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MASTER

***Effect of Molecular Multiple Scattering and
Surface Albedo on Atmospheric Photodissociation Rates***

F. M. Luther and R. J. Gelinas

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Effect of Molecular Multiple Scattering and Surface Albedo on Atmospheric Photodissociation Rates

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Results are presented from an extensive theoretical investigation aimed at evaluating the effect of molecular multiple scattering and surface albedo on photodissociation rates. Results are compared with similar calculations typical of most atmospheric photochemical models which only describe absorption in a direct solar beam. The effect of molecular multiple scattering and surface albedo on photodissociation rates, which can be sizable, depends strongly on solar zenith angle, surface albedo, altitude, and wavelength regime. Various atmospheric photodissociation processes are categorized by spectral type based upon the wavelength regime in which the photodissociation process occurs. Three basic wavelength regimes are noted, and results characteristic of each regime are presented. Adjustment factors are provided for generalizing the pure absorption calculations.

INTRODUCTION

At present, only the most elementary radiative transfer calculations are incorporated in atmospheric models containing photochemically active species. This is primarily due to nothing more than computer running time and capacity limitations. For example, even the simplest atmospheric kinetics models are beset with computational constraints that normally lead to invoking the assumption of a purely absorbing atomic and molecular atmosphere for determining solar fluxes and the corresponding photodissociation rates. As one proceeds to space- and time-dependent (transport-kinetic) atmospheric models, the repeated in-line calculation of even pure absorption photodissociation rates is so costly that further model assumptions of constant solar fluxes are invoked, often over space and time scales so coarse as to impair the basic physical interpretability of the original model foundations. These factors have been (and continue to be) sufficiently overriding that the roles of multiple scattering, the earth's surface reflection, and clouds and aerosols in evaluating photochemical rates have remained a side issue in atmospheric photochemical trace gas models; yet it is well-known that these radiative aspects can be significant in determining stratospheric and tropospheric radiative intensities at photodissociative wavelengths.

The importance of molecular scattering and surface albedo is suggested in the work of *McElroy and Hunten* [1966], in which these effects are applied to the interpretation of dayglow measurements for cases in which gaseous absorption may be neglected. *Prinn* [1970] included molecular scattering in calculations of ultraviolet radiative transfer and photolysis in Jupiter's atmosphere. These effects are also treated in the related work of *Callis et al.* [1975].

This paper is intended to bring to bear some results from reasonably general radiative transfer calculations on photodissociation rates for atmospheric models. Specifically, we include multiple molecular scattering and the earth's surface albedo in determining photodissociation rates. Effects of clouds and aerosols require more detailed model-dependent information and are not considered at this time. The data herein are parameterized by photodissociation spectral types, altitude, albedo, and solar zenith angle in order to provide a quantitative guide for sensitivity analysis on the pure absorption photodissociation rates without having to do the general in-line calculations. Sizable adjustment factors will be in-

dicated. The altitude range of 0–50 km and the wavelength range of 187.2–735.0 nm are exclusively considered, giving primary attention to absorption by O_2 , O_3 , and NO_2 .

RADIATIVE TRANSFER FORMULATIONS IN ATMOSPHERIC PHOTOCHEMICAL MODELS

Stratospheric and tropospheric models that contain photochemically active species have almost universally invoked an assumption of pure absorption for computing solar fluxes and photodissociation rates. We will briefly review the elements of that approach and describe some pure molecular absorption calculations that are performed for later reference.

The solution of the one-dimensional purely absorbing source-free radiative transfer equation at a particular altitude z_p (km), solar zenith angle θ_0 , and atmospheric composition $\{N_A(z)\}$ is given by

$$F_\lambda(z_p, \theta_0, \{N_A\}, t) = F_\lambda(\infty) \exp[-\tau_\lambda(z_p, \theta_0, \{N_A\}, t)] \quad (1)$$

where $F_\lambda d\lambda$ is the flux of photons (in number per square centimeter per second) in the wavelength interval $d\lambda$ about λ . $F_\lambda(\infty)$ represents the solar flux at 1 AU, and the optical depth τ_λ is given by

$$\tau_\lambda(z_p, \theta_0, \{N_A\}, t) \equiv \int_{z_p}^{\infty} dz \sum_A N_A(z, t) \sigma_T^A[\lambda, T(z)] \sec \theta_0(t) \quad (2)$$

In (2) the summation on A includes all atmospheric absorbers, each having number density $N_A(z, t) \text{ cm}^{-3}$ and a total absorption cross section $\sigma_T^A[\lambda, T(z)] \text{ cm}^2$. Most generally, $\sigma_T^A[\lambda, T(z)]$ is a function of the temperature $T(z)$. In this article we only consider atmospheric absorption by O_2 , O_3 , and NO_2 , only σ_{O_3} being dependent upon $T(z)$. Note that the solar zenith angle is generally a function of time t . Generally, $N_A(z)$ and $F_\lambda(\infty)$ can also be functions of time, but such dependences are usually neglected, whether justifiably or not.

The absorption cross sections for ozone and NO_2 are shown in Figure 1. The peak in the NO_2 cross section occurs near 400 nm, which is between the Huggins and the Chappuis bands of ozone. The ozone cross section is strongly peaked near 250 nm, and the peak in the cross section for the weaker Chappuis band occurs near 600 nm.

The photodissociation rate for transforming species i to species j is denoted by

$$J_{i \rightarrow j}(z_p, \theta_0, t) N_i(z_p, t)$$

where

$$J_{i \rightarrow j}(z_p, \theta_0, t) \equiv \int_{\lambda_{i \rightarrow j}} d\lambda \sigma_D^i[j, \lambda, T(z_p)] \cdot F_\lambda(z_p, \theta_0, \{N_A\}, t) \quad (3)$$

The microscopic photodissociation cross section $\sigma_D^i[j, \lambda, T(z_p)] \text{ cm}^2$ is often written in terms of the so-called quantum yield $Q_\lambda(i \rightarrow j)$ as

$$\sigma_D^i[j, \lambda, T(z_p)] \equiv \sigma_T^i[\lambda, T(z_p)] Q_\lambda(i \rightarrow j) \quad (4)$$

Given microscopic cross-section data, $F_\lambda(\infty)$, $\{N_A(z)\}$, and θ_0 , it is a straightforward matter to compute photodissociation coefficients. In our calculations we use $F_\lambda(\infty)$ derived from Ackerman's [1970] data, $N_{O_3}(z)$ from the U.S. Standard Atmosphere (1962) (also see the 1966 supplements), and $N_{O_2}(z)$ and $N_{NO_2}(z)$ from arbitrary model results [Chang, 1974] that are in reasonable agreement with observed data. The microscopic cross-section data are taken from a variety of sources described by Gelinas *et al.* [1973] (see also updates and additions to their report). Table 1 lists $T(z)$, $N_{O_2}(z)$, $N_{O_3}(z)$, and $N_{NO_2}(z)$ versus z from 0 to 55 km. Total column densities for O_2 , O_3 , and NO_2 are also given in Table 1.

It is necessary to treat the highly structured Schumann-Runge (S-R) bands of O_2 with special care because of the important 'window' at about 200 nm. (The ozone absorption coefficient assumes relatively large values at wavelengths greater than about 210 nm, and the O_2 Schumann-Runge band absorption (superimposed on an underlying continuum) is known to be relatively large at wavelengths shorter than about 195 nm. The strength and position of this lower cutoff is of central importance to ultraviolet solar fluxes and to some photodissociation rates.) The basic solar flux data $F_\lambda(\infty)$ are resolved only over rather broad intervals of wavelength width Δ , which may span hundreds of S-R spectral lines. In such intervals, group-averaged radiation fluxes $F_\Delta(z_p, \theta_0, t)$ are defined by

$$F_\Delta(z_p, \theta_0, t) = \Phi_\Delta(\infty) R_{O_2, O_3, NO_2}(\Delta, z_p, \theta_0, t) \quad (5)$$

where the O_2 , O_3 , NO_2 reduction factor is defined by

$$\begin{aligned} R_{O_2, O_3, NO_2}(\Delta, z_p, \theta_0, t) &= \frac{1}{\Delta} \int_{\Delta} d\lambda \exp \left\{ - \int_{z_p}^{\infty} dz [N_{O_2}(z, t) \sigma_T^{O_2}(\lambda, T(z)) \right. \\ &\quad + N_{O_3}(z, t) \sigma_T^{O_3}(\lambda, T(z)) \\ &\quad \left. + N_{NO_2}(z, t) \sigma_T^{NO_2}(\lambda, T(z))] \sec \theta_0(t) \right\} \quad (6) \end{aligned}$$

and

$$\Phi_\Delta(\infty) = \int_{\Delta} d\lambda F_\lambda(\infty) = F_\Delta(\infty) \cdot \Delta \quad (7)$$

The notation $\{N_A\}$ has been deleted because the atmospheric composition is now understood. The fact that available ozone and NO_2 absorption cross-section data are temperature-independent and only resolved over intervals Δ comparable to the solar flux data allows R_{O_2, O_3, NO_2} to be factored as

$$R_{O_2, O_3, NO_2}(\Delta, z_p, \theta_0, t) = R_{O_2}(\Delta, z_p, \theta_0, t) \cdot R_{NO_2}(\Delta, z_p, \theta_0, t) \quad (8)$$

with

Fig. 1. Absorption cross sections for O_2 and NO_2 .

$$R_{O_2}(\Delta, z_p, \theta_0, t) \equiv \exp [-\sigma_T^{O_2}(\Delta) \cdot N_{O_2}(z_p, \theta_0, t)] \quad (9)$$

$$\begin{aligned} N_{O_2}(z_p, \theta_0, t) &\equiv \int_{z_p}^{\infty} dz N_{O_2}(z, t) \sec \theta_0(t) \\ &\equiv \text{ozone column density cm}^{-2} \quad (10) \end{aligned}$$

Here $R_{NO_2}(\Delta, z_p, \theta_0, t)$ is defined analogously to $R_{O_2}(\Delta, z_p, \theta_0, t)$, and for O_3 ,

$$\begin{aligned} R_{O_3}(\Delta, z_p, \theta_0, t) &\equiv \frac{1}{\Delta} \int_{\Delta} d\lambda \\ &\cdot \exp \left\{ - \int_{z_p}^{\infty} dz N_{O_3}(z, t) \sigma_T^{O_3}(\lambda, T(z)) \sec \theta_0(t) \right\} \quad (11) \end{aligned}$$

The O_3 photodissociation rate is given by

$$J_{O_3 \rightarrow O}(z_p, \theta_0, t) = \sum_{\lambda \in \Delta} J_{O_3 \rightarrow O}(\Delta, z_p, \theta_0, t) \quad (12)$$

We assume $T(z) = T(z_p) = T_p$ in (11) and (12), which then reduce to

$$\begin{aligned} R_{O_3}(\Delta, z_p, \theta_0, t) &= \frac{1}{\Delta} \int_{\Delta} d\lambda \exp [-\sigma_T^{O_3}(\lambda, T_p) N_{O_3}(z_p, \theta_0, t)] \quad (13) \end{aligned}$$

and

$$\begin{aligned} J_{O_3 \rightarrow O}(\Delta, z_p, \theta_0, t) &= F_\Delta(\infty) R_{O_2}(\Delta, z_p, \theta_0, t) \\ &\cdot R_{NO_2}(\Delta, z_p, \theta_0, t) \int_{\Delta} d\lambda \sigma_T^{O_3}(\lambda, T_p) \\ &\cdot Q_\lambda(O_3 \rightarrow O) \exp [-\sigma_T^{O_2}(\lambda, T_p) N_{O_2}(z_p, \theta_0, t)] \quad (14) \end{aligned}$$

Expressions (13) and (14) are readily evaluated from the tabulations of Hudson and Mahle [1972]. They have performed the high-resolution integrations (over λ) and have tabulated R_{O_2} and $[J_{O_3 \rightarrow O} / (\Phi_\Delta(\infty) R_{O_2} R_{NO_2})]$ versus N_{O_3} for all interesting wavelengths, $\lambda \leq 205$ nm, in temperature-dependent (polynomial) forms. It should be noted that the presence of significant quantities of other absorbers having strong band structure in the O_3 Schumann-Runge region would necessitate more general high-resolution integrations for composite reduction factors to be performed in-line. Recall that the O_2 , O_3 , and NO_2 reduction factors are separable in (8) because $\sigma_T^{O_2}$ and $\sigma_T^{NO_2}$ do not have band structure comparable to $\sigma_T^{O_3}$ in the same spectral region.

In the examples that follow it is not necessary to show all the photodissociation coefficients of atmospheric interest because basic spectral types can be identified. A basis for classifying

TABLE 1. Values of Input Parameters

Height, km	Pressure, mbar	Temperature, K	Ozone Number Density, cm ⁻³	Oxygen Number Density, cm ⁻³	NO ₂ Number Density, cm ⁻³
55.0	0.4275	265.59	2.5725×10^{10}	2.4470×10^{13}	7.6040×10^4
52.5	0.5848	270.25	4.1808×10^{10}	3.2910×10^{13}	2.0438×10^5
50.0	0.7978	270.65	7.4409×10^{10}	4.4820×10^{13}	6.1539×10^5
47.5	1.0886	270.35	1.3455×10^{11}	6.1230×10^{13}	2.1392×10^6
45.0	1.4910	264.16	2.9218×10^{11}	8.5820×10^{13}	9.3970×10^6
42.5	2.0602	257.26	6.4248×10^{11}	1.2170×10^{14}	4.7596×10^7
40.0	2.8714	250.35	1.1843×10^{12}	1.7440×10^{14}	1.9125×10^8
37.5	4.0422	243.43	1.7839×10^{12}	2.5240×10^{14}	5.2476×10^8
35.0	5.7459	236.51	2.4365×10^{12}	3.6940×10^{14}	1.1048×10^9
34.0	6.6341	233.74	2.7217×10^{12}	4.3150×10^{14}	1.4024×10^9
33.0	7.6731	230.97	3.0093×10^{12}	5.0510×10^{14}	1.7212×10^9
32.0	8.8906	228.49	3.2823×10^{12}	5.9160×10^{14}	2.0452×10^9
31.0	10.3126	227.50	3.4696×10^{12}	6.8920×10^{14}	2.3452×10^9
30.0	11.9703	226.51	3.6729×10^{12}	8.0350×10^{14}	2.6097×10^9
29.0	13.9042	225.52	3.8783×10^{12}	9.3740×10^{14}	2.7941×10^9
28.0	16.1619	224.53	4.0682×10^{12}	1.0440×10^{15}	2.8645×10^9
27.0	18.7997	223.54	4.2522×10^{12}	1.2790×10^{15}	2.8266×10^9
26.0	21.8837	222.54	4.3701×10^{12}	1.4950×10^{15}	2.6753×10^9
25.0	25.4922	221.55	4.3781×10^{12}	1.7490×10^{15}	2.4450×10^9
24.0	29.7174	220.56	4.2537×10^{12}	2.0490×10^{15}	2.1809×10^9
23.0	34.6686	219.57	3.9821×10^{12}	2.4010×10^{15}	1.9083×10^9
22.0	40.4749	218.57	3.6349×10^{12}	2.8160×10^{15}	1.6668×10^9
21.0	47.2893	217.58	3.2171×10^{12}	3.3040×10^{15}	1.4420×10^9
20.0	55.2930	216.65	2.8002×10^{12}	3.8800×10^{15}	1.2501×10^9
19.0	64.6748	216.65	2.3715×10^{12}	4.5390×10^{15}	1.0751×10^9
18.0	75.6522	216.65	1.9838×10^{12}	5.3090×10^{15}	9.2068×10^8
17.0	88.4971	216.65	1.6367×10^{12}	6.2110×10^{15}	7.8004×10^8
16.0	103.5280	216.65	1.3307×10^{12}	7.2650×10^{15}	6.5124×10^8
15.0	121.1180	216.65	1.0654×10^{12}	8.5000×10^{15}	5.3172×10^8
14.0	141.7040	216.65	8.3114×10^{11}	9.9450×10^{15}	4.1738×10^8
13.0	165.7960	216.65	6.2839×10^{11}	1.1640×10^{16}	3.1730×10^8
12.0	193.9940	216.65	4.5202×10^{11}	1.3610×10^{16}	2.2714×10^8
11.0	226.9990	216.77	2.9622×10^{11}	1.5920×10^{16}	1.4266×10^8
10.0	264.9990	223.25	1.5010×10^{11}	1.8050×10^{16}	7.2402×10^7
9.0	308.0070	229.73	1.5294×10^{11}	2.0380×10^{16}	9.0920×10^7
8.0	356.5160	236.22	1.5594×10^{11}	2.2950×10^{16}	1.1126×10^8
7.0	411.0520	242.70	1.5877×10^{11}	2.5750×10^{16}	1.3217×10^8
6.0	472.1760	249.19	1.6189×10^{11}	2.8810×10^{16}	1.5329×10^8
5.0	540.4820	255.68	1.6537×10^{11}	3.2140×10^{16}	1.7349×10^8
4.0	616.6040	262.17	1.6940×10^{11}	3.5760×10^{16}	1.9123×10^8
3.0	701.2110	268.66	1.7440×10^{11}	3.9680×10^{16}	2.0440×10^8
2.0	795.0140	275.15	1.8081×10^{11}	4.3930×10^{16}	2.0839×10^8
1.0	898.7620	281.65	1.8902×10^{11}	4.8520×10^{16}	1.9318×10^8
0.0	1013.2500	288.15	2.0000×10^{11}	5.3490×10^{16}	1.4000×10^8

Total column densities are 8.2023×10^{14} cm⁻² for ozone, 4.5243×10^{14} cm⁻² for oxygen, and 4.2715×10^{14} cm⁻² for NO₂.

spectral types arises from the transmission properties of a pure molecular absorption atmosphere, as seen in Figure 2 for selected altitudes and a solar zenith angle of 60° (according to (1)). Three distinct regimes occur:

Regime 1: $187 \text{ nm} \leq \lambda \leq 290 \text{ nm}$

There is virtually no radiation transmitted to the lower elevations (0–10 km) for wavelengths shorter than 290 nm. Molecular species such as O₃, and others for which the dominant part of the photodissociation cross section lies in this spectral region, are therefore not directly photochemically active in the lower atmosphere. Such species will later be referred to as being of spectral type 1. Note (Figure 1) that at higher altitudes (≥ 20 km) there is the well-known O₂–O₃ window at about 200–210 nm. Above 30 km, transmission is nearly complete through this upper atmospheric window.

Regime 2: $290 \text{ nm} \leq \lambda \leq 330 \text{ nm}$

This is a transition region in which there is virtually no transmission to low altitudes for $\lambda < 290$ nm and complete

transmission at 330 nm at all altitudes of a purely absorbing atmosphere. The photodissociation of NO₂ to NO occurs predominantly in this range and is referred to herein as being of spectral type 2.

Regime 3: $330 \text{ nm} \leq \lambda \leq 735 \text{ nm}$

In this spectral region there is virtually complete transmission at all altitudes for a purely absorbing O₂–O₃–NO₂ standard atmosphere. Species having the dominant part of their photodissociation cross section in this range are referred to herein as being of spectral type 3.

Table 2 lists some of the important atmospheric photodissociation processes with spectral type based on a purely absorbing standard atmosphere and the designated references for source data. When a photodissociation process spans more than one of the spectral regimes given above, it is denoted by listing all the suitable regime numbers. For instance, ozone photodissociation to O(¹P) spans regimes 2 and 3 and is denoted as spectral type 2–3.

Fig. 2. Transmission properties of a purely absorbing molecular atmosphere for selected altitudes and a solar zenith angle of 60° .

RADIATIVE TRANSFER CALCULATIONS INCLUDING MOLECULAR MULTIPLE SCATTERING AND SURFACE ALBEDO

When molecular multiple scattering and surface albedo are included in the radiative transfer calculation, (1) is no longer the solution of the radiative transfer equation. However, the flux in the direct solar beam F_λ^* is given by an equation similar to (1):

$$F_\lambda^*(z_p, \theta_0, \{N_A\}, t) = F_\lambda(\infty) \exp[-\tau_\lambda^*(z_p, \theta_0, \{N_A\}, t)] \quad (15)$$

where the optical depth τ_λ^* along the slant path is given by

$$\begin{aligned} \tau_\lambda^*(z_p, \theta_0, \{N_A\}, t) \\ \equiv \int_{z_p}^{\infty} dz \sum_i N_i(z, t) \sigma_i^A[\lambda, T(z)] \sec \theta_0(t) \\ + \int_{z_p}^{\infty} dz \sum_i N_i(z, t) \sigma_i^R(\lambda) \sec \theta_0(t) \end{aligned} \quad (16)$$

In (16) the summation on i includes all atmospheric species, and σ_i^R is the Rayleigh scattering cross section for species i . $F_\lambda^*(z_p, \theta_0, \{N_A\}, t)$ differs from $F_\lambda(z_p, \theta_0, \{N_A\}, t)$ as defined by (1) in that attenuation due to both absorption and scattering is included in (15), whereas only absorption is included in (1).

The photodissociation coefficient also depends upon the scattered (diffuse) radiation as well as the direct solar flux as given by

$$\begin{aligned} J_{i \rightarrow j}(z_p, \theta_0, t) \equiv \int_{\lambda=11\lambda} d\lambda \sigma_D^i[\lambda, T(z_p)] \\ \cdot \left[F_\lambda^*(z_p, \theta_0, \{N_A\}, t) + \int_{\omega} I_\lambda(z_p, \omega) d\omega \right] \end{aligned} \quad (17)$$

where I_λ is the specific intensity of the diffuse radiation and ω is a solid angle. Including the effect of molecular multiple scattering and surface albedo in the calculation is simply expressed by changing the value of F_λ appearing in (3). For clarity we define

TABLE 2. Classification of Photodissociation Processes by Spectral Type

Photodissociation Process	Spectral Type	Data Source References
$\text{CH}_2\text{O} \rightarrow \text{CHO} + \text{H}$	2	McQuigg and Calvert [1969] and Calvert and Pitts [1966]
$\text{CH}_2\text{O} \rightarrow \text{CO} + \text{H}_2$	2	McQuigg and Calvert [1969] and Calvert and Pitts [1966]
$\text{CO}_2 \rightarrow \text{CO} + \text{O}$	1	Thompson et al. [1963]
$\text{H}_2\text{O} \rightarrow \text{HO} + \text{H}$	1	Thompson et al. [1963]
$\text{H}_2\text{O}_2 \rightarrow \text{HO} + \text{HO}$	2 for $z < 30$ km 1-2 for $z \geq 30$ km	Urey et al. [1929] and Holt et al. [1948]
$\text{HNO}_2 \rightarrow \text{HO} + \text{NO}$	3	Johnston and Graham [1973]
$\text{HNO}_2 \rightarrow \text{H} + \text{NO}_2$	3	Johnston and Graham [1973]
$\text{HNO}_2 \rightarrow \text{HO} + \text{NO}_2$	2 for $z < 25$ km 1-2 for $z \geq 25$ km	Johnston and Graham [1973]
$\text{HNO}_2 \rightarrow \text{H} + \text{NO}_2$	1	Johnston and Graham [1973]
$\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}(\text{D})$	2 for $z < 20$ km 1-2 for 20-40 km 1 for $z > 40$ km	Bates and Hays [1967] and Preston and Barr [1971]
$\text{N}_2\text{O} \rightarrow \text{N} + \text{NO}$	2 for $z < 20$ km 1-2 for 30-40 km 1 for $z > 40$ km	Bates and Hays [1967] and Preston and Barr [1971]
$\text{N}_2\text{O}_2 \rightarrow \text{NO}_2 + \text{NO}_2 + \text{O}$	2 for $z \leq 25$ km 1-2 for $z \geq 25$ km	Johnston and Graham [1973]
$\text{N}_2\text{O}_2 \rightarrow \text{NO}_2 + \text{NO}_2$	2 for $z \leq 25$ km 1-2 for $z \geq 25$ km	Johnston and Graham [1973]
$\text{NH}_3 \rightarrow \text{NH}_2 + \text{H}$	1	Thompson et al. [1963]
$\text{NO}_2 \rightarrow \text{NO} + \text{O}(\text{D})$	1	Hall and Blacet [1952],* Leighton [1961], and Dixon [1940]
$\text{NO}_2 \rightarrow \text{NO} + \text{O}$	2	Hall and Blacet [1952], Leighton [1961], and Dixon [1940]
$\text{NO}_2 \rightarrow \text{NO}_2 + \text{O}$	3	Johnston and Graham [1973]
$\text{NO}_2 \rightarrow \text{NO} + \text{O}_2$	3	Johnston and Graham [1973]
$\text{O}_2 \rightarrow \text{O} + \text{O}$	1	Ackerman [1970] and Hudson and Mahle [1972]
$\text{O}_2 \rightarrow \text{O} + \text{O}_2$	2-3	Ackerman [1970]
$\text{O}_2 \rightarrow \text{O}(\text{D}) + \text{O}_2$	2 for $z < 35$ km 1-2 for $z \geq 35$ km	Ackerman [1970] and Gelinas et al. [1973]†

* For $\lambda = 190\text{--}400$ nm.

† See also updates and additions to this report.

$$F_{\lambda}(\text{multiple scattering}) \equiv F_{\lambda}'(z_p, \theta_0, \{N_A\}, t) + \int_{\lambda^*} I_{\lambda}(z_p, \omega) d\omega \quad (18)$$

Henceforth F_{λ} (pure absorption) will refer to the flux defined by (1). Aside from substituting F_{λ} (multiple scattering) in place of F_{λ} (pure absorption) in (3), all other aspects of the photodissociation rate calculation are the same as for the purely absorbing molecular atmosphere. Since $F_{\lambda}'(z_p, \theta_0, \{N_A\}, t)$ is less than F_{λ} (pure absorption), F_{λ} (multiple scattering) may be greater than or less than F_{λ} (pure absorption), depending upon the intensity of the diffuse radiation.

In our calculations the model atmosphere extends between 0 and 55 km and is divided into 43 layers. The thickness of a layer is 1 km up to 35 km and 2.5 km between 35 and 55 km. Each atmospheric layer is subdivided into sublayers such that the vertical optical depth of each sublayer, including scattering and absorption, is less than 0.02. There may be as many as 500 sublayers, depending upon the total optical depth of the atmosphere. The radiative transfer equation is solved using the Gauss-Seidel iterative scheme to obtain the specific intensity at increments of 6° in the local zenith angle for each level. The spectral region between 187.2 and 735 nm is divided into 119 spectral intervals, of which 9 are in the Schumann-Runge bands of oxygen.

RESULTS

The effect of molecular multiple scattering and surface albedo on photodissociation rates is analyzed both in terms of

their effect on the photodissociation coefficients for individual reactions and in terms of their effect on F_{λ} . An understanding of the spectral variation of the effect on the flux will aid in interpreting the effect on the photodissociation coefficients, which results from an integration over wavelength.

In studying the spectral dependence of the effect on F_{λ} we present only the results for a solar zenith angle of 60° , but these are qualitatively typical of the results for other solar

Fig. 3c

Fig. 3d

Fig. 3a

Fig. 3b

Fig. 3e

Fig. 3. Flux ratio versus wavelength for a solar zenith angle of 60° and selected values of surface albedo R at altitudes z of (a) 40 km, (b) 30 km, (c) 20 km, (d) 10 km, and (e) 0 km.

zenith angles. Parametric variations of surface albedo were also made and are discussed below.

The flux ratio F_{λ} (multiple scattering) / F_{λ} (pure absorption) is shown in Figures 3a-3e for selected altitudes. At an altitude of 40 km there is little change in the flux for wavelengths less than 290 nm. It turns out that a minor decrease occurs in the flux in this spectral region except in the vicinity of the local peak near 230 nm, a point at which there is large attenuation of the solar flux. Since no solar radiation reaches the earth's surface at wavelengths less than 290 nm, there is no dependence on surface albedo in this spectral region.

The results for a surface albedo of 0.0 demonstrate the effect of molecular multiple scattering alone, which is shown to have its maximum effect near 330 nm. Molecular multiple scattering may cause as much as a 50% increase in F_{λ} over a relatively narrow spectral region. At wavelengths greater than 300 nm there is a strong dependence upon surface albedo which may lead to as much as a doubling of the flux for this solar zenith angle. For a surface albedo of 0.3 (approximate global mean) the flux is increased between 30 and 60% at wavelengths greater than 330 nm.

Looking at flux ratios for both 30 and 20 km, there is little change relative to the 40-km case at wavelengths greater than 300 nm. There is a significant change in flux ratios at wavelengths less than 300 nm, however. Large increases in flux ratios occur as large vertical optical depths ($\tau \approx 10$) are approached. Although these changes are large, the magnitude of the flux is so small at these optical depths that the change in flux should have a negligible effect on species concentrations at such altitudes. This is amply demonstrated in Figure 4 by the photodissociation of molecular oxygen (spectral type 1) for a solar zenith angle of 60°.

The region between 0- and 10-km altitude contains approximately 75% of the mass of the atmosphere. For this reason, most molecular multiple scattering occurs in this region of the atmosphere. As one moves downward from 10 km to the earth's surface, the downward flux is reduced due to back-scattering, and the amount of atmosphere available to scatter the radiation upward is reduced. Consequently, in moving from 10 km to the earth's surface, there is a dramatic decrease in F_{λ} for the multiple scattering case. Exceptions to this mechanism may occur in cases where surface reflection is sufficiently strong to compensate for this molecular scattering effect.

Fig. 4. Photodissociation coefficients versus height for the reaction $O_2 \xrightarrow{h\nu} O(^1D) + O$ for the pure absorption and multiple scattering cases at a solar zenith angle of 60°.

Fig. 5. Photodissociation coefficients versus height for the reaction $O_3 \xrightarrow{h\nu} O(^1D) + O_2$ for the pure absorption and multiple scattering cases at a solar zenith angle of 60° and selected values of surface albedo R .

The effect of both molecular multiple scattering and surface albedo on the photodissociation coefficients for specific reactions is now considered. Although we restrict our discussion to only a few reactions, they represent the variation in behavior that occurs as the spectral region of primary importance moves from regime 1 to regime 3:

Vertical profiles of the photodissociation coefficients for each of these reactions for a solar zenith angle of 60° are shown in Figures 5-7.

Reaction (19a) overlaps spectral regimes 1 and 2. The strong absorption in spectral regime 1 dominates for altitudes greater than 35 km. Consequently, there is no dependence upon surface albedo in this altitude range. As the flux in regime 1 becomes depleted, an event which occurs at altitudes below 35 km, the relative contribution of flux in regime 2 increases. Consequently, the sensitivity of results to surface albedo increases markedly with decreasing altitude.

Reaction (19b) spans spectral regimes 2 and 3; therefore the photodissociation coefficients at all altitudes depend strongly

Fig. 6. Photodissociation coefficients versus height for the reaction $NO_2 \xrightarrow{h\nu} NO + O$ for the pure absorption and multiple scattering cases at a solar zenith angle of 60° and selected values of surface albedo R .

Fig. 7. Photodissociation coefficients versus height for the reaction $\text{O}_3 \xrightarrow{h\nu} \text{O}(^1\text{P}) + \text{O}_2$ for the pure absorption and multiple scattering cases at a solar zenith angle of 60° and selected values of surface albedo R .

on surface albedo. The values for $R = 0.0$ show that molecular scattering alone significantly increases the stratospheric values of the photodissociation coefficients.

Reaction (19c) is in spectral regime 3. In this case, the effect of molecular scattering alone on the stratospheric values of the photodissociation coefficients is significantly reduced, but there is still a strong dependence upon surface albedo.

Up to this point we have considered the effects of molecular multiple scattering and surface albedo on the photodissociation coefficients for only one solar zenith angle. The functional dependence upon solar zenith angle for reactions (19a)-(19c) is shown in Figures 8-10, respectively. In each figure the ratio of photodissociation coefficients $J(\text{multiple scattering})/J(\text{pure absorption})$ is plotted for selected altitudes, and the results are parameterized over surface albedo and solar zenith angle (0° , 30° , 60° , and 78°).

There are certain features which are common to all three sets of results. In each case the ratio of photodissociation coefficients decreases with increasing solar zenith angle, and at a given altitude the curves for different values of surface albedo converge as the solar zenith angle increases. Remember that F_1 for the multiple scattering case consists of two components: the direct solar flux and the contribution due to diffuse radiation. The direct solar flux differs from the pure absorption flux only in terms of the additional attenuation due

Fig. 8. Ratios of photodissociation coefficients versus solar zenith angle for the reaction $\text{O}_3 \xrightarrow{h\nu} \text{O}(^1\text{D}) + \text{O}_2$ at selected heights.

Fig. 9. Ratios of photodissociation coefficients versus solar zenith angle for the reaction $\text{NO}_2 \xrightarrow{h\nu} \text{NO} + \text{O}$ at selected heights.

to the molecular scattering optical depth. The gaseous absorption optical thickness is the same for both cases. As the solar zenith angle increases, the direct solar flux for the multiple scattering case decreases in relation to the pure absorption flux because of the increased molecular scattering optical depth. The diffuse radiation is strongly dependent upon the flux of photons incident at the top of the atmosphere, which varies as the cosine of the solar zenith angle. As the solar zenith angle increases, a larger fraction of the total flux is diffuse, but the incident flux at the top of the atmosphere is reduced. The net effect is a decrease in the ratio of photodissociation coefficients with increasing solar zenith angle.

In the limit as $\theta_s \rightarrow 90^\circ$, no flux reaches the earth's surface. The results therefore become independent of surface albedo for a solar zenith angle of 90° . For this reason the photodissociation coefficients corresponding to different values of the surface albedo at a given altitude tend to converge as the solar zenith angle increases.

CONCLUSIONS

There is a strong spectral variation in the effect which molecular multiple scattering and surface albedo have on photodissociation rates. We have analyzed these effects for three basic spectral regimes: $187 \text{ nm} \leq \lambda \leq 290 \text{ nm}$, $290 \text{ nm} \leq \lambda \leq 330 \text{ nm}$, and $330 \text{ nm} \leq \lambda \leq 735 \text{ nm}$. In the first regime, surface

Fig. 10. Ratios of photodissociation coefficients versus solar zenith angle for the reaction $\text{O}_2 \xrightarrow{h\nu} \text{O}(^1\text{P}) + \text{O}_2$.

albedo has no effect on photodissociation rates because virtually no radiation reaches the earth's surface. Molecular scattering can cause large relative changes in F_{λ} at large optical depths in this spectral region, but these changes in absolute magnitude are very small when they are compared to $F_{\lambda}(\infty)$.

For regimes 2 and 3 the combined effect of molecular multiple scattering and surface albedo can cause several-fold increases in the stratospheric values of the photodissociation coefficient for large values of surface albedo, which implies that significant changes in photodissociation rates might occur over extensive areas of snow, ice, or cloud cover. The results are highly sensitive to solar zenith angle, especially for large values of surface albedo.

The effect of these results on the various species concentrations remains to be determined. The strong dependence upon solar zenith angle has serious implications in regard to the choice of solar zenith angle used in the fixed sun atmospheric photochemical models.

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How Important is Gaseous Absorption in the Visible?

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How Important is Gaseous Absorption in the Visible?

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Solar heating of the atmosphere and earth's surface is the driving force affecting the temperature structure, dynamics, and hydrologic cycle of the atmosphere. Therefore, perturbations to the atmospheric composition which affect the solar radiation budget may have significant climatic consequences. The following discussion addresses some of the important factors affecting gaseous absorption in the visible.

In contrast to the transfer of ultraviolet radiation, the atmosphere is highly transparent to visible radiation. Consequently, a large fraction of the incoming radiation at these wavelengths reaches the troposphere where it can be scattered by molecules, cloud droplets, particles, and the earth's surface. The radiative properties of the troposphere thus affect gaseous absorption in the stratosphere via the upward scattered radiation. Changes in the albedo of the troposphere (including the earth's surface) can have a significant effect on solar absorption in the stratosphere.

Fig. 1 shows the solar absorption by ozone as a function of ozone amount and surface albedo for a solar zenith angle of 60° . This calculation included multiple scattering and solar absorption in the visible and UV. In terms of the total solar absorption by ozone, a 5% decrease in total ozone column is approximately equivalent to a decrease in surface albedo of 0.07 at this solar zenith angle.

It is important to realize that the fractional change in O_3 absorption does not equal the fractional change in the O_3 column. The fractional change in O_3 absorption is approximately half the fractional change in O_3 column (Fig. 2).

This figure applies only to small changes in O_3 . This effect results from the saturation of the O_3 absorption in the Hartley band (200 to 300nm). Even with a reduction of 10% in the O_3 column, there is virtually no change in the amount of energy absorbed in this band. Most of the change in O_3 absorption occurs in the weaker Huggins (300 to 350nm) and Chappuis (420 to 720nm) bands.

Other gaseous species which absorb solar radiation include H_2O , O_2 , CO_2 , and NO_2 . Relatively small amounts of energy are absorbed by O_2 and H_2O in the 0.7 μ m region, and there are some minor absorption bands of CO_2 in the near infrared. Only a small fraction of the absorption by water vapor (several strong bands in the infrared) occurs in the stratosphere.

NO_2 absorption occurs primarily in the wavelength region from 300 to 710 nm and is only a small fraction (approx. 0.03) of the solar absorption by O_3 for the unperturbed atmosphere. The increase in NO_2 absorption is comparable to the decrease in O_3 absorption for a stratosphere perturbed by NO_x injection (Fig. 3). A key factor in this effect is that the fractional increase in the NO_2 column is many times greater than the fractional decrease in the O_3 column. Lawrence Livermore Laboratory's current one-dimensional transport-kinetics model predicts a value of 10.4 for the ratio of fractional changes in the total columns of NO_2 and O_3 and a value of 14.6 for the stratospheric columns. The values differ significantly from earlier values which were obtained using a faster reaction rate for $OH + HO_2$. Calculations of the perturbed solar radiation budget presently have a high degree of uncertainty due to uncertainties in the perturbed species concentrations.

In summary, calculations of the solar radiation budget are affected by uncertainties in the albedo of the earth's surface and clouds and uncertainties in the concentration profiles of trace species. Albedo measurements are

needed as a function of wavelength and solar zenith angle for different surface and cloud types. Changes in cloud fraction, which may be induced by natural or anthropogenic climatic perturbations, will affect the solar radiation budget, but changes in cloud fraction cannot be accurately predicted at the present time.

SOLAR ABSORPTION BY OZONE

Figure 1. Solar absorption by O_3 versus total O_3 columns for a solar zenith angle of 60° .

Figure 2. The ratio of the fractional change in O_3 absorption to the fractional change in total O_3 as a function of total O_3 for a solar zenith angle of 60° .

Figure 3. The perturbed solar radiation budget due to an NO_x injection at 17 km of 2.5×10^5 kg/yr as NO_2 . The solar zenith angle is 60° .

***What is the Importance of Multiple Scattering
in Calculations of Photodissociation Rates?***

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WHAT IS THE IMPORTANCE OF MULTIPLE SCATTERING
IN CALCULATIONS OF PHOTODISSOCIATION RATES?

A position paper by

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and

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Stratospheric and tropospheric models that contain photochemically active species have almost universally incorporated photodissociation rate calculations which only describe absorption in a direct solar beam. Models of this type shall be referred to as "pure absorption" calculations. When multiple scattering (including diffuse scattering of radiation from the earth's surface) is included in the calculation, there may be a significant increase in stratospheric photodissociation rates. There is a strong wavelength dependence for the effect of molecular multiple scattering and surface albedo on photodissociation rates. Correction factors for the flux used in the pure absorption calculation are shown in Fig. 1 for a solar zenith angle of 60° . In the wavelength region $187 \text{ nm} < \lambda < 290 \text{ nm}$, surface albedo has no effect on photodissociation rates because virtually no radiation reaches the earth's surface. Multiple scattering can cause large relative changes in the flux used in the photodissociation rate calculation at large optical depths, but these changes in absolute value are small when compared to the flux at the top of the atmosphere. At wavelengths greater than 290 nm, there may be as much as a 60% increase in the flux for a surface albedo of 0.25 and a solar zenith angle of 60° . The correction factors are nearly constant with height above 20 km, but they may vary significantly with height below 20 km, which is where most multiple scattering occurs.

Because of differences in the wavelength dependence of the photodissociation cross-sections, multiple scattering effects can differ significantly between reactions. Species concentrations may be affected directly by changes in the photodissociation coefficients or indirectly by subsequent chemical reaction with other species. The effect of multiple scattering on species concentrations was tested using the Lawrence Livermore Laboratory one-dimensional transport kinetics model. A simple, although rather crude, method was used to incorporate the effects of multiple scattering. Correction factors for the flux used in the pure absorption calculation were specified as a function of wavelength at each 10 km of altitude. Correction factors at other altitudes were computed by linear interpolation. The correction factors correspond to a solar zenith angle of 45° and a surface albedo of 0.2. This method is satisfactory

above 20 km where the effect of multiple scattering does not vary significantly with height, but it could lead to significant errors between 0-10 km. Consequently, the results of this experiment should be interpreted as a qualitative analysis rather than quantitative.

The changes in concentration of several key species due to multiple scattering relative to the pure absorption calculation are shown in Figs 2-8. Calculations were made with and without ClONO₂. Inclusion of ClONO₂ significantly affected the results for the chlorine containing species, but had a negligible effect on the other species. These curves correspond to the case with ClONO₂ unless otherwise specified.

Multiple scattering leads to a significant increase in NO concentration (Fig. 2) near 30 km due to photolysis of NO₂. There is very little HNO₃ above 30 km, so NO₂ decreases because it is essentially the only source of NO. NO photolysis is prescribed in the model, and it is not affected by the multiple scattering parameterization. NO photolysis is significant only at high altitudes (~40 km), and should not significantly affect the results at lower altitudes. HNO₃ photolysis is increased near 20 km where the concentration is large. A few percent decrease in HNO₃ at this altitude represents a significant increase in NO₂, which is in turn photolyzed to NO.

The increase in O(³P) in the region 20-30 km (Fig. 3) is due primarily to increased photolysis of O₃. Again, because of differences in ambient concentrations, a small percentage decrease in O₃ causes a large percentage increase in O(³P). The increase in O(³P) near 40 km is due primarily to increased photolysis of NO₂. The increase in O₃ at this height occurs because the chemical production of O₃ by O+O₂ is increased more than the photodestruction of O₃.

The increase in OH (Fig. 4) results from $\text{HNO}_3 \xrightarrow{h\nu} \text{OH} + \text{NO}_2$ and $\text{H}_2\text{O}_2 \xrightarrow{h\nu} 2\text{OH}$. The peak concentration in H₂O₂ occurs near 28 km, so a small percentage decrease in H₂O₂ in this region can cause a large percentage increase in OH.

Photodissociation of ClONO₂ (Fig. 5) affects several other chlorine containing species through a complex chain of reactions. Certain key reactions are:

The peak concentration of ClONO₂ occurs near 25 km, so photodestruction of ClONO₂ acts as a strong source of ClO in this region. The large increase in NO concentration between 20-30 km tends to destroy ClO, leading to a net decrease in ClO in this region (Fig. 6) and an increase in Cl (Fig. 7). The increase in Cl concentration leads to an increase in HCl concentration (Fig. 8) through reaction with CH₄.

The conclusions which can be drawn from this preliminary study are (1) that multiple scattering can have a very significant effect on species concentrations, particularly those which are associated with the products of photolysis and (2) that the magnitude of the effect on species concentrations may be significantly affected by model chemistry (e.g., whether or not ClONO_2 is included). Species which are significantly affected by multiple scattering include NO , $\text{O}(^3\text{P})$, OH , ClONO_2 , ClO , Cl , and HCl .

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In our calculations the model atmosphere extends between 0 and 55 km and is divided into 43 layers. The thickness of a layer is 1 km up to 35 km and 2.5 km between 35 and 55 km. Each atmospheric layer is subdivided into sublayers such that the vertical optical depth of each sublayer, including scattering and absorption, is less than 0.02. There may be as many as 500 sublayers, depending upon the total optical depth of the atmosphere. The radiative transfer equation is solved using the Gauss-Seidel iterative scheme to obtain the specific intensity at increments of 6° in the local zenith angle for each level. The spectral region between 187.2 and 735 nm is divided into 119 spectral intervals, of which 9 are in the Schumann-Runge bands of oxygen.

Fig. 3a

Fig. 3b

Fig. 3c

Fig. 3d

Fig. 3e

Fig. 3. Flux ratio versus wavelength for a solar zenith angle of 60° and selected values of surface albedo R at altitudes z of (a) 40 km, (b) 30 km, (c) 20 km, (d) 10 km, and (e) 0 km.

FIGURE 2

FIGURE 3-

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

FIGURE 8

Photodissociation Rate Calculations

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PHOTODISSOCIATION RATE CALCULATIONS*

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INTRODUCTION

Stratospheric and tropospheric models that contain photochemically active species have almost universally invoked an assumption of pure absorption for computing solar fluxes and photodissociation rates. This has been due primarily to nothing more than limitations involving computer running time and capacity. For example, even with the simplest representations of atmospheric kinetics, models are often beset with computational constraints that normally lead to invoking the assumption of a purely absorbing atomic and molecular atmosphere for determining solar fluxes and the corresponding photodissociation rates. These limiting factors have been (and continue to be) sufficiently overriding that the roles of multiple scattering, the earth's surface reflection, clouds, and aerosols have remained a side issue in evaluating photochemical rates in atmospheric photochemical

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trace gas models; yet it is well-known that these factors can be significant in determining stratospheric and tropospheric radiative intensities at photodissociative wavelengths.

We will briefly review the approach used in pure molecular absorption calculations, and we will discuss the effect of including multiple scattering effects in a stratospheric model.

RADIATIVE TRANSFER FORMULATIONS IN ATMOSPHERIC PHOTOCHEMICAL MODELS

The solution of the one-dimensional purely absorbing source-free radiative transfer equation at a particular altitude z_p (km), solar zenith angle θ_o , and atmospheric composition $\{N_A(z)\}$ is given by

$$F_\lambda(z_p, \theta_o, \{N_A\}, t) = F_\lambda(\infty) \exp[-\tau_\lambda(z_p, \theta_o, \{N_A\}, t)] \quad (1)$$

where $F_\lambda d\lambda$ is the flux of photons (in number per square centimeter per second) in the wavelength interval $d\lambda$ about λ . $F_\lambda(\infty)$ represents the solar flux at 1 AU, and the optical depth τ_λ is given by

$$\tau_\lambda(z_p, \theta_o, \{N_A\}, t) \equiv \int_{z_p}^{\infty} dz \sum_A N_A(z, t) \sigma_T^A[\lambda, T(z)] \sec \theta_o(t) \quad (2)$$

In Eq. (2) the summation on A includes all atmospheric absorbers, each having number density $N_A(z, t) \text{ cm}^{-3}$ and a total absorption cross section $\sigma_T^A[\lambda, T(z)] \text{ cm}^2$. Most generally, $\sigma_T^A[\lambda, T(z)]$ is a function of the temperature $T(z)$.

The photodissociation rate for transforming species i to species j is denoted by

$$J_{i \rightarrow j}(z_p, \theta_o, t) N_i(z_p, t)$$

where

$$J_{i \rightarrow j}(z_p, \theta_o, t) \equiv \int_{\text{all } \lambda} d\lambda \sigma_D^i[j, \lambda, T(z_p)] F_\lambda(z_p, \theta_o, \{N_A\}, t) \quad (3)$$

The microscopic photodissociation cross section $\sigma_D^i[j, \lambda, T(z_p)] \text{ cm}^2$ is often written in terms of the so-called quantum yield $Q_\lambda(i \rightarrow j)$ as

$$\sigma_D^i[j, \lambda, T(z_p)] \equiv \sigma_T^i[\lambda, T(z_p)] Q_\lambda(i \rightarrow j) \quad (4)$$

Given microscopic cross-section data, $F_\lambda(\infty)$, $\{N_A(z)\}$, and θ_o , it is a straightforward matter to compute photodissociation coefficients.

It should be noted that uncertainties still remain in the data used to calculate the photodissociation coefficients in the models. For example, major uncertainties remain in the branching of O_3 photolysis near 310 nm to either $O(^3P)$ or $O(^1D)$, in the branching and quantum yield for NO_3 photolysis, and in the methodology for calculating the photolysis of species having banded or line absorption cross-section structures, such as O_2 or NO .

RADIATIVE TRANSFER CALCULATIONS INCLUDING MOLECULAR MULTIPLE SCATTERING AND SURFACE ALBEDO

When molecular multiple scattering and surface albedo are included in the radiative transfer calculation, (1) is no longer the solution of the radiative transfer equation. However, the flux in the direct solar beam

F_{λ}^S is given by an equation similar to (1):

$$F_{\lambda}^S(z_p, \theta_o, \{N_A\}, t) = F_{\lambda}(\infty) \exp[-\tau_{\lambda}^S(z_p, \theta_o, \{N_A\}, t)] \quad (5)$$

where the optical depth τ_{λ}^S along the slant path is given by

$$\begin{aligned} \tau_{\lambda}^S(z_p, \theta_o, \{N_A\}, t) &= \int_{z_p}^{\infty} dz \sum_A N_A(z, t) \sigma_T^A[\lambda, T(z)] \sec \theta_o(t) \\ &+ \int_{z_p}^{\infty} dz \sum_i N_i(z, t) \sigma_R^i(\lambda) \sec \theta_o(t) \end{aligned} \quad (6)$$

In (6) the summation on i includes all atmospheric species, and σ_R^i is the Rayleigh scattering cross section for species i . $F_{\lambda}^S(z_p, \theta_o, \{N_A\}, t)$ differs from $F_{\lambda}(z_p, \theta_o, \{N_A\}, t)$ as defined by (1) in that attenuation due to both absorption and scattering is included in (5), whereas only absorption is included in (1).

The photodissociation coefficient also depends upon the scattered (diffuse) radiation given by

$$\begin{aligned} J_{i \rightarrow j}(z_p, \theta_o, t) &\equiv \int_{\text{all } \lambda} d\lambda \sigma_0^i[j, \lambda, T(z_p)] \\ &\cdot \left[F_{\lambda}^S(z_p, \theta_o, \{N_A\}, t) + \int_{\frac{1}{4}\pi} I_{\lambda}(z_p, \omega) d\omega \right] \end{aligned} \quad (7)$$

where I_{λ} is the specific intensity of the diffuse radiation and ω is a solid angle. Including the effect of molecular multiple scattering and surface albedo in the calculation is simply expressed by changing the value of F_{λ} appearing in (3). For clarity we define

$$F_{\lambda}^{MS}(\text{multiple scattering}) \equiv F_{\lambda}^S(z_p, \theta_o, \{N_A\}, t) + \int_{\frac{1}{4}\pi} I_{\lambda}(z_p, \omega) d\omega \quad (8)$$

Henceforth, F_{λ}^{PA} (pure absorption) will refer to the flux defined by (1). Aside from substituting F_{λ}^{MS} in place of F_{λ}^{PA} in (3), all other aspects of the photodissociation rate calculation are the same as for the purely absorbing molecular atmosphere. Since $F_{\lambda}^S(z_p, \theta_o, \{N_A\}, t)$ is less than F_{λ}^{PA} , F_{λ}^{MS} may be greater than or less than F_{λ}^{PA} , depending upon the intensity of the diffuse radiation.

MODEL DESCRIPTION

The effect of molecular scattering and surface albedo on ambient species concentrations and on model sensitivity has been assessed using a one-dimensional transport-kinetics model. The model has been described previously [Chang, 1975; Wuebbles and Chang, 1975], so only the main features of the model will be summarized.

The governing equation regarding the temporal variation in the number density of the i^{th} constituent c_i is given by the continuity equation,

$$\frac{\partial c_i}{\partial t} = P(c) - L(c) c_i - \frac{\partial}{\partial z} \left[K_z \rho \frac{\partial}{\partial z} \left(\frac{c_i}{\rho} \right) \right] \quad (9)$$

where $P(c)$ is the production of c_i due to photochemical interactions of the other c_j species; $L(c) c_i$ is the loss of c_i due to chemical interaction of c_i with the other c_j species; K_z is the vertical transport coefficient; $\rho = \rho(z)$ is the ambient air density; and t and z are time and altitude, respectively.

The model atmosphere extends from the ground to 55 km and is divided into 44 layers. A total of 92 chemical (and photochemical) reactions are included in the model; 45 reactions describe O_x , NO_x , and HO_x chemistry,

and 47 reactions describe ClO_x chemistry. These reactions are used to dynamically describe the stratospheric vertical distributions of 20 minor atmospheric species ($\text{O}(^3\text{P})$, O_3 , NO , NO_2 , N_2O , HNO_3 , OH , HO_2 , H_2O_2 , Cl , ClONO_2 , ClO , ClO_2 , OCIO , ClNO , ClNO_2 , HCl , CCl_4 , CF_2Cl_2 and CFCl_3). Three species (H , N , $\text{O}(^1\text{D})$) are assumed to be in instantaneous equilibrium, and the vertical distributions of N_2 , O_2 , H_2O , CH_4 and H_2 are assumed constant throughout the calculations.

The vertical transport in the model is parameterized through the so-called "eddy" mixing coefficient K_z (see Wuebbles and Chang, 1975; Chang, 1975). The numerical technique, which is a variable order, multistep, implicit method, used to solve Equation (1), is that described by Chang et al. (1974). The boundary conditions are species dependent and are assumed to be either fixed or time varying source dependent concentrations at the surface and flux conditions at 55 km, the upper boundary.

The chemical reaction rates used in the model are shown in Table 1. Other reaction rates in the model are based on the review by Hampson and Garvin (1975). Detailed spectral data used in the calculations are as described by Gelinas (1974).

The effect of multiple scattering was incorporated into the photodissociation rate calculation by applying correction factors to the flux F_λ used in the pure absorption calculation (Eq. (1)). These correction factors, which are given by the ratio $F_\lambda^{\text{MS}}/F_\lambda^{\text{PA}}$, were computed for the unperturbed species profiles using a highly detailed solar radiation model (Luther and Gelinas, 1976). A separate factor was computed for each of the 44 levels and for each of the 148 wavelength intervals between 133 and 735 nm. Different sets of correction factors

were computed for each assumed value of surface albedo A_s using a solar zenith angle of 45° . The correction factors were assumed to be constant in the calculations.

Examples of correction factors for a solar zenith angle of 60° are shown in Figure 1 as functions of wavelength for selected altitudes and various values of A_s . Since no solar radiation reaches the earth's surface at wavelengths less than 290 nm, there is no dependence on surface albedo in this spectral region. The results for a surface albedo of zero demonstrate the effect of molecular multiple scattering alone, which is shown to have its maximum effect near 330 nm. The correction factors are nearly constant with height above 20 km, but they may vary significantly with height in the region below 20 km, which is where most scattering events occur. Correction factors for a solar zenith angle of 45° are somewhat larger than those shown for 60° , but they are qualitatively similar [Luther and Gelinas, 1976].

RESULTS

The effects of including multiple scattering in the photodissociation rate calculation may be of three types: (1) the effect on photodissociation coefficients, (2) the effect on ambient species concentration profiles, and (3) the effect on model sensitivity to perturbations.

1. Photodissociation Coefficients

As shown by Figure 1, the effect of multiple scattering should be largest for those species having strong absorption cross-sections at wavelengths greater than 300 nm. Table 2 compares photodissociation

coefficients for pure absorption and for multiple scattering computed for the ambient model atmosphere. Only those photodissociation reactions significantly affected by multiple scattering are shown in Table 2. In an attempt to account for the diurnal variation of photodissociation in the model, the solar flux was halved in these calculations.

The importance of the significant changes in reaction rate coefficients is reflected in the species concentration profiles and in the model sensitivity.

2. Species Concentration Profiles

The concentration profiles for selected O_x , HO_x , NO_x , and ClX species are shown in Figures 2-5 for the ambient atmosphere prior to inclusion of multiple scattering and prior to the release of CFM's. These figures are included in order to define the reference conditions for assessing the fractional change in concentration caused by multiple scattering.

The changes in concentration of chemical species due to multiple scattering relative to the pure absorption calculation were computed for cases with and without $ClONO_2$. Inclusion of $ClONO_2$ significantly affected the results for the chlorine containing species, but it had a small effect on the other species (< 5% change in NO_2 and much less for other species). The following figures correspond to the case including $ClONO_2$ and with $A_s = 0.25$ unless otherwise specified.

The effect of multiple scattering on O_x species is shown in Figure 6. The large percentage increase in $O(^1D)$ near 10 km occurs where the ambient concentration is very small; nevertheless, it is significant in terms of stratospheric chemistry. The increases in $O(^3P)$ and $O(^1D)$ in the region 20-30 km are due to increased photolysis of O_3 . Because of differences in ambient concentrations, a small percentage decrease in O_3 causes large percentage increases in the other species. The increase in $O(^3P)$ near 40 km is due

primarily to increased photolysis of NO_2 . The increase in O_3 at this height occurs because the chemical production of O_3 by $\text{O} + \text{O}_2$ is increased more than the photolysis of O_3 .

Figure 7 shows the effect of multiple scattering on HO_x species. The increase in OH results from $\text{HNO}_3 \xrightarrow{h\nu} \text{OH} + \text{NO}_2$ and $\text{H}_2\text{O}_2 \xrightarrow{h\nu} 2\text{OH}$. The peak concentration in H_2O_2 occurs near 28 km, so a small percentage decrease in H_2O_2 in this region can cause a large percentage increase in OH. The increase in HO_2 is chemically linked to the increase in OH.

Figure 8 shows the effect of multiple scattering on NO_x species. There is a very large increase in NO near 20 km due to increased photolysis of NO_2 . NO_2 increases because of increased photolysis of HNO_3 . There is very little HNO_3 above 30 km, so NO_2 decreases in this region because it is essentially the only source of NO.

The effect of multiple scattering on ClONO_2 is shown in Figure 9. The concentration is reduced 20-40% between 20 and 30 km, which is the region of maximum ClONO_2 concentration. Photolysis of ClONO_2 affects several other chlorine containing species through a complex chain of reactions. Certain key reactions are:

The peak concentration of ClONO_2 occurs near 25 km, so photolysis of ClONO_2 acts as a strong source of ClO in this region. The large increase in NO between 20-30 km tends to destroy ClO, leading to a net decrease in ClO in this region (Figure 10) and an increase in Cl (Figure 11). The increase in

Cl leads to an increase in HCl (Figure 12) through reaction with CH_4 . These results also indicate that inclusion of ClONO_2 has a more significant effect on ClX species than the choice of surface albedo.

Ratios of total column abundances computed with multiple scattering to that with pure absorption were 0.94 (O_3), 0.975 (NO_2) and 1.21 (NO).

The above analysis is overly simplified considering the complexity and interaction of the various chemical cycles. Nevertheless, we have attempted to summarize the major mechanisms by which multiple scattering affects species concentrations.

3. Model Sensitivity

Model sensitivity was tested for two types of perturbations: release of CFM's at constant production levels and the stratospheric injection of NO_x . In each case calculations were made with and without ClONO_2 . The CFM calculation to steady state assumes that CFCl_3 and CF_2Cl_2 are released at 1973 rates as estimated by McCarthy (1974). The ozone reductions computed at steady state are shown in Table 3 for the various cases.

Multiple scattering significantly reduces the sensitivity of the model without ClONO_2 . The ozone reduction changed from -15.28% to -12.45% when multiple scattering was included with $A_s = 0.25$.

The model with ClONO_2 is the more complete model according to our present understanding. When multiple scattering is included in this model, there is a negligible change in model sensitivity for $A_s = 0.25$ in spite of significant changes in photodissociation rates and species concentrations. The decrease in sensitivity for the model without ClONO_2 occurs because multiple scattering shifts the balance between NO_2 and NO

toward NO. This increases the importance of the reaction $\text{ClO} + \text{NO}$ relative to $\text{ClO} + \text{O}$, thus decreasing the effectiveness of the chlorine catalytic cycle. The effect of including ClONO_2 is also reduced by multiple scattering. This occurs primarily because of increased ClONO_2 photolysis reducing the ClONO_2 concentration. Thus, while the O_3 destructiveness of the ClO_x catalytic cycle is reduced by multiple scattering, the ameliorating effect of ClONO_2 is also reduced. The net effect is that the CFM calculations including ClONO_2 with and without multiple scattering give approximately the same reduction in ozone. The model sensitivity depends upon the choice of A_s , as indicated by the reduced model sensitivity for $A_s = 0.75$.

Model sensitivity to stratospheric injections of NO_x is shown in Table 4. For these calculations, NO_x was injected globally at a rate of 2.5×10^9 kg/yr as NO_2 uniformly distributed over a 1-km thick shell centered at either 17 or 20 km altitude. Multiple scattering significantly increased the sensitivity of the model without ClONO_2 , but it had only a small effect (<5%) on the sensitivity of the model with ClONO_2 .

DISCUSSION

The results above provide a partial assessment of effect of including multiple scattering in the photodissociation rate calculation of transport-kinetics models. Multiple scattering significantly affects photodissociation rates, particularly at wavelengths greater than 290 nm, and this is reflected in the species concentration profiles. The degree to which multiple scattering affects model sensitivity to various perturbations depends upon model chemistry, solar zenith angle, and surface albedo. The assessment has not yet been extended to diurnal or two-dimensional calculations.

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TABLE 1

1976 Chemistry: O_x , NO_x and HO_x Chemistry

<u>Reaction</u>	<u>Rate</u>
$O_2 + h\nu \rightarrow O + O$	QJ(1)
$O_3 + h\nu \rightarrow O + O_2$	QJ(2)
$O_3 + h\nu \rightarrow O(^1D) + O_2$	QJ(3)
$O + O_2 + M \rightarrow O_3 + M$	$1.07 \times 10^{-34} \exp(510/T)$
$O + O_3 \rightarrow 2O_2$	$1.9 \times 10^{-11} \exp(-2300/T)$
$NO_2 + h\nu \rightarrow NO + O$	QJ(4)
$O_3 + NO \rightarrow NO_2 + O_2$	$9.0 \times 10^{-13} \exp(-1200/T)$
$O + NO_2 \rightarrow NO + O_2$	9.1×10^{-12}
$N_2O + h\nu \rightarrow N_2 + O(^1D)$	QJ(5)
$N_2O + O(^1D) \rightarrow N_2 + O_2$	7×10^{-11}
$N_2O + O(^1D) \rightarrow 2NO$	7×10^{-11}
$NO + h\nu \rightarrow N + O$	QJ(6)
$N + O_2 \rightarrow NO + O$	$1.1 \times 10^{-14} T \exp(-3150/T)$
$N + NO \rightarrow N_2 + O$	2.7×10^{-11}
$O(^1D) + H_2O \rightarrow 2OH$	2.1×10^{-10}
$O(^1D) + CH_4 \rightarrow OH + CH_3$	1.3×10^{-10}
$HNO_3 + h\nu \rightarrow OH + NO_2$	QJ(7)
$O_3 + OH \rightarrow HO_2 + O_2$	$1.6 \times 10^{-12} \exp(-1000/T)$
$O + OH \rightarrow O_2 + H$	4.2×10^{-11}
$O_3 + HO_2 \rightarrow OH + 2O_2$	$1.0 \times 10^{-13} \exp(-1250/T)$
$O + HO_2 \rightarrow OH + O_2$	3×10^{-11}
$H + O_2 + M \rightarrow HO_2 + M$	$2.08 \times 10^{-32} \exp(290/T)$
$O_3 + H \rightarrow OH + O_2$	$1.23 \times 10^{-10} \exp(-562/T)$

TABLE 1 1976 CHEM CONT

Reaction	Rate
$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$1.7 \times 10^{-11} \exp(-500/T)$
$\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	2.0×10^{-11}
$\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	$\frac{2.76 \times 10^{-13} \exp(880/T)}{1.166 \times 10^{18} \exp(222/T) + \text{M}}$
$\text{OH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3$	8.9×10^{-14}
$\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{OH}$	QJ(8)
$\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$	$1.7 \times 10^{-11} \exp(-910/T)$
$\text{N}_2 + \text{O}(^1\text{D}) + \text{M} \rightarrow \text{N}_2\text{O} + \text{M}$	2.8×10^{-36}
$\text{N} + \text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{O}$	1.4×10^{-12}
$\text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M}$	$3.96 \times 10^{-33} \exp(940/T)$
$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$	2.0×10^{-13}
$\text{H}_2 + \text{O}(^1\text{D}) \rightarrow \text{OH} + \text{H}$	2.9×10^{-10}
$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$	$1.0 \times 10^{-11} \exp(-550/T)$
$\text{N} + \text{O}_3 \rightarrow \text{NO} + \text{O}_2$	5.7×10^{-13}
$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	$1.2 \times 10^{-13} \exp(-2450/T)$
$\text{HO}_2 + h\nu \rightarrow \text{OH} + \text{O}$	QJ(9)
$\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$	$2.36 \times 10^{-12} \exp(-1710/T)$
$\text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$	$2.5 \times 10^{-33} \exp(2500/T)$
$\text{H}_2\text{O}_2 + \text{O} \rightarrow \text{OH} + \text{HO}_2$	$2.75 \times 10^{-12} \exp(-2125/T)$
$\text{O} + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_3$	$3.5 \times 10^{-11} \exp(-4550/T)$
$\text{CO} + \text{OH} \rightarrow \text{H} + \text{CO}_2$	1.4×10^{-13}
$\text{O}(^1\text{D}) + \text{M} \rightarrow \text{O} + \text{M}$	$2.2 \times 10^{-11} \exp(92/T)$
$\text{NO}_3 + h\nu \rightarrow \text{NO}_2 + \text{O}$	0.66
$\quad \quad \quad \rightarrow \text{NO} + \text{O}_2$	0.34

TABLE 1 1976 CHEM CONT

ClO_x Chemistry

Reaction	Rate
$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	$2.97 \times 10^{-11} \exp(-243/T)$
$\text{Cl} + \text{OCIO} \rightarrow 2\text{ClO}$	5.9×10^{-11}
$\text{Cl} + \text{O}_2 + \text{M} \rightarrow \text{ClO}_2 + \text{M}$	$1.7 \times 10^{-33} \left(\frac{300}{T}\right)$
$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$	$5.4 \times 10^{-12} \exp(-1133/T)$
$\text{Cl} + \text{ClO}_2 \rightarrow \text{Cl}_2 + \text{O}_2$	5×10^{-11}
$\text{Cl} + \text{ClO}_2 \rightarrow 2\text{ClO}$	1.4×10^{-12}
$\text{Cl} + \text{NO} + \text{M} \rightarrow \text{ClNO} + \text{M}$	$1.7 \times 10^{-32} \exp(553/T)$
$\text{Cl} + \text{ClNO} \rightarrow \text{Cl}_2 + \text{NO}$	3.0×10^{-11}
$\text{Cl} + \text{NO}_2 + \text{M} \rightarrow \text{ClNO}_2 + \text{M}$	$6.9 \times 10^{-34} \exp(2115/T)$
$\text{Cl} + \text{ClNO}_2 \rightarrow \text{Cl}_2 + \text{NO}_2$	3.0×10^{-12}
$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$	$3.38 \times 10^{-11} \exp(+75/T)$
$\text{NO} + \text{ClO} \rightarrow \text{NO}_2 + \text{Cl}$	$1.13 \times 10^{-11} \exp(+200/T)$
$\text{ClO} + \text{O}_3 \rightarrow \text{ClO}_2 + \text{O}_2$	$1.0 \times 10^{-12} \exp(-2763/T)$
$\text{ClO} + \text{O}_3 \rightarrow \text{OCIO} + \text{O}_2$	$1.0 \times 10^{-12} \exp(-2763/T)$
$\text{ClO} + \text{NO}_2 \xrightarrow{\text{M}} \text{ClNO}_3$	0.05*HNO ₃ formation (incl. diurnal effect)
$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{OCIO}$	$2.0 \times 10^{-12} \exp(-2300/T)$
$\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$	$2.0 \times 10^{-13} \exp(-1260/T)$
$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{ClO}_2$	$2 \times 10^{-13} \exp(-1260/T)$
$\text{HCl} + \text{O}(^1\text{D}) \rightarrow \text{Cl} + \text{OH}$	2×10^{-10}
$\text{ClNO}_3 + \text{HCl} \rightarrow \text{O}_2 + \text{HNO}_3$	0.0
$\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$	$2.0 \times 10^{-12} \exp(-310/T)$
$\text{O} + \text{HCl} \rightarrow \text{OH} + \text{Cl}$	$1.75 \times 10^{-12} \exp(-2273/T)$
$\text{ClO}_2 + \text{M} \rightarrow \text{Cl} + \text{O}_2 + \text{M}$	$1.5 \times 10^{-8} \exp(-4000/T)$
$\text{O} + \text{OCIO} \rightarrow \text{ClO} + \text{O}_2$	5.0×10^{-13}

TABLE 1 1976 CHEM CONT

 ClO_x Chemistry

<u>Reaction</u>	<u>Rate</u>
$\text{NO} + \text{OCIO} \rightarrow \text{NO}_2 + \text{ClO}$	3.4×10^{-13}
$\text{N} + \text{OCIO} \rightarrow \text{NO} + \text{ClO}$	6.0×10^{-13}
$\text{H} + \text{OCIO} \rightarrow \text{OH} + \text{ClO}$	5.7×10^{-11}
$\text{Cl} + \text{OH} \rightarrow \text{HCl} + \text{O}$	$2.0 \times 10^{-12} \exp(-1878/T)$
$\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2$	3.0×10^{-11}
$\text{Cl} + \text{HNO}_3 \rightarrow \text{HCl} + \text{NO}_3$	$4.0 \times 10^{-12} \exp(-1500/T)$
$\text{ClO}_2 + \text{HO}_2 \rightarrow \text{HCl} + 2\text{O}_2$	3.0×10^{-12}
$\text{Cl}_2 + h\nu \rightarrow 2\text{Cl}$	QCJ(1)
$\text{HCl} + h\nu \rightarrow \text{H} + \text{Cl}$	QCJ(2)
$\text{ClO}_2 + h\nu \rightarrow \text{ClO} + \text{O}(^1\text{D})$	QCJ(3)
$\text{ClO} + h\nu \rightarrow \text{Cl} + \text{O}$	QCJ(4)
$\text{ClO} + h\nu \rightarrow \text{Cl} + \text{O}(^1\text{D})$	QCJ(5)
$\text{ClNO} + h\nu \rightarrow \text{Cl} + \text{NO}$	QCJ(6)
$\text{ClNO}_2 + h\nu \rightarrow \text{Cl} + \text{NO}_2$	QCJ(7)
$\text{OCIO} + h\nu \rightarrow \text{ClO} + \text{O}(^1\text{D})$	QCJ(8)
$\text{OCIO} + h\nu \rightarrow \text{ClO} + \text{O}$	QCJ(9)
$\text{CF}_2\text{Cl}_2 + h\nu \rightarrow 2\text{Cl}$	QCJ(10)
$\text{CFCl}_3 + h\nu \rightarrow 2.5 \text{ Cl}$	QCJ(11)
$\text{CCl}_4 + h\nu \rightarrow 2\text{Cl}$	QCJ(12)
$\text{CFCl}_3 + \text{O}(^1\text{D}) \rightarrow 2\text{Cl}$	5.8×10^{-10}
$\text{CF}_2\text{Cl}_2 + \text{O}(^1\text{D}) \rightarrow 2\text{Cl}$	5.3×10^{-10}
$\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$	$5.7 \times 10^{-11} \exp(-2400/T)$
$\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{HCl} + \text{HO}_2$	$1.0 \times 10^{-11} \exp(-810/T)$
$\text{O} + \text{ClNO}_3 \rightarrow \text{ClO} + \text{NO}_3$	2.1×10^{-13}
$\text{OH} + \text{CH}_3\text{Cl} \rightarrow \text{H}_2\text{O} + \text{HO}_2 + \text{HCl}$	$1.58 \times 10^{-12} \exp(-1049/T)$

TABLE 2
COMPARISON OF PHOTODISSOCIATION RATES
CALCULATED WITH AND WITHOUT MULTIPLE SCATTERING

Altitude, km	J_{PA}	J_{MS}	J_{MS}/J_{PA}
$O_3 + h\nu \rightarrow O(^3P) + O_2$			
10	2.02×10^{-4}	3.01×10^{-4}	1.49
20	2.07	3.00	1.45
30	2.41	3.21	1.33
40	2.74	3.49	1.27
$O_3 + h\nu \rightarrow O(^1D) + O_2$			
10	5.83×10^{-6}	1.08×10^{-5}	1.85
20	7.97×10^{-6}	1.22×10^{-5}	1.53
30	5.78×10^{-5}	6.27×10^{-5}	1.08
40	9.32×10^{-4}	9.14×10^{-4}	0.98
$NO_2 + h\nu \rightarrow NO + O$			
10	4.72	7.77×10^{-3}	1.65
20	4.74	7.76	1.64
30	4.85	7.68	1.58
40	4.97	7.73	1.56
$HNO_3 + h\nu \rightarrow OH + NO_2$			
10	2.72×10^{-7}	4.82×10^{-7}	1.77
20	3.37×10^{-7}	5.18×10^{-7}	1.54
30	4.98×10^{-6}	5.11×10^{-6}	1.03
40	3.52×10^{-5}	3.52×10^{-5}	1.00

TABLE 2 CONT

Altitude, km	J_{PA}	J_{MS}	J_{MS}/J_{PA}
$H_2O_2 + h\nu \rightarrow 2OH$			
10	1.90×10^{-6}	3.35×10^{-6}	1.76
20	2.23×10^{-6}	3.46×10^{-6}	1.55
30	6.57×10^{-6}	7.29×10^{-6}	1.11
40	3.51×10^{-5}	3.52×10^{-5}	1.00
$ClO + h\nu \rightarrow Cl + O$			
10	1.72×10^{-5}	3.25×10^{-5}	1.89
20	2.55×10^{-5}	3.82×10^{-5}	1.50
30	1.92×10^{-4}	2.05×10^{-4}	1.07
40	1.64×10^{-3}	1.62×10^{-3}	0.99
$ClONO_2 + h\nu \rightarrow ClO + NO_2$			
10	3.31×10^{-5}	5.57×10^{-5}	1.68
20	3.43×10^{-5}	5.61×10^{-5}	1.64
30	5.22×10^{-5}	7.07×10^{-5}	1.35
40	2.24×10^{-4}	2.38×10^{-4}	1.06

TABLE 3

CHANGE IN THE OZONE COLUMN DUE TO THE ATMOSPHERIC RELEASE
OF CFM'S -- STEADY STATE VALUE AT CONSTANT PRODUCTION

CASE	CHANGE IN OZONE COLUMN - %		
	WITHOUT MULTIPLE SCATTERING	WITH MULTIPLE SCATTERING	RATIO
WITHOUT ClONO_2	-15.28	$A_s = 0.25$ -12.45	0.81
WITH ClONO_2	-8.97	-9.03	1.01
WITH ClONO_2	-8.97	$A_s = 0.75$ -6.91	0.77

TABLE 4

NO_x INJECTION 2.5×10^9 KG/YR AS NO₂

CASE	CHANGE IN OZONE COLUMN - %		
	WITHOUT MULTIPLE SCATTERING	MULTIPLE SCATTERING $A_s = 0.2$	RATIO
17-KM INJECTION:			
WITHOUT C/ONO ₂	-0.75	-0.97	1.29
WITH C/ONO ₂	-1.07	-1.10	1.03
20-KM INJECTION:			
WITHOUT C/ONO ₂	-3.23	-3.82	1.18
WITH C/ONO ₂	-3.93	-4.12	1.35

Fig. 1a

Fig. 1b

Fig. 1c

Fig. 1d

Fig. 1e

Fig. 1. Flux ratio versus wavelength for a solar zenith angle of 60° and selected values of surface albedo R at altitudes z of (a) 40 km, (b) 30 km, (c) 20 km, (d) 10 km, and (e) 0 km.

Fig. 2. Ambient concentration profiles of O_3 , $O(^3P)$, and $O(^1D)$.

Fig. 3. Ambient concentration profiles of OH, HO₂, and H₂O₂.

Fig. 4. Ambient concentration profiles of NO₂, NO, and HNO₃.

Fig. 5. Ambient concentration profiles of species containing chlorine.

Fig. 6. The change in O_x species concentrations due to multiple scattering with $A_s = 0.25$.

Fig. 7. The change in HO_x species concentrations due to multiple scattering with $A_s = 0.25$.

Fig. 8. The change in NO_x species concentrations due to multiple scattering with $A_s = 0.25$.

Fig. 9. The change in concentration of ClONO_2 , due to multiple scattering for $A_s = 0$ and 0.25.

Fig. 10. The change in concentration of ClO due to multiple scattering.

Fig. 11. The change in concentration of Cl due to multiple scattering.

Fig. 12. The change in concentration of HCl due to multiple scattering.

***First Annual Report of the Lawrence Livermore National
Laboratory to the High Altitude Pollution Program***

F. M. Luther et al.

**Lawrence Livermore National Laboratory
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PREFACE

During the fiscal year ending June 30, 1976, Lawrence Livermore Laboratory (LLL) participated in the High Altitude Pollution Program, which was instituted by the U.S. Department of Transportation's Federal Aviation Administration, under Reimbursable Agreement DOT-TSC-76-1 with the Transportation Systems Center in Cambridge, Massachusetts. This report describes the major accomplishments and significant findings of the LLL work performed to date. The overall research effort at LLL, which is primarily concerned with numerical modeling, has been divided into a number of subtasks according to research area. The successful accomplishment of these subtasks has required contributions and cooperation from many participants. The work reported here should be considered the collective effort of all those listed below.

Scientific Administration

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1. INTRODUCTION

The High Altitude Pollution Program (HAPP) was initiated by the Federal Aviation Administration for the purpose of ensuring that stratospheric aircraft engine emissions will not result in unacceptable effects on the biosphere. The objective of HAPP is to quantitatively determine the requirements for reduced cruise-altitude exhaust emissions and, through international and interagency cooperation, to ensure that, if necessary, appropriate regulatory action is taken. HAPP incorporates many related activities, including modeling, field measurements, laboratory measurements, engines and fuels assessment, regulation, and monitoring.

As an active participant in HAPP during the fiscal year ending June 30, 1976, Lawrence Livermore Laboratory (LLL) has undertaken an extensive effort in numerical modeling of the atmospheric response to aerospace utilization of the stratosphere. A modeling effort is important to HAPP for two primary reasons. First, modeling constitutes a means of relating engine emissions to changes in atmospheric composition. Because of the complex physical processes and feedback mechanisms involved, it is essentially impossible to assess the effects of emissions without incorporating these processes into a model and allowing them to interact. Second, modeling contributes to the interpretation and analysis of experimental results and helps determine the relative priorities for carrying out this work. The modeling effort at LLL covers four major areas of research: photochemical kinetics, coupled kinetics and transport, radiative transfer, and meteorological analysis.

Photochemical kinetics modeling must span gas-phase reaction processes and heterogeneous (i.e., gas-particle) reaction processes, constant and diurnally (and seasonally) varying photochemical reaction rates, a wide range of ambient temperatures and pressures, neutral and ionized species, processes with both accurately and poorly known rates of reaction, and species of both acknowledged and questionable importance in the stratosphere. Considerable attention has been directed toward evaluation of the sensitivity of reaction mechanisms to deficiencies in our knowledge of reaction rates, quantum yields, and reaction mechanisms.

The transport-kinetics models are intended for time-dependent calculations of the response of the stratosphere to injections of trace species by aerospace vehicles. These one- and two-dimensional models incorporate interactive radiative and chemical processes coupled with transport, which is described by prescribed mean winds and eddy diffusion coefficients

as appropriate. These models are designed to facilitate perturbation and sensitivity studies.

Radiative transfer modeling includes (1) application of highly detailed models to assessment of the effect on the radiation budget of perturbations to the stratospheric composition, and (2) development of simplified radiative transfer models for inclusion in the transport-kinetics models. Considerable attention has been directed toward including interactive radiative processes in the transport-kinetics models in order to assess possible feedback mechanisms.

Meteorological analysis provides guidance and support for the modeling efforts through in-depth studies of atmospheric processes and phenomena. A primary responsibility of this research is to develop test situations to validate various aspects of the numerical models.

In addition to these major research areas, special limited studies have been conducted using LLL's two-dimensional climate model (ZAM2). Climate model development at LLL is presently being supported by a related project involving assessment of the climatic effects of atmospheric nuclear explosions. This project, which is funded by the Division of Military Application of the Energy Research and Development Administration, and HAPP both take advantage of numerical modeling capabilities and scientific expertise developed at LLL during the Climatic Impact Assessment Program (CIAP) of the Department of Transportation. Although the same numerical models are used for both studies, the applications of the models are quite different. For example, the study of the climatic effect of nuclear explosions is primarily concerned with the time-dependent response of the atmosphere to pulse injections of NO_x , whereas the HAPP study is concerned with steady-state injections of NO_x . Tasks relating to model development or refinement benefit both projects, and consequently such tasks have been divided between the two projects. In this way each project's sponsor benefits from the participation of the other sponsor.

These two projects together constitute LLL's stratospheric research program. The various research activities included in the program and their interrelationships are diagrammed in Fig. 1. Except for the two-dimensional transport-kinetics model, we are beyond the model development stage. Because of rapidly changing chemistry and rate data, most of the effort in the transport-kinetics area during the past year has been devoted to model improvement and sensitivity studies. Research in the radiation transfer

area has concentrated on the development of subroutines for inclusion in the transport-kinetics and climate models. Several sensitivity and validation studies were conducted using the two-dimensional climate model (not sponsored by HAPP), and the results from these studies agreed well with other models. Meteorological analysis has consisted primarily of comparing model results with observations when possible and developing validation tests for the models.

A long-range objective of the research program is the development of a capability for assessing the possible climatic effects of various atmospheric perturbations. Currently, our assessments of perturbed species concentrations consider a large number of photochemical reactions and are capable of treating radiative and diurnal processes in detail, and they assume that the effects of transport on atmospheric composition can be represented parametrically. Our climatic assessments treat many interrelated

thermodynamic and hydrologic processes, and the perturbed chemical composition is treated as a given quantity. Ultimately, our assessments will include interaction between the chemistry and the dynamics.

The sensitivity studies conducted during the past year were intended to increase our understanding of the characteristics of the numerical models and the uncertainties associated with their results. The perturbations (e.g., NO_x injections) used in these studies were chosen so as to cause a significant model response rather than on the basis of an expected SST fleet size. The reader is cautioned, therefore, not to interpret the results as predictions of the effects of aerospace operations, but rather as indications of the model sensitivity. Predictions of the effects of aerospace operations on atmospheric composition must include the simultaneous injection of several species (e.g., NO_x , H_2O , and SO_2). During the next year simultaneous injections will be considered.

Fig. 1. Flow chart showing the approach LLL has taken in its stratospheric research program.

2. RESEARCH ACTIVITIES

Because of the complex nature of the work, most of the research tasks represent the combined effort of several scientists rather than individual contributions. It is not possible to separate the tasks by research area because of the team approach. Major tasks that have been completed are reported here in considerable

detail. Work still in progress and several shorter tasks that have been finished are summarized at the end of this section. Those contributions which we feel are particularly significant have been, or are in the process of being, submitted for publication in technical journals.

2.1 NO_x CATALYTIC OZONE DESTRUCTION: SENSITIVITY TO RATE COEFFICIENTS

In recent years it has been suggested that several of man's activities could result in a reduction of stratospheric ozone. This would increase the UV-B* flux at the earth's surface, and presumably result in an increase in the incidence of skin cancer. It has also been suggested that changes in stratospheric ozone might alter the climate (Grobecker et al. 1974). Among others, NO_x from stratospheric aircraft flights (Johnston 1971, Crutzen 1972), NO_x from nuclear tests (Foley and Ruderman 1973), and nuclear warfare (MacCracken and Chang 1975, National Academy of Sciences 1975a) have been proposed as capable of reducing stratospheric ozone. In order to estimate the magnitudes of these hypothesized effects, considerable effort has been devoted to the construction of numerical models of the stratosphere (Grobecker et al. 1974, National Academy of Sciences 1975b, Interdepartmental Committee for Atmospheric Sciences 1975) and acquisition of data to be used for model input and to verify model results. The major reasons for current credence in the models have been that they have used measured inputs (so that the components of the model are presumed to be separately tested) and that the models generate concentrations of stratospheric species that fall within the sometimes rather wide range of measured values.

While the above considerations are necessary for model credibility, they are not conclusive for several reasons. First, the models are known to be incomplete in various ways. All use more or less severe approximations in treating photon flux densities. All 1-D and 2-D (one dimensional and two-dimensional) models use parameterized transport. All the models use an incomplete representation of the chemistry (for example, ionic processes and heterogeneous processes are omitted or very crudely represented in existing models). Second, comparison of computed and observed concentrations is subjective since most

parameters reveal a substantial range of measured values and hence some selection must be made of the actual data to be compared. Finally, each of the input parameters has some uncertainty associated with it (e.g., in the case of the chemical rate data the uncertainties that have been estimated for many of the processes range from a few percent up to a factor of 10 (Hampson and Garvin 1975)).

The first two problems mentioned are in a sense philosophical and may not be addressable in the framework of existing "mean state" models with admittedly restricted degrees of freedom. The estimated effects of processes known to be omitted are a few percent or less. Although ionic processes have recently been suggested to be important (Ruderman et al. 1976), this argument is speculative. However, the third source of uncertainty can be examined:

In principle there are several techniques available to study quantitatively the propagation of error in a complex model (Dickinson and Gelinas 1975, Cukier et al. 1973, Schaibly and Schuler 1973, and Atherton et al. 1975). Unfortunately, at present these techniques are prohibitively expensive and are difficult to apply. Nonetheless, it is feasible to perform experiments which examine model sensitivity to perturbations in individual rate coefficients or ensembles of rate coefficients chosen with the intent of maximizing or minimizing the model response to an incremental change in some other parameter. This would then provide approximate bounds for the model's sensitivity to rate coefficient uncertainties. In this study we adjust the rate constants involved in a model of the HO_x, NO_x, and O_x reactions in the stratosphere and then examine the effects on the response of the model to an NO_x injection. This technique is useful in determining extreme ranges of possible effects, and in identifying highly sensitive parameters or groups of parameters. It is recognized that this is not very useful in estimating the probability of errors of any given magnitude. But it could give qualitative lower-limit estimates of the expectation of an effect. For even this to be done, it is necessary to estimate the

*Ultraviolet flux in the biologically active wavelength region, 280-320 nm.

distribution of expected error in the individual rate coefficients and the sensitivity of the model to subsets of the rate coefficients.

The quantitative meaning of the uncertainties quoted by Hampson and Garvin (1975) and used in this study is not easily specified. The quoted uncertainties were intended to define a range that would be expected by a panel of experienced chemical kineticists to contain the correct value (Hampson 1976). We have examined data published after the evaluations given by Hampson and Garvin for six reactions of particular importance to our model and some $O(^1D)$ reactions.* We find that for lower stratospheric conditions the mean divergence between new data and the value cited by Hampson and Garvin was about 1.2 times the cited uncertainty, but that the error distribution was very different from a normal distribution.

If, in spite of the above finding, one treats the quoted uncertainties as estimates of the expected errors (i.e., 1 σ), then the expectation that all of the varied rate coefficients will depart at least as far from the "best" values as those used in a test model, and in the same sense, will be roughly $(0.16)^n$ where n is the number of adjusted rate coefficients. However,

*The reactions examined were K6, K10, K11, K12, K14, K18, K19, K20, K26, and the reactions of $O(^1D)$ with N_2 , O_2 , and CO_2 . Only relative rates were compared for the $O(^1D)$ reactions with species other than CO_2 , which were the source of absolute rate data in Hampson and Garvin.

because the model is insensitive to many of the rate coefficients and very sensitive to a few, this methodology provides only a lower limit to the expectation of a model with a sensitivity at least as divergent from the "best" model as the model tested. If many of the parameters varied are insensitive, this lower limit would be so extreme as to be meaningless.

The basic model used for these experiments was the LLL one-dimensional model used in the CIAP documentation (Grobecker et al. 1974, Grobecker 1975). Its structure has been described elsewhere (Chang et al. 1974). This model includes the chemical reactions given in Table 1. It treats the following species dynamically (by parameterized vertical transport) as well as photochemically: O , O_3 , NO , NO_2 , HNO_3 , HO , HO_2 , H_2O_2 , N_2O . Steady-state approximations are made for $O(^1D)$, N , and H , and the concentration profiles of H_2O and CH_4 are prescribed.* The various species concentrations are solved numerically at 44 levels extending to an altitude of 55 km. In this study both the carbon cycle (except insofar as methane is a source of HO_x) and the halogen cycles were omitted. The response of the model to the choice of eddy diffusion profile was examined by Chang (1974). For this study we used the LLL diffusion profile derived in the earlier study (Chang et al. 1974). (See Fig. 2.) Nine sets of rate coefficients were examined:

*This version of the basic model is chosen specifically to provide continuity with the CIAP Report.

Table 1. Reactions and rate parameters for the various models used.

Reaction		Photolysis rates at the indicated altitudes for Model A ₂		
		55 km	30 km	15 km
$O_2 + h\nu \rightarrow 2O$	J1	7.76×10^{10}	1.90×10^{11}	8.42×10^{16}
$O_3 + h\nu \rightarrow O + O_2$	J2	2.80×10^{-4}	2.41×10^{-4}	2.07×10^{-4}
$O_3 + h\nu \rightarrow O(^1D) + O_2$	J3	4.79×10^{-3}	5.85×10^{-5}	7.90×10^{-6}
$NO_2 + h\nu \rightarrow NO + O$	J4	5.03×10^{-3}	4.85×10^{-3}	4.74×10^{-3}
$N_2O + h\nu \rightarrow N_2 + O(^1D)$	J5	4.14×10^{-7}	2.89×10^{-8}	1.44×10^{-15}
$NO + h\nu \rightarrow N + O$	J6	1.35×10^{-6}	8.90×10^{-10}	7.30×10^{-37}
$HNO_3 + h\nu \rightarrow OH + NO_2$	J7	6.38×10^{-5}	4.78×10^{-6}	3.21×10^{-7}
$H_2O_2 + h\nu \rightarrow 2OH$	J8	8.25×10^{-5}	6.39×10^{-6}	2.22×10^{-6}
$HO_2 + h\nu \rightarrow OH + O$	J9	1.98×10^{-4}	3.40×10^{-6}	1.70×10^{-10}
$NO_3 + h\nu \rightarrow NO + O_2$	J10 ₁	(Either J10 ₁ or J10 ₂ is assumed to be the only fate of NO_3 as is indicated by model subscript.)		
$NO_3 + h\nu \rightarrow NO_2 + O$	J10 ₂			

Reaction		Arrhenius A-factor ^a for indicated model			Temperature dependence ^b
Formula	Number	A	B	C	
$O + O_2 + M \rightarrow O_3 + M$	K1	1.07×10^{-34}	0.91×10^{-34}	1.26×10^{-34}	+ 510.
$O + O_3 \rightarrow 2O_2$	K2	1.9×10^{-11}	1.5×10^{-11}	2.4×10^{-11}	-2300.
$O_3 + NO \rightarrow NO_2 + O_2$	K3	9×10^{-13}	11.6×10^{-13}	7×10^{-13}	-1200.
$O + NO_2 \rightarrow NO + O_2$	K4	9.1×10^{-12}	10.4×10^{-12}	7.9×10^{-12}	-
$N_2O + O(^1D) \rightarrow N_2 + O_2$	K5	1.1×10^{-10}	0.7×10^{-10}	1.74×10^{-10}	-
$N_2O + O(^1D) \rightarrow 2NO$	K6	1.1×10^{-10}	0.7×10^{-10}	1.74×10^{-10}	-
$N + O_2 \rightarrow NO + O$	K7	1.1×10^{-14}	0.7×10^{-14}	1.74×10^{-14}	-3150.
$N + NO \rightarrow N_2 + O$	K8	2.7×10^{-11}	2.1×10^{-11}	3.4×10^{-11}	-
$N + NO_2 \rightarrow 2NO$	K9	6×10^{-12}	6×10^{-12}	0.	-
$O(^1D) + H_2O \rightarrow 2OH$	K10	3.5×10^{-10}	2.8×10^{-10}	4.4×10^{-10}	-
$O(^1D) + CH_4 \rightarrow OH + CH_3$	K11	4×10^{-10}	3.2×10^{-10}	5×10^{-10}	-
$O_3 + OH \rightarrow HO_2 + O_2$	K12	1.6×10^{-12}	0.8×10^{-12}	3.2×10^{-12}	-1000.
$O + OH \rightarrow O_2 + H$	K13	4.2×10^{-11}	2.7×10^{-11}	6.7×10^{-11}	-
$O_3 + HO_2 \rightarrow OH + 2O_2$	K14	1.0×10^{-13}	0.5×10^{-13}	2.0×10^{-13}	-1250.
$O + HO_2 \rightarrow OH + O_2$	K15	8×10^{-11}	2×10^{-11}	32×10^{-11}	- 500.
$H + O_2 + M \rightarrow HO_2 + M$	K16	2.08×10^{-32}	2.44×10^{-32}	1.77×10^{-32}	+ 290.
$H + O_3 \rightarrow OH + O_2$	K17	1.23×10^{-10}	1.0×10^{-10}	1.55×10^{-10}	- 562.
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	K18	3×10^{-11}	6×10^{-11}	1.5×10^{-11}	- 500.
$HO_2 + OH \rightarrow H_2O + O_2$	K19 ^c	2×10^{-11c}	2×10^{-10}	1.5×10^{-11}	-
$OH + NO_2 \xrightarrow{M} HNO_3$	K20 ^d	4×10^{-12}	2×10^{-12}	8×10^{-12}	- ^d
$OH + HNO_3 \rightarrow H_2O + NO_3$	K21	8.9×10^{-14}	4.5×10^{-14}	1.8×10^{-13}	-
$H_2O_2 + OH \rightarrow H_2O + HO_2$	K22	1.7×10^{-11}	2.7×10^{-11}	1.1×10^{-11}	-910.
$N_2 + O(^1D) + M \rightarrow N_2O + M$	K23	2.8×10^{-36}	5.6×10^{-36}	1.4×10^{-36}	-
$N + NO_2 \rightarrow N_2O + O$	K24	9×10^{-12}	9×10^{-12}	1×10^{-12}	-
$NO + O + M \rightarrow NO_2 + M$	K25	3.96×10^{-33}	2×10^{-33}	8×10^{-33}	+ 940.
$NO + HO_2 \rightarrow NO_2 + OH$	K26	2×10^{-13}	6.3×10^{-14}	6.3×10^{-13}	-
$OH + OH \rightarrow H_2O + O$	K27	1×10^{-11}	1.6×10^{-11}	0.63×10^{-11}	- 550.
$N + O_3 \rightarrow NO + O_2$	K28	5.7×10^{-13}	1.8×10^{-12}	1.8×10^{-13}	-
$NO_2 + O_3 \rightarrow NO_3 + O_2$	K29	1.23×10^{-13}	1.55×10^{-13}	1×10^{-13}	-2470.
$OH + CH_4 \rightarrow H_2O + CH_3$	K30	2.36×10^{-12}	2.15×10^{-12}	2.6×10^{-12}	-1710.
$OH + OH + M \rightarrow H_2O_2 + M$	K31	2.5×10^{-33}	4×10^{-33}	1.6×10^{-33}	+2503.
$H_2O_2 + O \rightarrow OH + HO_2$	K32	2.75×10^{-12}	2.34×10^{-12}	3.23×10^{-12}	-2125.
$O(^1D) + M \rightarrow O + M$	K33	5.85×10^{-11}	4.14×10^{-11}	8.26×10^{-11}	-
$CH_3 \xrightarrow{O_2} 2HO_2 + CO$		(Assumed to be the only fate of CH_3 .)			

^aConstant A in $K = A \exp(C/T)$ in units of cm^3/s (cm^6/s for three-body processes).

^bConstant C in $K = A \exp(C/T)$.

^cModel A' differs from A only in that K19 is set to 2×10^{-10} , the value used in most of the CIAP experiments.

^dK20 is pressure-dependent. In our model $K20 = K[M]/(1.12 \times 10^{18} + [M])$ where K is value tabulated above. This is a fit to the altitude-dependent expression given by Hampson and Garvin (1975).

Fig. 2. K_2 profiles that have been used by various investigators. The Chang (1974) profile was used to examine the nine sets of rate coefficients described in the text.

1. Model A_1 used the rate coefficients given in Hampson and Garvin (1975) with the rate coefficient for the reaction $\text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ (K19) set to $2 \times 10^{-11} \text{ cm}^3/\text{s}$. This is the low end of the range quoted, and the value currently preferred by us (Kaufman 1975, Lloyd 1974). Branch 1 was assumed for J10.

2. Model A_2 differed from model A_1 in that branch 2 was assumed for J10.

3. Model A'_1 differed from model A_1 in that K19 was set to the high end of the range, i.e., 2×10^{-10} , the value used for most of the CIAP computations. Branch 1 was assumed for J10.

4. Model A'_2 differed from model A'_1 by assuming branch 2 for J10.

5. Model B assumed all the rate coefficients were in error by the estimated uncertainty indicated by Hampson and Garvin (1975)* and were varied within this range with the intent of maximizing the destruction of O_3 by a given amount of NO_x , minimizing the destruction of O_3 by ambient O_x and HO_x , and minimizing the ambient concentrations of NO_x and HO_x . Branch 1 was assumed for J10.

*When a rate constant was reported to be known with higher accuracy, but only at room temperature, and the room-temperature rate constant was less than $10^{-12} \text{ cm}^3/\text{s}$, a ± 3 -fold uncertainty was assumed.

6. Model C_1 varied all rate coefficients within the same range of uncertainty with the intent of minimizing the destruction of O_3 by a given quantity of NO_x , maximizing O_3 destruction by ambient O_x and HO_x , and maximizing the ambient concentrations of NO_x and HO_x . Branch 1 was assumed for J10.

7. Model C_2 differed from model C_1 by assuming branch 2 for J10.

8. In an attempt to identify the reactions most responsible for the change in model behavior, a model C'_1 , analogous to model C_1 , was developed in which only a limited set of rate coefficients was adjusted. Branch 1 was assumed for J10.

9. Model C'_2 differed from model C'_1 by assuming branch 2 for J10.

It should be noted that the uncertainties in the photodissociation rates, which are probably even larger than the uncertainties in thermal rate coefficients, were not treated here. Several approximations are involved in the calculation of photodissociation rates, and these approximations are the subject of concurrent research.

The following computations were carried out:

1. An ambient condition was computed for each of the models.

2. The condition after 300 years of NO_x injection at 2000 molecules/ $\text{cm}^3 \cdot \text{s}$ throughout a 1-km-thick layer at 17 km altitude, the average cruise altitude of the Concorde SST, hereafter designated as NO_x -17.*

3. All models were used to compute the condition after 300 years with the above NO_x injection at 20 km, a possible cruise altitude for an "advanced" SST (NO_x -20).

4. Same as cases 2 and 3 with injection at 35 km (NO_x -35).

5. Ambient conditions (case 1) were recomputed for all models with the water column increased by 10%, roughly the magnitude of the increase in stratospheric water content expected from the hypothetical fleet of 500 Boeing SST's (Grobecker 1975) ($1.1 \times \text{H}_2\text{O}$).

6. Case 2 was repeated with the water column increased by 10% ($1.1 \times \text{H}_2\text{O}$, NO_x -17).

The calculated O_3 columns and the percent of O_3 deviation (ΔO_3) from the respective ambient conditions are given in Table 2. The effect of the choice of diffusion profile was examined for cases 1 and 2 and the results are summarized in Table 3. The K_2 profiles studied are given in Fig. 2.

*This emission rate corresponds to a very large Concorde fleet, numbered in thousands of planes. For comparison we examined a few cases assuming a tenfold smaller injection rate and found the resultant perturbations to be about ninefold smaller, suggesting an almost linear relationship between injection rate and resultant perturbation.

Table 2. Calculated ambient and perturbed O_3 column densities (10^{18} cm^{-2}) and percent deviation from the respective ambient O_3 column densities (ΔO_3) for the perturbation cases 1-6 as described in the text. See text for description of models

Case		CIAP model (high value of K19)		"Best" model (low value of K19)		Maximized re- sponse to NO_x	Minimized response to NO_x		Response to NO_x mini- mized on four rates	
		A_1	A_2	A_1	A_2	B	C_1	C_2	C_1	C_2
		J10 yields	J10 yields	J10 yields	J10 yields	J10 yields	J10 yields	J10 yields	J10 yields	J10 yields
		$NO + O_2$	$NO_2 + O$	$NO + O_2$	$NO_2 + O$	$NO + O_2$	$NO + O_2$	$NO_2 + O$	$NO + O_2$	$NO_2 + O$
1. Ambient	O_3	7.765	7.993	7.422	7.555	7.577	6.893	6.997	7.338	7.415
2. NO_x -17	O_3	7.428	7.712	7.292	7.467	6.996	7.013	7.152	7.383	7.490
	ΔO_3	-4.34%	-3.52%	-1.75%	-1.16%	-8.06%	+1.74%	+2.22%	+0.61%	+1.01%
3. NO_x -20	O_3	7.005	7.316	7.035	7.250	6.370	7.004	7.182	7.323	7.467
	ΔO_3	-9.79%	-8.47%	-5.21%	-4.03%	-15.92%	+1.61%	+2.64%	-0.20%	+0.70%
4. NO_x -35	O_3	6.426	6.767	6.377	6.614	5.674	6.450	6.663	6.663	6.837
	ΔO_3	-17.24%	-15.34%	-14.06%	-12.46%	-25.11%	-6.42%	-4.77%	-9.20%	-7.80%
5. $1.1 \times H_2O$	O_3	7.767	7.992	7.408	7.539	7.588	6.857	6.959	7.312	7.387
	ΔO_3	+0.03%	-0.01%	-0.14%	-0.21%	+0.15%	-0.52%	-0.54%	-0.35%	-0.38%
6. $1.1 \times H_2O$, O_3		7.435	7.715	7.282	7.454	6.979	6.978	7.114	7.357	7.462
NO_x -17	ΔO_3	-4.25%	-3.48%	-1.84%	-1.34%	-7.89%	+1.23%	+1.67%	+0.26%	+0.63%

Table 3. Calculated ambient (case 1) and perturbed (case 2) O_3 column densities (10^{18} cm^{-2}) and percent deviation from the respective ambient O_3 column densities (ΔO_3) for four eddy diffusion coefficient profiles as described in the text. See text for description of models

Eddy diffusion coefficient profile	Model A_1	Model A_2	Model B	Model C_1	Model C_2
Chang (1974):					
Case 1-ambient	7.422	7.555	7.577	6.893	6.997
Case 2- NO_x -17	7.292	7.467	6.966	7.613	7.152
ΔO_3	-1.75%	-1.16%	-8.06%	+1.74%	+2.22%
Crutzen (1975):					
Case 1-ambient	7.444	7.648	7.267	7.102	7.271
Case 2- NO_x -17	7.346	7.575	6.896	7.150	7.345
ΔO_3	-1.32%	-0.95%	-5.10%	+0.68%	+1.02%
Wofsy (1975):					
Case 1-ambient	7.845	8.090	7.577	7.474	7.675
Case 2- NO_x -17	7.462	7.814	6.460	7.509	7.835
ΔO_3	-4.88%	-3.41%	-14.74%	+0.47%	+2.08%
Hansen (1974):					
Case 1-ambient	7.463	7.713	7.090	7.272	7.497
Case 2- NO_x -17	6.964	7.358	5.888	7.149	7.572
ΔO_3	-6.68%	-4.60%	-16.95%	-1.69%	+1.00%

Fig. 3. Calculated equilibrium concentration profiles for O_3 compared with observations from Krueger (1973). Note that for Figs. 3-7 all surface concentrations are input, not calculated.

Fig. 4. Calculated equilibrium concentration profiles for NO_2 compared with data summary of Ackerman (1975).

The computed ambient concentration profiles are compared with observations in Figs. 3-7 for models A₁, B, and C₁. (For most species model A' closely resembled model B and model C' resembled model C. Differences due to the J10 branch were barely detectable on these semilog plots.) Only profiles for species for which we could find measurements are given here.

As can be seen, the computed ambient states for the species that have been measured in the stratosphere are rather similar for all three models (labeled simply as A, B, and C in the figures). The concentrations plotted represent diurnally averaged conditions as parameterized by a "half sun" condition (the photolysis rates used are one-half of the noontime rate as calculated by the model). Only for the QH measurements of Anderson (1976) can computed concentration profiles be said to disagree with measurement by more than the spread in recent measurements. From Fig. 7 model B would be the

most likely to be judged inadequate. However, in order to be more definitive, one must carry out detailed sensitivity analyses involving diurnal models on the details of HO_x chemistry since OH variations are highly time-dependent.

Based on present kinetics data, models B and C are highly improbable. The fact that they gave computed profiles agreeing as well as model A with present observations indicates that such agreement is insufficient to validate a model. This seems to suggest that for observational data to be used to discriminate among models the concentrations must be known within a factor of two at the very least. If, as seems probable, many trace species vary substantially in time and space, the above statement pertains to the accuracy with which the concentration distribution must be known, a much more expensive undertaking than a single measurement.

Perturbations in the O₃ column computed for a 17-km injection of NO_x (case 2) are plotted on a

Fig. 5. Calculated equilibrium concentration profiles for NO compared with data summary of Ackerman (1975).

linear scale in Fig. 8. As can be seen, the tropospheric perturbations, largely influenced by the CH_4 and NO_x smog reactions (Chameides and Walker 1973, Johnston and Quiveis 1974), are quite small compared to the stratospheric perturbations. This is in part due to our use of fixed concentrations as a surface boundary condition. We have experimented with the lower boundary condition sufficiently to demonstrate that this type of surface boundary condition has a negligible effect on computed stratospheric profiles, although the tropospheric sensitivities are significantly affected by the boundary conditions.

The opinion has been expressed that model predictions of O_3 destruction for a given NO_x injection are accurate to within a factor of 2 or 3 (Grobecker et al. 1974). As can be seen in Table 2, the perturbations in the O_3 column calculated from the base case (model A) and the most sensitive case (model B) differed by a factor of roughly 5 for a 17-km injection, 3 for a 20-km injection, and only 1.6 for a 35-km injection. Thus, in the case of maximizing the effect of an NO_x injection the uncertainty is comparable to that expected, and is not severe. Further, more than half the computed difference resulted from the variation of K19 (compare models A

and A' for case 2). However, in the case of minimizing O_3 destruction (model C), an NO_x injection at 17 km resulted in an *increase* in O_3 equal to about 25% of the decrease in the base case. For a 35-km injection of NO_x all of the models predicted an O_3 decrease, the model C decrease being about 40% as large as that of model A. Thus, the range of predicted effects is small for a high altitude injection, and the uncertainty is modest for maximizing the effect of an NO_x injection; however, the uncertainty is very substantial (encompassing a reversal of the effect) in the case of minimizing the effect of a given NO_x injection at low altitudes.

If it were necessary to vary all 33 thermal rate coefficients to the limit of their uncertainty in order to obtain this reversal, the expectation of its being realized would be almost nonexistent. However, we examined the results of the model C computation and were able to identify several key parameters that are responsible for the reversal of the calculated effect. We found in model C that at low altitudes O_3 is regulated primarily by the HO_x cycle and that the most important parameters were those regulating the HO_x concentrations, the reactions of HO_x with odd oxygen, and the reactions

Fig. 6. Calculated equilibrium concentration profiles for HNO_3 compared with data summary of Ackerman (1975).

Fig. 7. Calculated equilibrium concentration profiles for OH compared with observations by Anderson (1976) and Davis (1975). Most of Anderson's data were taken at high zenith angles, whereas Davis's data were taken at low zenith angles. Thus, the "half-sun" correction should not be applied in making comparisons with the Anderson data.

and

These reduce the efficiency of the NO_x and HO_x cycles in the lower stratosphere where the NO_x destruction cycle is already inefficient because NO_2 is usually photolyzed there resulting in the regeneration of odd oxygen.

To improve our understanding we have sought to separate the odd oxygen destruction roles of the Chapman, NO_x , and HO_x cycles. Since the cycles are known to be coupled (e.g., the NO_x and HO_x cycles

are coupled through K20, K21, and K26), it is unclear which quantities would be most illuminating. As a beginning we have defined the net odd oxygen destruction rate (D) of each of the cycles as follows:

$$D(\text{Chapman}) \equiv 2K2[\text{O}][\text{O}_3].$$

(O_2 photolysis is omitted because we wish to compare destruction terms.)

$$D(\text{NO}_x) = K3[\text{NO}][\text{O}_3] + K4[\text{NO}_2][\text{O}] + K25[\text{NO}][\text{O}][\text{M}] + K29[\text{NO}_2][\text{O}_3] \\ - K4[\text{NO}_2] - K6[\text{NO}] - K7[\text{N}][\text{O}_2] - K8[\text{N}][\text{NO}] - K24[\text{N}][\text{NO}_2] \\ + K28[\text{N}][\text{O}_3] - 110[\text{NO}_3] \text{ (if Branch 1 is assumed).}$$

(All reactions involving [N] are trivial below 50 km, as is also NO photolysis; $J10[NO_3]$ is treated as equal to the rate of NO_3 formation.)

$$D(HO_x) = K12 [O_3][OH] + K13 [O][OH] + K14 [O_3][HO_2] + K15 [O][HO_2] \\ + K17 [O_3][H] + K18 [O^1D][H_2O] - K27 [OH]^2 - J9 [HO_2]$$

(The last two terms are of little significance.)

Vertical profiles of these quantities evaluated under ambient or equilibrium conditions of models A_2 , B, and C_2 are compared in Fig. 9. The largest differences between the models appear in $D(HO_x)$, in $D(\text{Chapman})$ above 40 km, and in $D(NO_x)$

below 27 and above 45 km. Table 4 was prepared to reflect these differences quantitatively. It gives for each model the relative fraction of the integral (over the altitude range indicated) of the odd oxygen destruction rate ascribable to each of the three cycles.

The model most comparable to the models used in CIAP is A' . The instantaneous rates widely quoted from Johnston (1975) are included for comparison. The differences in results reflect differences in methodology and definitions as well as differences in rate coefficients and species concentration profiles. Our results were obtained from a 1-D time-dependent model with coupled kinetics and transport extending from 0 to 55 km using photolysis rates averaged over the diurnal cycle by taking half the rates calculated for a 45° zenith angle. Johnston's values were obtained

Fig. 8. Calculated perturbations in the O_3 profile for a 17-km injection of NO_x (case 2) plotted as departures from the ambient profiles (case 1) of the models indicated.

Fig. 9. Calculated equilibrium profiles of odd oxygen destruction rates as defined in text for models A, B, and C. Where $D(\text{NO}_x)$ forms cusps at the left border, it changes sign. Regions of net ozone production by NO_x are shaded.

from a nondynamic model integrated between "tropopause" and 45 km, but using photolysis rates for specific altitudes, latitudes, and times of day. Little quantitative significance should be attached to these integrated destruction rates since they do not accurately reflect the relative importance of the various processes in determining total O_3 . In an effort to estimate the relative importance of these processes in determining total column densities, we have weighted the various local destruction rates by the product of the local O_3 concentration and the local lifetime* for each level and integrated the results from 11 to 55 km. These weighted loss rates are insensitive to the choice of the integration limits so long as the top is above 45 km and the bottom is below 12 km.

In an effort to identify the most sensitive reactions we generated additional models by varying smaller subsets of the 33 K's listed in Table 1. We found that varying as few as three rates, K14, K18, and K26, was sufficient for an NO_x injection at 17 km to produce an increase rather than a decrease in the O_3 column. Model C' uses the values of the three K's cited above plus K20 from model C and the rest from model A. As seen in Table 2 this is sufficient for a 17-km injection of NO_x to produce an O_3 increase more than one-third as large as that produced in model C.

We also examined the effect of increased stratospheric water vapor both alone and in

*The local O_3 lifetime was defined as the ratio of the local O_3 concentration to the arithmetic sum of the net chemical loss rates and the flux of O_3 through each level.

Table 4. Relative fractions of integrated odd oxygen destruction rates ascribable to the Chapman, NO_x , and HO_x cycles for various models over the indicated domains. For "weighted" integrations the loss terms for each level were multiplied by the local O_3 concentration and the local lifetime (lifetime determined by both chemistry and transport)

Model	D (Chapman)			D (NO_x)			D (HO_x)		
	11-50 km	11-45 km	Weighted 11-55 km	11-50 km	11-45 km	Weighted 11-55 km	11-50 km	11-45 km	Weighted 11-55 km
B	0.37	0.26	0.05	0.58	0.71	0.90	0.05	0.03	0.05
A ₂	.36	.29	.06	.50	.62	.81	.15	.09	.13
A ₁	.24	.23	.07	.43	.53	.66	.33	.24	.27
A ₂	.24	.23	.07	.43	.52	.64	.33	.24	.29
C ₂	.25	.23	.09	.40	.50	.50	.35	.27	.41
C ₂	0.13	.14	0.07	0.32	.38	0.45	0.55	.48	0.49
Johnston (1975) ^a	-	0.17	-	-	0.70	-	-	0.12	-

^aJohnston used a nondynamic model to simulate a three-dimensional system. His integration was between a variable tropopause and 45 km.

combination with an NO_x injection at 17 km. As can be seen in Table 2 (case 5 compared to case 1), a 10% increase in stratospheric water vapor increased the O_3 column in model B and decreased it in A, C, and D. When the increased water vapor was imposed on a 17-km NO_x injection, the effects on the O_3 column were almost additive (case 6 compared to cases 2 and 5).

These experiments have led us to the following conclusions:

1. A value of $2 \times 10^{-11} \text{ cm}^3/\text{s}$ for K19 leads to an O_3 reduction due to a fixed NO_x injection less than half that predicted during the CIAP program.
2. The matching of computed profiles of species concentration against observations does not at present provide a definitive criterion for choosing between models, even for models as different in their response as those described here. However, HNO_3 , OH , and HO_2 differ most between the models and thus would provide the sharpest discriminators if observational data were of equal quality for all species. The observed OH data are more easily consistent with the lower value for K19.
3. Species concentration profiles must be known to better than a factor of 2 before they can be used to discriminate between models differing widely in sensitivity to NO_x injections.

4. The reactions

are of greatest importance in determining the effect on the O_3 column of an NO_x injection in the lower stratosphere. None of these processes (except, perhaps, K20) has a well-established rate coefficient under stratospheric conditions. The best chance of reducing these uncertainties is through very accurate laboratory determinations of these rate coefficients.

5. Finally, it is worth noting that uncertainty resulting from imperfect knowledge of the rates for the Chapman and NO_x O_3 destruction cycles is small (less than a factor of 2); the largest variations in the model results arose from the uncertainty in the rates for the HO_x cycle and the processes coupling the NO_x and HO_x cycles. It is also suggested in Table 2 (case 5, models A and C) that for sets of rate coefficients that tend to minimize the response to NO_x , a major injection of water vapor in the lower stratosphere could significantly reduce the depth of the O_3 layer.

2.2 SENSITIVITY OF OZONE REDUCTION FROM CHLOROFUOROMETHANES TO PARAMETER UNCERTAINTIES

Since the effect of chlorofluoromethanes (CFM's) on atmospheric ozone was initially predicted by Molina and Rowland (1974), a number of papers have been published (for example, Wofsy et al. 1975, Crutzen and Isaksen 1975, Turco and Witten 1975) describing investigations of these effects made with various one-dimensional models of the stratosphere. In this study, we examined the sensitivity of one such 1-D stratospheric model to uncertainties in some of the important parameters used in it. In particular, we examined the sensitivity of the effect of CFCl_3 and CF_2Cl_2 on total global ozone due to changes in key chemical rates and diffusion coefficients.

The calculations in this study were made with LLL's one-dimensional time-dependent model of the troposphere and stratosphere. In this model 92 chemical (and photochemical) reactions are used to dynamically describe the stratospheric vertical distributions of 20 minor atmospheric species (O^3P , O_3 , NO , NO_2 , N_2O , HNO_3 , OH , HO_2 , H_2O_2 , Cl , Cl_2 , ClO , ClO_2 , OCIO , ClNO , ClNO_2 , HCl , CCl_4 , CF_2Cl_2 , and CFCl_3) while three (H , N , O^3D) are assumed to

be in instantaneous equilibrium. Vertical distributions of N_2 , O_2 , H_2O , CH_4 , and H_2 were assumed constant throughout the calculations.

The chemical rates for six reactions important to the chlorine cycle are shown in Table 5. Other reaction rates in the model are based on the review by Hampson and Garvin (1975). Solar flux, absorption cross sections, and the calculation of photodissociation rates are as described by Gelinas (1974).

Sensitivity to Diffusion Coefficients

The vertical transport in a one-dimensional "globally" averaged model of the stratosphere is parameterized through the so-called eddy diffusion coefficient. There does not yet exist a unique approach for the derivation of a suitable set of eddy diffusion coefficients, and each modeler has his own justification for choosing a particular diffusion profile. Because there are no unambiguous reasons for choosing one profile over another, the sensitivity of the model to that choice must be examined. The various diffusion coefficients used in this study are shown in Fig. .

Table 5. Rates used for key reactions

Reaction	Rate	Source
$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	$2.97 \times 10^{-11} \exp(-243/T)$	Average of Davis et al. (1975) and Anderson et al. (1975)
$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$	5.3×10^{-11}	Watson (1974)
$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$	$5.4 \times 10^{-12} \exp(-1133/T)$	Davis et al. (1975)
$\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$	$2.0 \times 10^{-12} \exp(-310/T)$	Anderson et al. (1975)
$\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$	$2.6 \times 10^{-11} \exp(-56/T)$	Anderson et al. (1975)
$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	2×10^{-11}	Low value quoted by Hampson and Garvin (1975)

For each of the three diffusion coefficients (Chang 1974, Crutzen and Isaksen 1975, and Wofsy 1975), the following series of calculations was carried out: (1) a natural atmosphere containing no chlorine, (2) a natural atmosphere containing chlorine assuming an HCl mixing ratio of 10^{-9} by volume at the surface and a constant CCl_4 flux at the surface, and (3) model 2 plus the fluorocarbons CFCl_3 and CF_2Cl_2 introduced at the surface starting in 1950 and running through 1975 based on world fluorocarbon production data (McCarthy 1974).

In addition possible scenarios beyond 1975 have been examined with model 3: (3a) continued growth in fluorocarbon production at a rate of 10% per year, (3b) continued constant production at the 1973 production levels, (3c) continued constant production at one-half of the 1973 production level, (3d) constant production at 1973 level until a sharp cutoff in 1978 or in 1983 (model 3e).

In comparing the calculations for the three diffusion profiles, it was found that when compared to their respective chlorine-free atmospheres the inclusion of chlorine caused a reduction of total ozone of 0.50% for the Chang profile, 0.56% for the Crutzen profile, and 0.62% for the Wofsy profile. With the chlorofluoromethanes (model 3) at the end of 1975 there is a calculated reduction in total ozone (relative to the respective chlorine-containing atmospheres, model 2) of 0.77% with the Chang profile, 1.08% with the Crutzen profile, and 1.00% with the Wofsy profile. These results indicate an uncertainty due to choice of eddy diffusion profiles of approximately a factor of 0.83 to 1.17 from the mean in the ozone reduction predicted at the end of 1975. Inclusion of other natural sources of stratospheric chlorine omitted in this model would only alter the baseline level of O_3 and have minimal effect on the predicted perturbations due

to chlorofluoromethanes, especially with respect to this relative uncertainty.

The differences in predicted effects using the different diffusion profiles can be attributed to the different rates at which free chlorine (created by the photodissociation of CFCl_3 and CF_2Cl_2 mostly above 30 km) is transported to levels below 30 km. The Crutzen and Wofsy profiles allow more rapid transport of the free radical chlorine to levels where the chlorine catalytic cycle has its strongest effect on stratospheric ozone.

Figure 10 shows the reduction in total ozone calculated for the case of a continued growth in CFCl_3

Fig. 10. Sensitivity to the diffusion profile assumed is shown in these calculations of the decrease in total ozone that would result from a continued growth of 10% per year in chlorofluoromethane production beyond 1975.

and CF_2Cl_2 production beyond 1975 of 10% per year (model 3a) which corresponds to approximately a seven-year doubling time. As is expected, all predicted perturbations increase exponentially. For this scenario, the reduction of global total ozone is 5.0 to 6.92% by the end of 1990 and 13.6 to 17.8% by the year 2000. It is significant to note that there is only a three-year difference among the predictions as to the time when a given reduction in ozone is reached.

A constant production rate at 1973 levels for the chlorofluoromethanes (model 3b) was assumed in the calculated total ozone reductions shown in Fig. 11. The shaded area shows the range of ozone projections as a function of time when the 1973 production rate is used. The time after 1975 to reach a total ozone depletion of 5% ranges from 23 to 33 years, depending on the choice of diffusion profile. By the year 2000, there is a range of uncertainty of 1.3% (5.3%, Wofsy; 4%, Chang) in the predicted reduction in total ozone. Also shown in Fig. 11 is the calculated ozone depletion resulting from a constant production rate at one-half the 1973 level (model 3c). At this lowered release rate, a meaningful uncertainty range can be assigned to the projected steady-state values as well as the times needed to approach them. The different eddy diffusion models lead to ultimate ozone depletions of 6.5% (Chang) to 7.8% (Wofsy). For both scenarios the characteristic times differ very little; the time needed to reach one-half the final equilibrium depletion is 38 years for the Chang diffusion and 34 years for the Wofsy diffusion.

Fig. 11. Calculated decrease in total ozone that would result from a constant production of chlorofluoromethanes at the 1973 rate and at one-half the 1973 rate. Shaded bands show range of values resulting from assumption of different diffusion profiles.

The effect of stopping production of the chlorofluoromethanes is shown in Fig. 12. For this case (model 3d) constant production at 1973 levels was assumed until the end of 1978 when all releases were assumed to cease. For each of the tested diffusion profiles, the destruction of ozone continues for some time following the stopping of production. This happens because the troposphere, acting as a reservoir, continues to furnish a source of CFCl_3 and CF_2Cl_2 to the stratosphere. The minimum in the total ozone level occurs approximately at 8 to 13 years after production is halted, depending on the choice of the diffusion profile. At the peak reduction in ozone, there was a calculated range of 0.60-0.83% additional ozone destroyed from the 1978 levels, resulting in a peak ozone reduction ranging from 1.75 to 2.32%. As seen in Fig. 12, it takes 55 to 75 years (i.e., until 2033 or 2053) to return to the already reduced ozone levels of 1978 (when production was halted). For the three diffusion profiles studied, if the release of chlorofluoromethanes were halted in 1978, ozone reduction would continue for another decade (with an uncertainty of ± 3 years) to a peak ozone reduction a factor of 1.5 greater than the 1978 reduction, and it would take 55-75 years to return to the 1978 ozone concentrations.

With production at 1973 levels continued until the end of 1983, total ozone continues to fall for 7-10 years with a peak reduction ranging from 2.4 to 3.2% (approximately 30% greater than the 1983 values), and it would take 33-50 years to return to

Fig. 12. Calculated decrease in total ozone that would result if chlorofluoromethane production were stopped in 1978 or in 1983. Shaded bands show range of values resulting from assumption of different diffusion profiles.

the reduced 1983 ozone levels. Consequently, a five-year delay in halting production of chlorofluoromethane would entail an increase in peak ozone reduction by a factor of 1.4 lasting over an additional period of 30-50 years.

Sensitivity to Reaction Rates

Another uncertainty to be examined is the sensitivity to key reaction rate coefficients important to stratospheric chlorine chemistry. For each of six reactions, currently used rates were changed to test the sensitivity to potentially controversial rate choices. As a reference case the diffusion profile labeled Chang was used in each of these calculations. Because of this, it is the ratio of the change in O_3 relative to the standard case rather than the absolute magnitude that is of interest. It is reasonable to expect that similar fractional changes would hold for the other diffusion profiles, although the actual reductions would be somewhat different.

For the reaction $Cl + O_3 \rightarrow ClO + O_2$, the currently used value in the model is an average of two recent measurements by Davis et al. (1975) and Anderson et al. (1975). Both of these measurements agree quite well at stratospheric temperatures. However, until recently the value used for this reaction in most models (e.g., in the model of Wofsy et al. 1975) was 1.85×10^{-11} , the value given in the Watson (1974) chlorine chemistry review. Using this rate in our model, we found that the reduction in ozone by the end of 1975 increased by a factor of 1.56. Since the rates examined have a ratio of approximately 1.7 at stratospheric temperatures, the change in the ozone perturbation was nearly proportional to the increase in the rate of this reaction.

To study the sensitivity to the reaction $ClO + O \rightarrow Cl + O_2$, we varied the reaction rate coefficient from the value in Watson (1974) of 5.3×10^{-11} to a value approximately 17% lower, 4.4×10^{-11} . The reason for choosing this lower value is that it represents a recent preliminary measurement for this reaction at the University of Pittsburgh (Kaufman, private communication, 1975). With the lower value the 1975 calculated reduction in ozone was reduced by a factor of 0.88.

The rate coefficient for the reaction $ClO + NO \rightarrow Cl + NO_2$ currently used in our model, $2.6 \times 10^{-11} \exp(-50/T)$, is based on recent measurements at the University of Pittsburgh (F. Kaufman, private communication, 1975). Until recently, the rate coefficient recommended in Watson (1974), 1.7×10^{-11} , was used. With the value of 1.7×10^{-11} , the calculated reduction in total ozone for the end of 1975 increased by a factor of 1.13.

The measurement by Davis et al. (1975) of 5.4

$\times 10^{-12} \exp(-1133/T)$ for the rate coefficient of the reaction $Cl + CH_4 \rightarrow HCl + CH_3$ is the value currently used in our model. However, there is still uncertainty regarding this quantity. It differs from the earlier measurement recommended by Watson (1974), $5.6 \times 10^{-11} \exp(-1790/T)$. This rate coefficient has a large effect on the 1975 reduction of total ozone, the old value leading to an ozone reduction about a factor of 1.4 greater than the new value used in our base case.

The $OH + HCl \rightarrow H_2O + Cl$ reaction rate coefficient of $2 \times 10^{-12} \exp(-310/T)$ measured by Anderson et al. (1975) is the one currently used in our model. It agrees well at stratospheric temperatures with the value of $2.8 \times 10^{-12} \exp(-410/T)$ recommended in Watson (1974). Using the Watson rather than the Anderson et al. value changes the 1975 reduction in ozone by a factor of 0.96.

The reaction $OH + HO_2 \rightarrow H_2O + O_2$ is extremely important in determining the amount of stratospheric hydroxyl, OH. The OH distribution likewise is important in determining the conversion rate of HCl to atomic chlorine available for the ozone-destroying catalytic cycle. Though the rate coefficient for this reaction has not been directly measured, there are data which support a range of values (as recommended in Hampson and Garvin 1975), from 2×10^{-11} to 2×10^{-10} . Theory and combustion experiments tend to support the lower part of the range, although the lower temperature experiments support the high end of the range. If the range of values for this rate coefficient are used in the 1-D model, it is found that the 1975 reduction in total ozone is reduced by a factor of 0.32 for the faster rate of 2×10^{-10} . The range of uncertainty for the reaction $Cl + HO_2 \rightarrow HCl + O_2$ may also be large, but was not examined in this study. Only the estimated rate of $3 \times 10^{-11} \text{ cm}^3/\text{s}$ was used (this rate coefficient has not been measured).

Another sensitivity that is of interest is the possible presence of synergistic effects when several rate coefficients are varied. One test of this is to study the cumulative uncertainty in the rates of these reactions by choosing the rates of the six reactions such that they would maximize or minimize the effect on total ozone. Using the previously discussed values, the rates were chosen in the following manner:

	Maximize	Minimize
$Cl + O_3$	HI	LO*
$ClO + O$	HI*	LO
$ClO + NO$	LO	HI*
$Cl + CH_4$	LO	HI*
$OH + HCl$	HI*	LO
$OH + HO_2$	LO*	HI

*Indicates base case rates shown in Table 5.

HI and LO refer respectively to the faster and slower rate at stratospheric temperatures. An approximate factor of 9 was found for the ratio of predicted 1975 ozone reduction in the two extreme cases. This agrees well with the bounds obtainable through direct multiplicative superposition of the individual sensitivity factors, i.e., $(1.56)(1.42)(1.13) = 2.5$ versus the direct maximum factor of 2.3 and $(0.88)(0.96)(0.31) = 0.26$ versus the direct minimum factor of 0.25. Consequently, we conclude that there is no important synergistic effect among these six reaction rates. It should be emphasized that this max-min uncertainty range was obtained by taking some extreme values in reaction rate coefficients and does not represent the "most probable" range of uncertainty. In fact, using the individual sensitivity factors as reported above and some reasonable estimates for the expected uncertainty in individual rate coefficients, one could derive a "most likely" uncertainty range that could be significantly smaller than the present max-min range.

All of the above uncertainty analysis applies to the calculation of the ozone reduction in 1975. This provides a basis for estimating the uncertainty in the steady-state ozone reduction that is calculated in a constant-production scenario. With a constant rate of injection of CFM's into the atmosphere, the approach to the steady state of percent ozone reduction is shown in Fig. 11. These curves are well described by an exponential expression of the form $A(1 - e^{-\lambda t})$. The time-dependent term, $e^{-\lambda t}$, represents the atmospheric residence time. For the CFM's this residence time, $1/\lambda$, depends predominantly on the eddy diffusion coefficients (which determine the rate of CFM injection into and the HCl removal from the stratosphere) and on the rate of CFM photolysis. For

ozone reductions less than 15%, $1/\lambda$ depends only weakly on the chemical rate constants since the amount of HCl in the stratosphere is nearly unaffected by changes in these constants. On the other hand, these rate constants strongly affect the catalytic chain length for ozone destruction, which appears in the multiplicative constant A. This implies that a change in rate constant has, to a good approximation, the effect of a linear scaling of the entire time-dependent curve. Thus, the relative uncertainties estimated for the 1975 ozone reductions are applicable to the steady state limit of a constant-production scenario.

It should be noted that these experiments did not examine the full range of uncertainties associated with the chemical rate inputs to the model. Each of the other 86 reactions in the model has some uncertainty, and numerous reactions are omitted from the model either because there are no available data or because the reactions are considered insignificant. A "maximum" and "minimum" analysis for the complete reaction set could lead to unrealistic profiles for many species in the ambient atmosphere. Such simulations have not been carried out. The sensitivity of the model to omitted processes (e.g., heterogeneous reactions, ionic reactions) remains at present an uninvestigable problem, and potentially a serious source of error in stratospheric models.

Among the reactions that were studied, $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ stands out as the most critical. Since the stratospheric OH concentration is very sensitive to the precise value of this reaction rate coefficient and since direct laboratory measurements of this rate coefficient are very difficult, a good *in situ* measurement program may provide some very useful, although indirect, data to narrow the range of uncertainties involved.

2.3 SOLAR ABSORPTION IN A STRATOSPHERE PERTURBED BY NO_x INJECTION

While much attention has been directed toward nitrogen dioxide as a chemical reactant capable of reducing the ozone layer of the stratosphere, little attention has been directed toward its role as an absorber of solar radiation. Solar absorption by nitrogen dioxide had not been expected to be significant compared with solar absorption by ozone because many radiative equilibrium models have generated reasonable stratospheric temperature profiles without including nitrogen dioxide (e.g., Manabe and Strickler 1964). However, as will be shown, the increase in solar absorption by nitrogen dioxide may counter a significant fraction of the decrease in solar absorption by ozone following stratospheric injection of NO_x (oxides of nitrogen).

The radiative transfer model used for these calculations assumes a cloudless, plane-parallel atmosphere in which there is molecular multiple scattering and gaseous absorption above an isotropically scattering ground. The wavelength region between 187.2 and 735 nm, in which molecular oxygen, ozone, and nitrogen dioxide are the dominant gaseous absorbers, is divided into 119 spectral intervals. The atmosphere between 0 and 55 km is divided into 43 layers, which are 1 km thick up to 35 km and 2.5 km thick from 35 to 55 km. Each atmospheric layer is divided into sublayers which have an optical depth, including scattering and absorption, of less than 0.02. There may be as many as 500 sublayers depending upon the total optical depth of the

atmosphere. The Gauss-Seidel iterative scheme is used to solve the radiative transfer equation to obtain the radiative intensity at increments of 6° in the local zenith angle at each level. Components of the radiative intensity are then integrated over the upper and lower hemispheres to obtain the diffuse fluxes.

The absorption cross sections were derived from a variety of sources described in Gelnas (1974). The vertical profiles of temperature, pressure, and oxygen concentration correspond to the U.S. Standard Atmosphere (1962), and the concentration profiles for O_3 and NO_2 were derived from transport-kinetics calculations.

The two cases considered are NO_2 injections (as NO_2) at 17 or 20 km at the rate of 2000 molecules/cm³·s uniformly distributed over a 1-km-thick layer. This injection rate (2.5×10^{12} g/year) corresponds to that of a fleet of several thousand supersonic transports (Grobecker et al. 1974). The stratospheric column densities of O_3 and NO_2 for each of the three cases are shown in Table 6. The unperturbed O_3 profile corresponds to

Table 6. Stratospheric column densities (above 13 km) for O_3 and NO_2 (molecules/cm²)

Case	O_3	NO_2
Unperturbed	7.92×10^{18}	4.06×10^{15}
17-km injection	7.50×10^{18}	5.43×10^{15}
20-km injection	7.03×10^{18}	6.80×10^{15}

0.305 atm·cm of O_3 . The 17-km injection corresponds (by model calculation) to a 5.3% reduction in stratospheric O_3 and a 33.7% increase in stratospheric NO_2 , whereas the 20-km injection corresponds to an 11.2% reduction in O_3 and a 67.5% increase in NO_2 . In each case, the fractional change in the NO_2 column density is approximately six times the fractional change in the O_3 column density.

For each of the three sets of concentration profiles, O_3 and NO_2 solar absorption rates were computed for values of the solar zenith angle θ ranging from 0° to 78° and values of the surface albedo a_s ranging from 0 to 1. For the unperturbed case, the stratospheric O_3 absorption ranged from 2.95% ($\theta = 0^\circ$, $a_s = 0$) to 7.23% ($\theta = 78^\circ$, $a_s = 1$) of the incoming solar radiation. For the unperturbed case, the stratospheric NO_2 absorption ranged from 0.072% ($\theta = 0^\circ$, $a_s = 0$)

to 0.365% ($\theta = 78^\circ$, $a_s = 1$) of the solar radiation incident at the top of the atmosphere. This result verifies that the solar absorption by NO_2 is normally only a small fraction (0.024 to 0.050) of the solar absorption by O_3 .

The ratio of the increase in stratospheric solar absorption by NO_2 (with respect to the unperturbed case) to the decrease in absorption by O_3 is given in

Table 7. The ratio of the increase in NO_2 absorption to the decrease in O_3 absorption for a surface albedo of 0.25

Case	Solar zenith angle			
	0°	30°	60°	78°
17-km injection	0.38	0.40	0.45	0.50
20-km injection	0.35	0.37	0.41	0.47

Table 7 for selected solar zenith angles and a surface albedo of 0.25. This ratio varies significantly with solar zenith angle but only slightly with surface albedo. The ranges of this ratio for the 17- and 20-km injections indicate that the increase in NO_2 absorption significantly compensates (30-50%) for the decrease in O_3 absorption.

The change in stratospheric composition increases the solar radiation transmitted to the troposphere, resulting in increased tropospheric heating. More radiation is scattered upward from the troposphere and a larger fraction of this radiation escapes to space because of the increased transmission of the stratosphere. This leads to an increase in the planetary albedo and a decrease in the net solar heating of the atmosphere/earth system. An analysis of the perturbed solar radiation budget for the 20-km injection case is shown in Fig. 13 for a solar zenith angle of 60° . The increase in stratospheric absorption by NO_2 , the increase in tropospheric heating, and the increase in radiation lost to space combine to equal the decrease in stratospheric absorption by O_3 . The relative magnitudes of these various components vary with surface albedo. For small values of surface albedo, most of the net decrease in stratospheric heating goes into increased tropospheric heating. For large values of surface albedo, most of the net decrease in stratospheric heating is lost to the system as radiation scattered to space. The increase in NO_2 absorption is approximately a constant fraction of the decrease in O_3 absorption for all values of surface albedo, as was previously mentioned.

Fig. 13. Calculated decrease in stratospheric absorption by O_3 (upper curve) and the three components that make up this quantity as a function of surface albedo. This example is for the 20-km injection case and a solar zenith angle of 60° .

Although perturbations to the stratospheric composition due to NO_x injection lead to increased solar heating of the troposphere, it does not necessarily follow that these perturbations cause an increase in surface temperature. Perturbations to the longwave (IR) radiation budget must also be considered when computing changes in surface temperature. Because of the reduction in solar heating of the stratosphere, the stratospheric temperature will decrease. This reduction in emitting temperature combined with the reduction in ozone concentration results in a decrease in the downward longwave radiative flux entering the

troposphere. This cooling effect tends to counteract the increased solar heating of the troposphere. Ramanathan et al. (1975) found that the longwave effect dominates the solar effect for global mean conditions. Using a radiative-convective model and a perturbation similar to the 20-km injection case, they computed a change in surface temperature of -0.1 K.

At biologically important wavelengths (280-320 nm), solar absorption by NO_2 has only a small effect on the amount of solar radiation reaching the earth's surface. In this spectral region the optical thickness of O_3 is several orders of magnitude greater than the optical thickness of NO_2 ; thus the flux of UV-B radiation incident at the earth's surface is much more sensitive to changes in O_3 column density. Neglecting solar absorption by NO_2 leads to a slight overestimate of the biological effects from stratospheric injection of NO_x . For the 17- and 20-km injection cases considered, neglecting solar absorption by NO_2 caused the change in UV-B radiation at the earth's surface to be overestimated by 2%.

The fact that a significant fraction of the decrease in net stratospheric heating is lost to the system as radiation scattered to space has important implications for radiative equilibrium models and climatic models dependent on radiative energy balance calculations. The effect on planetary albedo of changes in atmospheric composition must be included to accurately compute the perturbed solar radiation budget. Not including the albedo effect may even lead to predicted changes in surface temperature of the wrong sign (Ramanathan et al. 1975). The effect of solar absorption by NO_2 should also be included in these models for case studies involving significant changes in NO_2 column density. Other species, such as water vapor and aerosols, should also be included in more complete analyses of SST effects, but they would not affect the qualitative results presented here.

2.4 EFFECT OF NO PHOTOLYSIS ON NO_y MIXING RATIOS

It has been suggested that the only significant sink for odd nitrogen in the stratosphere is through transport of HNO_3 to the troposphere. As a result, if NO were to be injected in the middle or lower stratosphere, the change in odd nitrogen ($NO_y \equiv NO + NO_2 + HNO_3 + N$) mixing ratio above the height of injection would be nearly constant (National Academy of Sciences 1975b, pp. 114-119).

Photolysis of nitric oxide and the subsequent reactions of nitrogen atoms with nitric oxide act as

a sink for odd nitrogen in the upper stratosphere. This paper reports an investigation of the importance of this net NO_y sink by means of a one-dimensional transport-kinetics model (Chang et al. 1974). In this model the reactions

provide a chemical sink for odd nitrogen in the upper stratosphere. Using the Chang (1974) eddy diffusion profile, a parameterization of NO photolysis as shown by Cieslik and Nicolet (1973), and the chemical reactions used by Duewer et al. (1976), we carried out the following experiments:

1. We computed an ambient NO_y mixing ratio and a perturbed NO_y mixing ratio due to an injection of NO at a rate of 2000 molecules/ $\text{cm}^3 \cdot \text{s}$ in a 1-km-thick layer centered at 17 km using our standard chemistry (with the rate constant for $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ equal to $2 \times 10^{-11} \text{ cm}^3/\text{s}$). We then repeated the calculation with the rates of the NO photolysis sink set equal to zero.

2. Both of the above sets of calculations were repeated for the Hunten eddy diffusion profile (Climatic Impact Committee 1975, p. 42) and for the Crutzen eddy diffusion profile (Crutzen and Isaksen 1975).

The NO_y mixing ratios resulting from the above calculations are given in Fig. 14. A comparison of the results with and without the NO photolysis sink implies that this sink for NO_y is responsible for both decreasing $[\text{NO}_y]$ at all altitudes and for a decrease in NO_y mixing ratio with altitude above about 30 km.

It is worth noting, however, that for the perturbed cases the changes in mixing ratio are not constant with altitude even when the photolysis sink (the only chemical sink for NO_y in the model) is removed. This is a result of a change in the net rate of the "natural" production of NO_y from the reaction

This source term changes because the ozone concentration changes. The ozone reduction leads to a decrease in $\text{O}(^1\text{D})$ concentrations at high altitudes where the proportional change in solar flux is less than the change in ozone concentration, and an increase in $\text{O}(^1\text{D})$ at low altitudes where the change in solar flux density more than compensates for the change in ozone. The changes in N_2O (because of altered solar flux) are relatively minor. The net change in the production of NO_y from $\text{O}(^1\text{D}) + \text{N}_2\text{O}$ in the model with NO photolysis suppressed is given in Fig. 15 for the three diffusion profiles.

The net changes in the ozone column for the above calculations are given in Table 8. In examining the ozone reductions it should be noted that the rate coefficients used in the current calculations are the recommended values from Hampson and Garvin (1975), with $2 \times 10^{-11} \text{ cm}^3/\text{s}$ for $\text{OH} + \text{HO}_2$. Thus, there are numerous minor changes and one major change in the rate coefficients used here compared to those used to generate the CIAP findings (Grobecker

Fig. 14. Plots of calculated ambient NO_y mixing ratio (ambient) and changes in NO_y mixing ratio (ΔNO_y) after a 17-km NO_x injection as described in the text. Solid curves are calculations with the normal model, dashed curves are calculations with the NO photolysis sink suppressed.

et al. 1974). Although omission of the N atom sink for NO_y makes a very substantial difference in the NO_y mixing ratio above 30 km, it causes only a minor increase in the percentage ozone perturbation for NO_x injections. This results because both the ambient and perturbed NO_y mixing ratios are reduced by the sink. The ozone perturbation is more strongly affected for the Hunten profile, which was used in the formula developed by NAS (National Academy of Sciences 1975b, p. 42), than for the other diffusion profiles considered.

The effect of the N atom reactions on the O_3 response of the model to a ClO_x injection is opposite in sign and larger than their effect on the O_3 response

to an NO injection. We find that the stratosphere is substantially less sensitive to chlorofluorocarbons when the N atom sink is removed from our model than when

Fig. 15. Calculated change in the odd nitrogen production rate in models with the NO photolysis sink suppressed.

Table 8. Ozone columns (molecules/cm²) and percent deviations

	Chang K_2	Hunten K_2	Crutzen K_2
Normal, ambient O_3	7.4334×10^{18}	7.4627×10^{18}	7.4437×10^{18}
Normal, 17-km NO source	7.2920×10^{18}	6.9644×10^{18}	7.3459×10^{18}
ΔO_3	-1.75%	-6.68%	-1.31%
No N atom, ambient O_3	7.2752×10^{18}	7.148×10^{18}	7.1165×10^{18}
No N atom, 17-km NO source	7.1467×10^{18}	6.630×10^{18}	7.0195×10^{18}
ΔO_3	-1.77%	-7.25%	-1.36%

it is included. A model that computed a 0.51% reduction in ozone due to chlorofluorocarbons in 1976 using our full chemistry computed only a 0.30% ozone reduction in 1976 when NO photolysis was neglected. This effect occurs because the reaction

reduces the efficiency of both the chlorine and NO_x

ozone destruction cycles, and the effect of this reaction is especially dependent on the NO_x mixing ratio above 35 km.

Thus, although models of the effects of NO_x injections on the stratosphere are not very sensitive to the NO photolysis sink for NO_x, inclusion of this sink is quite important for models of the effects of chlorofluorocarbons in the stratosphere. Indeed, the concentration of NO above 35 km is an important and poorly validated quantity in current models.

2.5 OTHER INVESTIGATIONS USING THE 1-D TRANSPORT-KINETICS MODEL

Transient Effects in the Transport-Kinetics Model

When the time-dependent response of the LLL one-dimensional model to a constant NO_x injection is computed, there is an initial period when the model computes an increase or very slowly growing decrease in total ozone. An initial increase in total ozone is obtained when the rate of the reaction of OH with HO₂ is taken to be near 2×10^{-11} cm³/s (model A, described earlier in Sec. 2.1) and the injection altitude is 17 km or less.

This behavior arises because, in the region below about 20 km, a local increase in NO_x results in an increase in the local concentration of ozone in that model, and if the injection altitude is much below 20 km, ozone is increased, until injected NO_x is transported up into the region above 20 km where it causes ozone destruction.

The increase in ozone at lower altitudes results from a combination of three factors. Given the rate coefficient used, the most important of these (in terms of the total ozone column) is the interference in HO₂ cycle destruction of ozone caused by NO_x. The intimately related methane smog reaction has a similar effect, and is the major source of the tropospheric ozone increase. The effect of high altitude reductions in ozone on the radiation reaching the lower stratosphere results in an increase in lower stratospheric ozone at later times, but has little effect on the early transient behavior.

The LLL treatment of methane oxidation uses the following reactions:

This shortcut mechanism yields roughly the correct amount of HO₂ production while underestimating O₃

production by about one-third. It avoids an increase in the number of species, and produces significant errors only in the troposphere, which is controlled by boundary conditions in any case.

The transient behavior calculated using the Chang (1974) eddy diffusion profile (Fig. 2) for a 17-km injection of NO_x at a rate of 2000 molecules/cm³·s in a 1-km-thick layer is illustrated in Fig. 16, and the transient behavior for a 10-km NO_x injection of equal magnitude is illustrated in Fig. 17. The references to branch 1 or branch 2 concern the assumed products of NO₃ photolysis. In calculating the curves labeled branch 1, NO₃ photolysis was assumed to yield NO + O₂, and in calculating those labeled branch 2, NO₂

Fig. 16. Calculated change in the total O₃ column vs time as a result of an NO_x injection (as NO₂) of 2000 molecules/cm³·s in a 1-km-thick layer centered at 17 km.

Fig. 17. Calculated change in the total O_3 column vs time as a result of an NO_x injection (as NO_2) of 2000 molecules/cm³·s in a 1-km-thick layer centered at 10 km.

+ O were the assumed products. Figure 18 presents the altitude-dependent change in ozone concentration after 0.2, 0.8, 2, 5, and 10 years for the 10-km NO_x injection assuming branch 1.

The results described here are of qualitative significance. They are sensitive to the choice of poorly-known rate constants, and are expected to be quite sensitive to the eddy diffusion profile. The greatest uncertainty is associated with low altitude injections of NO_x . Thus, the qualitative results should be treated cautiously.

New Eddy Diffusion Coefficient Profile

A new vertical eddy diffusion coefficient profile has been derived for the 1-D transport-kinetics model. This profile was designed to improve the fit with methane and nitrous oxide measurements in the upper stratosphere. It was necessitated by the requirement for improved representation of transport in the upper stratosphere where the distribution of chlorofluoromethanes becomes important. The new eddy diffusion coefficient profile (shown in Fig. 19) provides for increased transport in the upper stratosphere.

Fig. 18. Calculated change in ozone concentration vs altitude after 0.2, 0.8, 2, 5, and 10 years for the 10-km NO_x injection of Fig. 17.

Effect of ClONO₂ in the Stratospheric Model

The effect of adding ClONO₂ to the 1-D transport-kinetics model is shown in Table 9. The

Fig. 19. New vertical eddy diffusion coefficient profile (Chang 1976) compared with the previously used profile (Chang 1974).

actual reaction rate for formation of ClONO₂ is unknown at present, but preliminary measurements (Kaufman 1976, Birks 1976, DeMore 1976, all private communication) have indicated the rate coefficient is between 0.05 and 0.1 times that for formation of HNO₃. Case 0 refers to the model without ClONO₂. In case 1 the ClONO₂ production rate was assumed to be 0.1 times that of HNO₃, and in case 2 the ClONO₂ production rate was assumed to be 0.05 times that of HNO₃. A reaction rate of $2 \times 10^{-13} \text{ cm}^3/\text{s}$ (Davis 1976, private communication) was used for the ClONO₂ + O(³P) in cases 1 and 2. The photolysis rate calculated in the model for ClONO₂ includes the recently revised absorption cross sections from Spencer, Molina, and Rowland (1976), and the new Chang diffusion profile (Fig. 19) was used in all calculations.

As seen in Table 9, the effect of ClONO₂ is to reduce the effectiveness of the ClO_x released by the chlorofluoromethanes by approximately a factor of 2. With constant production of the chlorofluoromethanes at 1973 levels, the ozone reduction by the year 2176 changes from 13.68% without ClONO₂ to 7.47% for case 2 which has ClONO₂ produced at 0.05 times the rate of HNO₃. In the model, the effect of ClONO₂

Table 9. Percent change in total ozone from ambient atmosphere (containing CCl₄ and CH₃Cl) due to chlorofluoromethanes

	1974	1976	2176 (constant production at 1973 levels)
Case 0 (without ClONO ₂)	0.61	0.86	13.68
Case 1 (with ClONO ₂ = 0.1 HNO ₃)	0.23	0.30	4.87
Case 2 (with ClONO ₂ = 0.05 HNO ₃)	0.38	0.51	7.47
Case 2 (with ClONO ₂ and rate change):			
OH + HO ₂ → H ₂ O + O ₂ (2×10^{-11} ; 2×10^{-10})	0.02	0.03	—
Cl + O ₃ → ClO + O ₂ ($2.97 \times 10^{-11} e^{-243/T}$; 1.85×10^{-11})	0.43	0.59	—
ClO + O → Cl + O ₂ ($3.38 \times 10^{-11} e^{-75/T}$; 5.3×10^{-11})	0.38	0.53	—
ClO + NO → Cl + NO ₂ ($1.13 \times 10^{-11} e^{-200/T}$; 1.7×10^{-11})	0.40	0.55	—
Cl + CH ₄ → HCl + CH ₃ ($5.4 \times 10^{-13} e^{-1133/T}$; $5.6 \times 10^{-11} e^{-1790/T}$)	0.41	0.56	—
OH + HCl → H ₂ O + Cl ($2.0 \times 10^{-12} e^{-310/T}$; $2.8 \times 10^{-12} e^{-410/T}$)	0.33	0.45	—

occurs primarily below the altitudes of importance for the ClO_x catalytic cycle. The peak concentration of ClONO_2 occurs at approximately 25 km. At this altitude, the effect of ClONO_2 is primarily to reduce

the available NO_x (for the NO_x - O_3 cycle) in a region where O_3 removal is dominated by NO_x , thus compensating somewhat for the reduction of ozone occurring above due to ClO_x . The peak concentrations

Fig. 20. Calculated concentrations of ClO and ClONO_2 at various altitudes vs time of day, based on diurnally varying model and constant-sun model.

of ClONO_2 for both cases 1 and 2 are less than the upper limit of 10^9 molecules/cm³ given by Murcay (1976).

Also shown in Table 9 is the effect of varying the same six reactions discussed above when ClONO_2 is included in the model. The rates shown in parentheses indicate the rates normally used in the model (on the left) and the rates used to test the model's sensitivity (on the right). Whereas changing the rate coefficient for $\text{OH} + \text{HO}_2$ from 2×10^{-11} to 2×10^{-10} cm³/s had reduced the effectiveness of ClO_x by a factor of 3.1 without ClONO_2 , the effect with ClONO_2 is to reduce the change in total ozone by a factor of 17 (from 0.51% to 0.03%) for the year 1976. This increased sensitivity is attributed to ClONO_2 tying up NO_x in an atmosphere where O_3 is predominantly controlled by NO_x when $\text{OH} + \text{HO}_2$ is 2×10^{-10} cm³/s (this rate will reduce the OH available to react with NO_2 to produce HNO_3 , resulting in increased NO and NO_2 levels relative to when the rate is 2×10^{-11}).

Diurnal calculations have also been carried out for the model containing ClONO_2 . The diurnal variations of ClO and ClONO_2 after the 12th day (starting from the constant-sun model results) are shown in Fig. 20. The diurnal calculation shows less diurnally averaged ClONO_2 as compared with values from the constant-sun calculation (see crosses in Fig. 20). This is due to conversion of some of the ClONO_2 to HCl through the diurnal variation of NO_x and ClO_x species.

Effects of $\text{O}_3 \xrightarrow{h\nu} \text{O}(^1\text{D}) + \text{O}_2$ Quantum Yields Near Threshold

In comparing our model results with similar results from the Michigan and NCAR groups, we found that

the LLL model yielded about half the total stratospheric NO_x contained in the other models. The reason was that the other modeling groups were assuming a unit quantum yield for $\text{O}(^1\text{D})$ production from ozone photolysis at wavelengths shorter than 310 nm and zero at longer wavelengths (as recommended by Hampson and Garvin 1975), whereas we were using the formulation

$$\phi(\text{O}^1\text{D}) = 1 - \frac{1}{1 + e^{(\lambda - 303)/1.6}} \quad \text{for } \lambda < 305 \text{ nm},$$

$$\phi(\text{O}^1\text{D}) = \frac{1}{1 + e^{(\lambda - 303)/4.8}} \quad \text{for } 305 < \lambda < 330 \text{ nm},$$

which was recommended by Johnston (1973). Use of Johnston's expression reduces the lower stratospheric $\text{O}(^1\text{D})$ production by about a factor of 2 relative to the 310-nm step function and accounts for most of the differences in NO_x between the LLL model and the other models. Because an abrupt threshold is theoretically unlikely and seems incompatible with recent results, we believe the form of expression used in our model to be superior to the 310-nm step function. However, we recognize that the temperature dependence and precise value of $\text{O}(^1\text{D})$ in the 300-to-315-nm range is quite uncertain. Thus the expression used is significantly uncertain. The sensitivity of stratospheric NO_x to an incremental NO_x injection is fairly sensitive to the ambient NO_x concentration (in an atmosphere with doubled NO_2 the response of total ozone in model A to a 17-km NO_x injection changed from a base case 1.75% decrease to a 1.35% decrease). Also, depending on the importance of chlorine nitrate, the response of ozone to a source of stratospheric chlorine may be quite sensitive to the ambient NO_x concentration.

2.6 COMPARISON OF MODEL RESULTS WITH OBSERVATIONS

Catalytic Destruction of Ozone

We have been collecting observational data believed to have a bearing on the validity of the catalytic destruction of stratospheric O_3 . The data qualitatively confirm the current theory for short-period responses of O_3 at levels above 30 km to polar cap absorption events (PCA's) and changes in solar flux. Above 30 km the stratosphere is in photochemical equilibrium, and ozone should be controlled by photochemistry in this region. The data reveal that dynamics may be the dominant controlling process affecting long-term trends in ozone below 30 km.

Specific examples of differences between model

results and observational data are cited below. These differences reveal areas where we have limited understanding about the processes that may be affecting ozone. Further research is needed to satisfactorily explain these differences.

1. O_3 and nuclear tests. Since 1962, total O_3 has increased to mean levels higher than observed before atmospheric nuclear testing. Consequently catalytic destruction of ozone by NO_x generated during nuclear tests could not be the only controlling mechanism affecting ozone during this period.

2. O_3 and PCA's. There is no apparent dose response relationship either in terms of the relative

intensities of the PCA's of 1959, 1960, 1966, and 1972 or in terms of the colatitude of the O_3 data.

3. Correlation of O_3 with sunspots. One method in which ozone might be affected by solar activity adopts the following argument (Ruderman and Chamberlain 1975): An increase in sunspot activity $\rightarrow$ increased solar wind $\rightarrow$ decreased cosmic ray flux into the upper atmosphere $\rightarrow$ decreased NO production $\rightarrow$ increased ozone. This theory is not consistent with the observed variations of total ozone. O_3 oscillations decreased in amplitude as the sunspot amplitude increased up to 1969. Total O_3 increased from a peak sunspot maximum of 1957 to the very low sunspot maximum of 1969. Before 1954, O_3 oscillations lagged sunspots by about three years; after 1963 the variations appear almost in phase. O_3 amplitudes exceed amplitudes computed from the Ruderman and Chamberlain (1975) theory by about tenfold. There are rather large hemispheric differences in the apparent 11-year oscillations in O_3 .

4. Seasonal changes in total O_3 . The area with the best long-period O_3 data, Western Europe, shows between 1955 and 1970 a 14% increase in winter O_3 and only 4% in summer O_3 . This suggests processes other than photochemistry.

5. High O_3 mixing ratios in polar night. Heath (1974) reported BUW observations of a 4-mbar O_3 mass mixing ratio of 23 ppm at $70^\circ N$ on 2 January 1971, 44% above the maximum of 16 ppm normally observed in the tropical stratosphere. Unless the high O_3 measurement is due to instrument difficulties, this is highly suggestive of a nonphotochemical O_3 source not included in any current models.

6. Total O_3 following Agung eruption. Uniform global mixing of the estimated 1-MT stratospheric injection of Cl is computed (Ryan and Mukherjee 1975) to cause a decline in total O_3 of approximately

5%. If the bulk of the Cl from Agung remained in the southern hemisphere as did the bulk of the Agung dust, even larger changes in O_3 should have occurred there. O_3 observations show, if anything, an increase in total O_3 following the eruption.

Due to the sparseness and possible unreliability of some of the data, most of these differences cannot be resolved at the present time. We have indicated, however, several areas in which more data of a reliable nature would be very helpful.

Effect of Sudden Stratospheric Warmings on Global Ozone

To simulate and facilitate further investigation of the possibility that variation in the global ozone amount is caused by sudden stratospheric warmings (SSW's), observed SSW's were tabulated by year, date, and measure of intensity. It was noted that in the winters having major SSW's (1962-63 and 1967-68), total O_3 not only rose to higher levels sooner but also remained above the minor SSW winter of 1966-67 throughout the following spring and summer. The data since 1955 indicate that a minor SSW is the normal situation in the northern hemisphere and only the major warmings are abnormal. One can then hypothesize that the O_3 trend since 1958, down until 1962 and up since 1963, is due to major SSW's alone. This would also explain why the trend in the southern hemisphere appears to be much weaker or even reversed, since fewer and weaker SSW's occur in the southern hemisphere. Christie's (1973) O_3 analysis fits this hypothesis very well, as shown in Fig. 21, where the years with major SSW's have been circled. The fit with O_3 trend analyses of others is not so good, but this appears to be a problem plaguing all current theories. Later analysis suggests that late-season major SSW's culminating after the end of January have little effect on mean annual O_3 for the following year, e.g., the major SSW of 19 January through 6 February 1957. Admittedly, some of these arguments are speculative, but it is hoped that these ideas will stimulate further research and exchange of ideas which might clarify this possible climatic mechanism.

Fig. 21. Time series of annual mean values of ozone deviation. Circles indicate years with major sudden stratospheric warmings. (After Christie 1973.)

2.7 POSSIBLE CAUSE OF THE PRE-1970 INCREASE IN OZONE

The upward trend in total O_3 in the northern hemisphere from about 1957 to 1970 might be attributable to a change in the general circulation. Those proposing such explanations (e.g., Komhyr et al. 1971, Crutzen 1972) have tended to be nonspecific as to what changes have occurred, since we are lacking in understanding in this area. Empirical deduction seems to indicate that a weakening of the Hadley circulation and consequently of the exchange of air between the troposphere and the stratosphere would lead to an increase in stratospheric O_3 . This conclusion rests strongly on the opinion prevailing prior to the unveiling of the NO_x catalytic cycle that the troposphere was the major sink for stratospheric O_3 . Current theory is remarkably consistent in showing that in the extratropical lower stratosphere, O_3 concentrations are in excess of those predicted by photochemical equilibrium. A slowdown in tropospheric-stratospheric exchange would appear to allow more time for O_3 in this region to decay to the photochemical equilibrium concentrations, but that effect may well be overpowered by other effects. A slowdown in tropospheric-stratospheric exchange also reduces the upward rate of transfer of N_2O to the 25-to-30-km level, where it is oxidized to NO by $O(^1D)$, and allows more time on the way up for the N_2O to be photodissociated, producing N_2 rather than NO . And secondly, since the Hadley cell is driven by tropical convection which in turn maintains upward pressure on the tropical tropopause, any weakening can be expected to allow a lowering and warming of the tropical tropopause. This in turn would allow a higher mixing ratio of H_2O through the cold trap of the tropical tropopause.

Thus a weakening of the Hadley circulation with resultant slowing of the tropospheric-stratospheric exchange has at least three consequences, all of which appear to lead to increases in the stratospheric reservoir of O_3 :

1. It reduces the rate of transfer of O_3 from the storage region of the lower stratosphere to underlying well-mixed troposphere and O_3 -destroying surface boundary layer (i.e., it reduces the tropopause value of the K_2 of the 1-D model). This should result both in a reduction in the tropospheric concentration and surface destruction rate of O_3 and an increase in total O_3 in the storage reservoir of the lower stratosphere.

2. It slows the upward flux of N_2O , thus allowing more time for photodissociation and reducing the fraction that is oxidized by $O(^1D)$ to form NO . It also presumably allows more time for operation of the unknown tropospheric sink, thus assuring that an even smaller fraction survives to produce NO in the stratosphere.

3. It allows a lowering and warming of the tropical tropopause, which in turn allows a higher H_2O mixing ratio to pass through the tropical tropopause cold trap and to increase the humidity of the stratosphere. This in turn ties up a larger fraction of stratospheric NO_y as HNO_3 , reducing the fraction capable of attacking O_3 catalytically.

There remains the nagging problem that the pre-1970 increase in total O_3 appears to have been a phenomenon only of the northern hemisphere while the Hadley cell is usually regarded as a global phenomenon. This is not necessarily an insurmountable problem. We know that the northern hemisphere (winter) Hadley cell is stronger than the southern hemisphere (summer cell) — twice as strong according to Reed and Vlcek (1969), and almost ten times as strong according to Dütsch (1972) — and that the tropical tropopauses of both hemispheres vary in unison on an annual cycle, i.e., highest and coldest in January and February (pushed up by the northern-hemisphere Hadley cell) and lowest and warmest in July and August when the weak southern-hemisphere Hadley cell is operative (Smith 1963). This seems to indicate that the Hadley circulation and its control of the tropical tropopause and tropospheric-stratospheric exchange is strongly asymmetric, due presumably to both the distribution of land and sea and the eccentricity of the earth's orbit; the former amplifies latitudinal temperature gradients to strengthen the northern-hemisphere Hadley cell, and the latter causes the received solar flux in January to exceed that of July by nearly 7%, again strengthening the northern hemisphere cell. Thus, restriction to the northern hemisphere of the pre-1970 increase in O_3 becomes an additional argument supporting a relationship between the increase and the tropospheric-stratospheric exchange rate since the latter and the nuclear test hypothesis are the only ones proposed which would lead to a hemispheric as opposed to a global phenomenon.

Finally, it is necessary to establish that there was a progressive weakening of the Hadley circulation and a slowdown in tropospheric-stratospheric exchange for approximately a decade prior to 1970-71. This is attested to by the following evidence.

1. Angell and Korshover (1974) found a 5-to-7-mbar/decade increase in tropical tropopause pressure which appeared to have begun about 1957. Associated with it was a warming of the tropical tropopause at Singapore and Gan of approximately 1 K/decade, which they suggested might be related to the increase in H_2O mixing ratio in the lower stratosphere observed by Mastenbrook (1971) over Washington, D.C., between 1964 and 1970.

2. Measurements of Junge layer stratosphere aerosols by both airborne collectors and remote sensing reported a minimum and virtual disappearance of the layer in mid-1971 (Fox et al. 1973). While the major thinning of the layer from 1963 to this time has been related to the M. Agung and subsequent volcanic eruptions, the 1971 levels represented a significant decline over the pre-Agung values reported by Junge and Friend. This is even more apparent after application to the pre-Agung data of the 5-to-6-fold correction for impactor collection efficiency which now appears appropriate (Cadle and Grams 1975). Since gaseous sulfur and particulates, like all other material not episodically injected into the stratosphere (as by volcanoes, etc.), must enter through the Hadley circulation, the pre-Agung-to-1971 thinning of the Junge layer suggests a weakening of the Hadley circulation.

3. Winstanley (1973) reported for the Sahel strip

of Africa and India a continuing decline in summer monsoonal rainfall since the late 1920's, apart from a temporary reprieve in the early 1950's. The recent drought was the result of the cumulative effects of a decade of below-average monsoon rainfall with less and less rain each year through 1970.

Since tropical convection cells penetrating the tropical tropopause are likely to decrease even more than summer ITCZ (intertropical convergence zone) and monsoonal rainfall in general, Winstanley's data also indicates a progressive weakening (from about 1957 to 1970) of the Hadley circulation and, thus, of tropospheric-stratospheric exchange.

The above, of course, does not constitute proof, but does appear to indicate rather strongly that a progressive 10-to-13-year-long weakening of the Hadley cell and of tropospheric-stratospheric exchange is responsible for the progressive northern-hemisphere increases in total O_3 observed up through 1970.

2.8 WORK IN PROGRESS

Temperature Feedback in a Stratospheric Model

Perturbations to the stratospheric composition affect the stratospheric temperature profile via the solar and longwave radiation balance. Changes in temperature affect chemical reaction rates, which in turn feed back on stratospheric composition. The temperature feedback mechanism has long been recognized as potentially important in mitigating perturbations to the ozone concentration, but it has only recently been included in stratospheric models. Barnett et al. (1975) have investigated the temperature dependence of ozone concentration near the stratopause, and they showed that a decrease in temperature tends to increase the ozone concentration.

In order to investigate the effect of temperature feedback on the concentration of ozone, LLL's one-dimensional transport-kinetics model was coupled to a stratospheric radiative transfer model. The temperature profile is determined using a radiative equilibrium calculation with convective adjustment. The model includes solar absorption and longwave interaction by O_3 , H_2O , and CO_2 along with solar absorption by NO_2 . The techniques adopted for treating longwave radiative transfer are the same as those described by Ramanathan (1974). A band absorbance formulation is used to treat the 9.6- μm band of O_3 and the fundamental and several weak bands of CO_2 and its isotopes in the 15- μm region. An emissivity formulation is used to treat longwave radiative transfer by H_2O . Solar absorption by O_3 is treated using the empirical formulation given by Lindzen and Will (1973). Band absorbance

formulations are also adopted for treating solar absorption by H_2O and CO_2 . The empirical formulation of Luther (1976) is used for solar absorption by NO_2 . Solar absorption by O_3 and NO_2 are treated independently because absorption by these species is weak in the region where their absorption bands overlap. Solar radiation scattered from the troposphere is included assuming an albedo of 0.3.

A single cloud layer is included at 6.5 km with 42% cloud cover as suggested by Cess (1974). The lapse rate within the troposphere is assumed to be wet adiabatic (6.5 K/km), and the temperature at the earth's surface is specified to be 288 K. The tropopause height and the temperature profile within the stratosphere are computed by the model. The CO_2 mixing ratio is assumed to be 320 ppm by volume.

The temperature profile generated by the radiative equilibrium model is shown in Fig. 22. This profile is similar to temperature profiles observed at tropical latitudes. The temperature profile from the *U. S. Standard Atmosphere* (1962), which represents a midlatitude average, is shown for comparison since this profile is frequently assumed for transport-kinetics calculations which neglect temperature feedback. The unperturbed temperature profile, which we will hereafter refer to as the "ambient," is similar in shape to the standard atmosphere but is a few degrees warmer above 20 km. The higher temperature is related to the model-generated ozone concentration. There is excellent agreement when the midlatitude ozone profile from the *U. S. Standard Atmosphere Supplements* (1966) is used to generate an ambient

Fig. 22. Temperature profile derived by the model for unperturbed conditions compared with the U. S. Standard Atmosphere temperature profile.

temperature profile. Large-scale dynamical processes are neglected in the determination of the temperature profile. The processes have a significant effect on the temperature profile near the tropopause at midlatitudes. Including these effects would likely lessen the temperature gradient above the tropopause.

The model was applied to two perturbations to test the significance of temperature feedback on ozone concentration. The perturbations considered were stratospheric injection of NO_x and fluorocarbon production.

Stratospheric injection of NO_x . The effect of stratospheric injections of NO_x by supersonic transports (SST's) on ozone concentration was computed for four cases:

1. No temperature feedback; U. S. Standard Atmosphere (1962) temperature profile assumed.
2. No temperature feedback; ambient temperature profile from radiative equilibrium model assumed.
3. With temperature feedback.
4. Temperature feedback without including solar absorption by NO_2 .

The first case is an assumption frequently made in transport-kinetics calculations. The second case is the reference condition for comparison with the temperature feedback calculation, which is the third case. The fourth case is included to indicate the significance of neglecting solar absorption by NO_2 . These calculations are not intended to imply the effect

of a particular fleet of SST's since they do not include the injection of other species such as H_2O and SO_2 . Once the significance of temperature feedback is determined for the NO_x perturbation alone (which can be compared with other calculations), then the case of temperature feedback with multiple perturbations will be considered.

The reduction in the ozone column caused by the stratospheric injection of NO_x is shown in Fig. 23 for the case with temperature feedback. The NO_x injection rate as NO_2 represents a global average value uniformly distributed over a 1-km-thick layer centered at the indicated altitude. The ozone reduction is a steady state value obtained from a time-dependent calculation as it approached equilibrium. Relatively large levels of injection of NO_x are required to reduce the ozone column more than a few percent. The ozone reduction values in Fig. 23 are smaller than previously reported (Chang 1975) by about a factor of 2 due to changes in the chemistry, especially the $\text{OH} + \text{HO}_2$ reaction rate. The reaction rate presently used for $\text{OH} + \text{HO}_2$ is $2 \times 10^{-11} \text{ cm}^3/\text{s}$, whereas previously we used the upper limit $2 \times 10^{-10} \text{ cm}^3/\text{s}$ (Hampson and Garvin 1975).

The ratio of the ozone reduction for each given case to the ozone reduction with temperature feedback is

Fig. 23. Calculated ozone reduction vs. NO_x injection rate for 17- and 20-km injection heights.

shown in Fig. 24 for the 17-km injection. There are significant differences between the various cases for small NO_x injection rates. The two cases without temperature feedback demonstrate the sensitivity of the calculation to the assumed temperature profile. The ozone reduction using the *U. S. Standard Atmosphere* (1962) temperature profile is as much as 13% greater than for the ambient temperature profile, the difference decreasing with increasing NO_x injection rate.

The ozone reduction with temperature feedback but without solar absorption by NO_2 is substantially less than for the other cases. Neglecting solar absorption

by NO_2 , which is important for the perturbed stratosphere, leads to an overestimate of the stratospheric temperature change and, consequently, an overestimate of the temperature feedback effect.

The results for the 20-km injection case are shown in Fig. 25. Although the range of NO_x injection rates is the same as in the previous figure, the range of ozone column reduction is much greater. The results are similar to the 17-km injection case, but the difference between the various cases is not quite as large. The ozone reduction with temperature feedback is about 5% less than that with fixed ambient temperature for

Fig. 24. Calculated ratio of ozone reduction for a given case to ozone reduction with feedback vs NO_x injection rate for a 17-km injection height. Calculation assumes the NO_x injection is uniformly distributed in a 1-km-thick layer centered at injection height.

Fig. 25. Calculated ratio of ozone reduction for a given case to ozone reduction with feedback vs NO_x injection rate for a 20-km injection height.

small NO_x injection rates, and the crossover occurs near 14% ozone reduction.

Fluorocarbon Production. The natural atmosphere for these calculations contained HCl with an assumed mixing ratio of 10^{-9} by volume at the earth's surface and a constant CCl_4 flux at the surface. The fluorocarbons CFCl_3 and CF_2Cl_2 were introduced at the surface starting in 1950 and running through 1975 based on world fluorocarbon production data (McCarthy 1974). The computed reduction in the ozone column resulting from the atmospheric release of fluorocarbons during this period of time is shown in Fig. 26.

The reduction in the ozone column at the end of 1975 is 0.62% for the case with temperature feedback. The ozone reduction for the fixed-temperature

calculation using the ambient temperature profile is a factor of 1.09 greater than for the case with temperature feedback. With the *U. S. Standard Atmosphere* (1962) temperature profile, the ozone reduction is a factor of 1.18 greater. As in the case of NO_x injection, the results are sensitive to the assumed temperature profile for the fixed-temperature calculations, and temperature feedback significantly mitigates the ozone reduction. Temperature feedback reduces the maximum percentage change in ozone, which occurs near 40 km. The maximum change in absolute concentration occurs at 28 km.

Summary of Temperature Feedback Investigations. The effect of temperature feedback on ozone concentration has been investigated for two perturbations to the atmospheric composition.

Temperature feedback was found to have a similar effect for both the stratospheric injection of NO_x and fluorocarbon production. In both cases temperature feedback had a 5-10% restoring effect on the ozone column for small ozone reductions. Comparing calculations based on either fixed-temperature profiles, temperature feedback, or temperature feedback neglecting solar absorption by NO_2 revealed these additional important points:

1. Fixed-temperature calculations are quite sensitive to the assumed temperature profile.
2. Calculations of $\Delta\text{O}_3/\text{O}_3$ due to NO_x injection alone including temperature feedback may be as much as 20% less than those using the U. S. *Standard Atmosphere* (1962) temperature profile.
3. Calculations that neglect solar absorption by NO_2 significantly overestimate the effect of temperature feedback for perturbations involving NO_x injection.

As the chemical kinetics and transport models of the stratosphere continue to improve in detail, the effects due to temperature feedback will become increasingly important and must be considered in any assessment of potential perturbations to the atmospheric composition.

Variation of Tropospheric Minor Species

We are examining the latitudinal and diurnal variations of tropospheric minor species with particular attention to OH. This is an initial effort to improve the transport-kinetics model's capability to treat tropospheric residence times for modeling of aircraft injections and also for possible replacement chlorofluoromethanes in aerosols and refrigeration. According to model calculations, most of the tropospheric OH is contained within the tropical region ($\pm 30^\circ$ latitude). Diurnal calculations indicate a sinusoidal variation in the daytime concentration of OH at tropospheric altitudes, with the maximum concentration occurring at noon. Very small nighttime OH concentrations are predicted.

Since the HO_x species (OH, HO_2 , and H_2O_2) have very short lifetimes in the troposphere (on the order of a few seconds for OH and 10^4 seconds for HO_x as calculated by the model), it is possible to calculate the altitudinal and latitudinal variation of OH in the troposphere with the 1-D model without considering horizontal transport. The primary formation of OH in the troposphere comes through the reactions $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ and $\text{O}(^1\text{D}) + \text{CH}_4$, while the loss of OH is controlled by $\text{OH} + \text{CO}$ and $\text{OH} + \text{CH}_4$. Profiles

Fig. 26. Calculated change in ozone column due to fluorocarbon production between 1950 and 1976.

Fig. 27. Diurnally and seasonally averaged values of OH concentration vs latitude and height in the troposphere. Contour values are concentrations (10^6 molecules/cm³).

of temperature, H₂O, CH₄, CO, and O₃ (through photolysis to provide O(¹D)) were specified in the model and varied with latitude according to available measurements. The latitudinal distribution of water vapor was taken from Oort and Rasmussen (1971), the O₃ data are from Dütsch (1969), the temperature profiles versus latitude are from Louis (1974), and the CO data are from Seiler (1974). The model was then used to calculate the diurnal OH concentrations for various seasons and latitudes. A comparison of these calculations with the available measured OH distribution derived from the model is shown in Fig. 27. As indicated above, 71% of the tropospheric OH is contained within the band 30°S–30°N.

The derived OH concentrations were used to determine the tropospheric chemical lifetime for a number of fluorocarbon species based on chemical degradation via OH radical. The calculated lifetimes are shown in Table 10. The reaction rates for these species with OH are based on measurements by Davis (1976). The tropospheric residence time of these species is

Table 10. Estimated tropospheric chemical lifetimes for some fluorocarbons

Fluorocarbon	Lifetime (τ ; years)
CH ₃ Cl	0.4
CH ₂ Cl ₂	0.2
CCl ₃ H	0.2
CH ₃ Br	0.5
CH ₂ FCI	0.5
CHF ₂ Cl	4.6
CHFCl ₂	0.7
CH ₃ CF ₂ Cl	7.1
C ₂ Cl ₄	0.2
CH ₃ Cl ₃	1.4

important in determining whether their future use will lead to an impact on stratospheric ozone.

Model Sensitivity to Tropospheric N_2O Concentrations

We have investigated the effect of doubling the tropospheric N_2O concentrations in our standard model and in models designed to maximize or minimize the effect of an N_2O increase. We found ozone decreases of 2.6% (minimum reduction), 7.5% (standard), and 11.2% (maximum reduction) for the Chang (1974) eddy diffusion profile. Thus, the response to a doubling of tropospheric N_2O was moderate, and the range of uncertainties was not drastic.

Nuclear Weapons Sensitivity Studies

The time-dependent response of the model to massive injections of NO_x such as might result from the explosion of hundreds to thousands of megatons of nuclear weapons was calculated. This work is still incomplete and will not be described in detail at this time. However, one significant finding was that a pulse injection of NO_x in the lower stratosphere comparable to that expected from a few hundred megatons total yield using 1-to-3-Mt devices resulted in a transient increase in total ozone when models A_1 , A_2 , C_1 , C_2 , C_1' , or C_2' (described in Sec. 2-1 of this report) were used. This suggests that single test clouds might result in local ozone increases after a few days, making the results of such studies even harder to interpret as tests of theory. We are currently regenerating the coding necessary to study single clouds.

Two-Dimensional Transport-Kinetics Model Development

During the last year, numerous changes were made in the two-dimensional transport-kinetics model of the earth's atmosphere, in the mean wind and eddy diffusion coefficient data, in the chemical kinetics data, and in the various computer codes used to process input and output data. Numerous runs have been made to verify the behavior of the transport-kinetics model, and to verify the transport model by comparison with experimental data for several passive tracers. Current work is under way to improve the accuracy of the latitudinal dependence of photodissociation.

The seasonal average mean wind data of Louis was fitted with Fourier series to provide a full global time-dependent mean wind. The eddy diffusion data of Luther was modified to improve accuracy in the stratosphere. Global multipliers were added to allow modification of the mean wind and eddy diffusion coefficients. A capability of simulating particulate settling, using the Stokes-Cunningham formula, was added to allow comparison of the model with experimental measurements for various natural and artificial tracers for which particulate settling may be significant.

The transport equations were replaced with a new mass-consistent formulation, which is much better behaved when the mean wind field is not mass-consistent, as when horizontal or vertical components are modified by the global multipliers. A variable input parameter was added which allows choice of any weighted combination of first-order (upstream) or second-order (central) spatial differencing to model advection by the mean wind. This allows testing and partial control of the effects of numerical diffusion and dispersion. An option to keep concentrations fixed at any selected altitude was added. The upper boundary condition was modified to improve stability and avoid negative concentrations which could result from certain combinations of steep gradients and wind direction. These changes were tested in a tracer version of the 2-D model with no chemical kinetics and a single passive tracer, with a variety of runs simulating periods up to three years and with different initial and boundary conditions. Stability and accuracy were greatly improved, and correct steady-state solutions were obtained for those cases with known solutions. The full transport-kinetics model was run to simulate a six-month period, with encouraging results.

The tracer code was used to simulate the distribution of plutonium-238 released by the burnup of a SNAP-9A nuclear power source in the stratosphere in April 1964, which was described by Telegadas (1968). Various combinations of the particle size and density were used to model settling. It appears that settling significantly affected the actual distribution, and could not be modeled quantitatively with a single particle size.

The tracer model was also used to simulate the distribution of excess carbon-14 in the atmosphere released by atmospheric nuclear tests. The several simulations began with the measured distribution in March-May 1963, reported by Telegadas (1971), and simulated up to three years using various multipliers for components of the mean wind and eddy diffusion coefficients. The model-predicted distribution of excess carbon-14 for July 1964 is shown in Fig. 28, and the measured distribution is shown in Fig. 29. Good quantitative agreement was obtained for the maximum mixing ratio and for the integrated total load in the whole atmosphere, the troposphere, the stratosphere, and in the northern hemisphere. All were within 18% of the measured values. Agreement with measured concentrations at particular locations was qualitatively good in general and quantitatively good at lower latitudes. The main differences were occurrence of the maximum mixing ratio at about 25 km instead of 20 km, and concentration contours displaced toward higher altitudes in the polar regions.

The best overall agreement was obtained by multiplying Louis's mean wind data by 0.5 and Luther's horizontal eddy diffusion coefficients by 0.5. A different vertical profile of the vertical eddy diffusion coefficient with smaller values in the stratosphere would probably reduce the altitude error in the maximum mixing ratio and polar concentration contours.

The tracer model was also used to simulate the distribution of tungsten-185, as described in Stebbins (1961), resulting from a release of about 10 MCi at 18 km, 10°N latitude, on August 15, 1968. Several runs were made beginning with the distribution described for December 1968. Fair agreement with the measured distributions and with Louis's simulations was obtained for the first eight months of the

simulation. For longer times, results diverged, probably due to the lack of a model for rainout of the tungsten-185 in the troposphere. The best results for the first few months were obtained with Louis's mean wind values reduced in half. The vertical profiles again indicated that the vertical eddy diffusion coefficients should be reduced in the stratosphere.

The full transport-kinetics code is presently being tested with new chemical reaction rates and a full annual variation of the solar zenith angle for each latitude. Rapid changes in concentrations at the boundary of the terminator near the winter pole may require modifications in the model to avoid the use of prohibitively small time steps or failure of the differential equation solver to converge.

Fig. 28. Distributions of excess carbon-14 for July 1964 as calculated with the two-dimensional model.

Uncertainties in the Odd Nitrogen Budget of the Stratosphere

In an effort to improve our understanding of current stratospheric models, including their uncertainties and limitations, a review was undertaken of the odd nitrogen budget of the stratosphere as computed by

the models. This review has revealed: (1) an uncertain consensus that $N_2O + O(^1D)$ is the principal, if not the only, source of stratospheric NO_x ; (2) estimates of the strength of the N_2O source published since 1970 vary by more than an order of magnitude (0.2 to 4×10^8 molecules/cm²·s); (3) additional NO_x sources

Fig. 29. Measured distribution of excess carbon-14 for June-August 1964. Values are in units of 10^5 atoms per gram of CO_2 . Number of samples the value is based on is shown in parentheses.

which have been proposed include cosmic rays, downward transport from the thermosphere, oxidation of NH_3 (which alternatively may be an NO_x sink), and upward transport of NO_2 through the tropopause, as well as surmised but yet to be identified sources.

Aerosols and the Radiation Budget: One-Wavelength Versus Full-Flux Calculations

We have compared one-wavelength solar radiation calculations with full-flux calculations (0.285 to 2.5 μm) in order to assess the limitations and uncertainty of the results when only one wavelength in the visible is used. Comparisons were made for a standard atmosphere with tropospheric and stratospheric aerosols. Calculations at 0.55 μm greatly overestimate Mie scattering, but good agreement with the full-flux calculation has been obtained by scaling the aerosol optical depth to the flux-weighted aerosol optical depth.

In the past, assessments of the solar radiative effects of aerosols have been made using one-wavelength calculations in the visible spectrum. One-wavelength calculations have the advantage that they require much less computer time than the full-flux calculations. Their disadvantage is that they are less accurate than the full-flux calculations. If a method could be found for correcting the one-wavelength calculation, then extensive calculations on the solar effects of stratospheric aerosols could be undertaken at a reasonable cost.

Two corrections must be made to the one-wavelength calculation. One correction applies to the fact that the radiative properties of the aerosol at the given wavelength (usually 0.55 μm) are not representative of the full-flux radiative properties. This can be corrected to a large degree for weakly absorbing aerosols by scaling the one-wavelength results for the changed fluxes by the ratio of the flux-weighted aerosol optical depth to the optical depth at 0.55 μm . The second correction applies to the difference in the solar flux incident on the aerosol. In the case of stratospheric aerosols, the total downward flux incident from above is accurate to within a few percent of the full-flux value. However, the one-wavelength calculation overestimates the flux reaching the earth's surface. Consequently, the error in the flux incident on the aerosols from below depends upon the surface albedo. In the case of tropospheric aerosols the downward flux and the upward flux incident on the aerosols are overestimated by approximately the same factor, so the error is nearly independent of surface albedo and can be corrected effectively with a constant scaling factor.

The change in the upward-scattered flux at the top

of the atmosphere due to a stratospheric aerosol layer between 18 and 22 km is shown in Fig. 30 as a function of solar zenith angle and surface albedo. The solid lines correspond to the full-flux calculation, and the broken lines correspond to the scaled one-wavelength calculation at 0.55 μm . The one-wavelength results have been scaled by a factor of 0.75, which is the ratio of the flux-weighted aerosol optical depth (computed using the total downward flux at 22 km) to the optical depth at 0.55 μm . The aerosol optical depth is 0.05; a zero-order logarithmic size distribution (Toon and Pollack 1976) is assumed; and the wavelength-dependent real and imaginary indices of refraction are taken from Palmer and Williams (1975) for 75% H_2SO_4 . The scaled one-wavelength calculation duplicates all of the major features of the full-flux calculation (e.g., regions of increase or decrease in solar heating and the local maximum). There is very good agreement for small surface albedo.

The change in the net downward flux at 12 km due to the stratospheric aerosol layer is shown in Fig. 31. A decrease in the net flux indicates a decrease in the solar heating of the troposphere. The calculations show that this particular aerosol layer can lead to an increase in the solar heating for small solar zenith angles and large surface albedo.

The significant variation of the change in solar heating with solar zenith angle and surface albedo indicates that global mean calculations in which a solar zenith angle of 60° and a surface albedo of 0.3 are assumed may vary significantly from diurnal average calculations. Future assessments of the solar radiative effects of aerosols should take into account diurnal, latitudinal, and seasonal variations (as well as variations in surface albedo).

Climatic Effect of Contrails

A series of experiments to test the climatic effect of increased cirrus clouds due to jet contrails is currently under way using the two-dimensional climate model ZAM2. One experiment consists of increasing the computed cirrus cloudiness at all latitudes by a factor of 1.2. Gary Hunt at the British Meteorological Office has performed a similar experiment, and we will compare our results with his. Results will also be compared with those from the two-dimensional COMESA model, which uses a series of latitudinally arranged one-dimensional radiative equilibrium models similar to those of Manabe and Möller (1961). Another experiment attempts to simulate the global climatic effect of increased cirrus along a flight corridor. In this experiment, the cirrus cloud cover between latitudes 30 and 50°N will be incrementally increased by 0.10.

Fig. 30. Calculated change in upward flux at 40-km altitude as a function of surface albedo and solar zenith angle. Solid curves are full-flux calculation; dashed curves are one-wavelength ($0.55\text{-}\mu\text{m}$) calculation.

Fig. 31. Calculated change in net flux at 12-km altitude as a function of surface albedo and solar zenith angle. Solid curves are full-flux calculation, dashed curves are one-wavelength (0.55- μm) calculation.

3. FUTURE WORK

Future work will be directed toward further refinement and application of a variety of specialized numerical models and supporting research. Refinements which are planned for the one-dimensional transport-kinetics model include incorporating the effects of multiple molecular scattering and surface reflection on photodissociation rates, incorporating a parameterization of the water vapor budget into the model, and refining the tropospheric chemistry so as to include the full methane cycle and smog chemistry. The model will be used for a number of sensitivity studies to assess the effects of these refinements as well as the effects of new reaction rates or photochemical pathways as

data become available. Future perturbation studies will emphasize multiple perturbations (e.g., NO_x and H_2O with background Cl_x).

The two-dimensional model will undergo further development. Additional tracer studies are planned to refine the prescribed transport, and simulation studies are planned to validate model chemistry.

Calculations of the latitudinal and seasonal variations of the solar effects of perturbed stratospheric species will be conducted using concentration profiles generated by the two-dimensional model. Special studies will be made using the two-dimensional climate model ZAM2 to assess the climatic sensitivity to these perturbations.

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***Anthropogenic Perturbations to the Stratosphere:
Assessment of Environmental Effects***

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ANTHROPOGENIC PERTURBATIONS TO THE STRATOSPHERE:
ASSESSMENT OF ENVIRONMENTAL EFFECTS

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ABSTRACT

LLL has participated in atmospheric and geophysical science research for many years. At first this activity was associated with the nuclear weapons program and examined such areas as the radioactive fallout produced by nuclear experiments in the atmosphere and plutonium contamination resulting from accidents involving nuclear weapons. Later the interest expanded to the study of theoretical geophysical hydrodynamic methodology. Applied research in the ecological effects of underground Plowshare nuclear explosions was also pursued. As a result of these activities, the Laboratory developed a broad base of experience and technical talents in the many fields necessary for understanding and solving atmospheric and geophysical problems for different classes of pollutants and sources.

In 1972, LLL began to assess the potential chemical and climatic effects of engine effluents from fleets of supersonic transports. Since then additional studies have begun at LLL concerning potential reductions in stratospheric ozone due to other anthropogenic pollutants. The rapid evolution of our understanding of atmospheric chemistry and other physical processes has led to significant changes in the environmental assessments over the past few years. Here we summarize the most significant findings, and we present LLL's current assessments for several stratospheric perturbations.

INTRODUCTION

During the past few years, many threats to the stratospheric ozone layer have been proposed. Since 1972, LLL has been making assessments of the chemical and climatic impact of engine effluents from high altitude supersonic and subsonic aircraft. Since 1975, LLL has also been assessing the effect on the biologically and climatically important ozone layer of nitrogen oxides which are produced by atmospheric nuclear explosions. In addition, we are also assessing the potential environmental effects of chlorofluoromethanes (CFMs) which are used as aerosol spray propellents, refrigerants, and foaming agents.

This report summarizes LLL's capabilities and ongoing efforts in stratospheric research, discusses the major scientific elements of each of the problem areas mentioned above, reviews some of the results from previous assessments, and presents LLL's current assessments.

THE IMPORTANCE OF OZONE

To provide a framework for evaluating the effects of anthropogenic perturbations on stratospheric chemistry, it is necessary to understand the basic structure and composition of the atmosphere. Due to differences in the dominant physical processes, the atmosphere is usually represented as being divided into layers, the boundaries of which correspond to temperature minima or maxima (Fig. 1). The troposphere extends from the ground to an altitude of about 16 km near the equator and 8 km near the poles. In the troposphere the mean temperature decreases with increasing altitude, and the level of transition from decreasing to increasing or constant temperature with height is called the tropopause. Above this, the temperature increases generally through this region called the stratosphere to a maximum near 50 km, a level known as the stratopause. Above the stratosphere lie the mesosphere, thermosphere, and ionosphere, which are not central to our research interest, hence they will not be described in detail.

The temperature structure of the atmosphere results from the interaction between the solar and infrared radiation fluxes and the chemical composition of the atmosphere, with atmospheric transport serving to balance convectively unstable thermal stratifications. Because of the temperature structure, the stratosphere is stable with respect to convective overturning, and this leads to very limited vertical motions. Because of this stability, the mean residence time of a tracer in the stratosphere is of the order of 1 to several years while in the much less stable troposphere it is of the order of 1 to 10 days. In the troposphere rain rapidly

removes water soluble substances, but this scavenging process does not occur in the stratosphere.

Almost all the ozone is in the stratosphere (Fig. 2). Although it is customary to speak of an ozone layer, the concentration of ozone in fact never exceeds a few parts per million. The total amount of ozone in a vertical column corresponds to only about 3 mm of pure ozone at STP. Vertical profiles of ozone concentration typically show a maximum concentration near 23 km in middle latitudes.

Ozone is an effective absorber of ultraviolet (uv) radiation, essentially preventing radiation at wavelengths shorter than 290 nm from reaching the earth's surface. (Oxygen is also an effective absorber of radiation at wavelengths shorter than 242 nm). Ozone also absorbs solar radiation in the visible as well as longwave (infrared) radiation. Solar absorption by ozone is the primary warming mechanism for the stratosphere (Fig. 3) with smaller contributions due to solar absorption by water vapor, carbon dioxide, O_2 and NO_2 . Longwave radiation is exchanged predominantly by carbon dioxide, water vapor, and ozone. Changes in ozone abundance and vertical distribution are important because they affect the solar and longwave radiation budgets, which has climatic consequences, and they affect the amount of uv radiation reaching the earth's surface, which has biological consequences. The uv effect depends only upon the change in the total ozone column, whereas the climatic effects also depend upon the vertical distribution of the change in ozone concentration.

Perhaps the most widely discussed effect associated with increased uv resulting from a decrease in the amount of the ozone is the projected increase in incidence of skin cancer in humans. The non-melanoma forms of

skin cancer, which are rarely fatal, have been definitely linked to excessive long-term exposure to ultraviolet light, and they are most frequently found on exposed areas of the body in members of light-skinned races. Malignant melanoma has an associated high mortality rate, but the rate of occurrence is very small compared to the non-melanoma types of skin cancer. Although malignant melanoma has been linked statistically with uv exposure, biologists have been unable to provide any information which indicates a causal relationship.

In order to estimate the uv radiation dose contributing to skin cancer, the uv flux at a given wavelength is weighted by the erythemat (skin reddening) efficiency curve and integrated over wavelength. Most of the contribution to erythema dose comes from radiation in the wavelength region 280-320 nm. The erythema dose varies with latitude, season, ozone amount, and receiver orientation. Daily integrated erythema dose is shown as a function of latitude in Fig. 4. Because of the strong attenuation near 300 nm due to solar absorption by ozone, the percent increase in erythema dose may be significantly larger than the percent reduction in ozone. In Fig. 5, we see that a 10% reduction in ozone leads to approximately a 20% increase in daily erythema dose at middle latitudes.

Although skin cancer is the primary concern, it should also be pointed out that increased uv radiation also has some beneficial effects. There are reports that uv therapy lowers the frequency of respiratory infections,^[1] and uv treatments are used to treat skin diseases, such as psoriasis and acne. Ultraviolet radiation also enhances the production and metabolism of vitamin D₃ in the skin.

The potential reduction and redistribution of ozone due to stratospheric pollutants could lead to significant climatic effects. A reduction in stratospheric ozone alone leads to a cooling of the stratosphere and a warming of the troposphere since more solar radiation reaches the troposphere. At the same time less longwave radiation would be emitted downward into the troposphere, which would tend to cool the troposphere. An increase in the stratospheric concentration NO_2 tends to warm the stratosphere by increasing the amount of solar absorption. The increased solar absorption by NO_2 could even exceed the decrease in solar absorption by ozone locally near the level of injection of NO_x .^[2] Chlorofluoromethanes absorb and emit longwave radiation in the window region of the infrared spectrum where the atmosphere is otherwise relatively transparent. Increased concentrations of CFMs would absorb longwave radiation emitted from the earth's surface and increase the downward longwave emission, thus tending to warm the lower atmosphere. Because the changes in the solar and longwave fluxes depend not only upon the total amount of ozone and other species but also on their redistribution with altitude and latitude, quantitative evaluations of the effects are, as yet, insufficiently precise to establish the sign of the net climatic effect.

A quantitative assessment of the climatic effects due to perturbations to the atmospheric composition must include many physical processes and feedback mechanisms in addition to the perturbed solar and longwave radiation fields. The simplified one-dimensional climate models consider a global average energy balance. The more advanced multidimensional models consider the energy and momentum balances, the hydrologic cycle, and a detailed surface energy balance. Calculations using two-dimensional and

three-dimensional climate models suggest that an increase in the global mean surface temperature would be accompanied by an increase in the intensity of the hydrologic cycle, thus increasing global mean precipitation.^[3] Uncertainties regarding cloud feedback processes and how cloudiness will be affected by climate change make it difficult to accurately quantify the climatic changes at the present time.

OZONE PRODUCTION AND LOSS

The production of ozone in the stratosphere occurs through a series of photochemical reactions known as the Chapman cycle.^[4] Molecular oxygen is photolyzed by light at wavelengths less than 242 nm to yield oxygen atoms, which then combine rapidly with molecular oxygen to form ozone. About one-fifth of the photochemical removal of ozone occurs by reaction with atomic oxygen to regenerate molecular oxygen and by photolysis of ozone at high altitude. In the middle and lower stratosphere, ozone removal is largely accounted for by catalytic cycles in which species X extracts an oxygen atom from ozone and is then regenerated in a reaction with atomic oxygen

Such cycles have been recognized for X = H, HO, NO, Cl, and Br. Engine effluents from high altitude aircraft are a source of additional nitrogen oxides (NO_x) and hydrogen oxides (HO_x). Atmospheric nuclear explosions

produce NO in the fireball, and the NO is then injected into the atmosphere at the cloud stabilization height, which occurs in the stratosphere for high-yield weapons. Chlorofluoromethanes which are released at the ground are slowly transported upward into the middle stratosphere where they are photolyzed; thus releasing Cl. The rocket exhaust from the space shuttle will release chlorine directly into the stratosphere. Current research in stratospheric modeling attempts to understand the complex chemical interactions involving these catalytic cycles and the impact of the above man-made perturbations on the natural balances.

LLL'S STRATOSPHERIC ASSESSMENT CAPABILITIES

The modeling effort at LLL covers five major areas of research: photochemical kinetics, coupled kinetics and transport, radiative transfer, climate modeling, and meteorological analysis. The modeling of photochemical kinetics must span gas-phase reaction processes and heterogeneous (i.e., gas-particle) reaction processes, constant and diurnally (and seasonally) varying photochemical reaction rates, a wide range of ambient temperatures and pressures, neutral and ionized species, processes with both accurately and poorly known rates of reaction, and species of both acknowledged and questionable importance in the stratosphere. We are directing considerable attention to the problem of evaluating the sensitivity of the model to deficiencies in our knowledge of reaction rates, reaction mechanisms, and the quantum yields for photolysis.

Numerical models in which chemical kinetics and transport are coupled are used to study the structure of the atmosphere and to assess the potential stratospheric response to injections of trace species. The models currently available for modeling the stratosphere are either one-dimensional (vertical) or two-dimensional (vertical and latitude) transport-kinetics models. Three-dimensional models with somewhat limited chemical modeling are being developed but not at LLL.

The one-dimensional models are intended to include as complete a set of the important chemical reactions as is feasible along with detailed photochemistry, however they use a very highly parameterized representation of the vertical transport. Some models are capable of diurnal calculations, but most include some form of averaging over the day-night cycle. Our models are designed for time-dependent perturbation and sensitivity studies, whereas others are strictly steady-state.

The two-dimensional models are structured so that they can provide an indication of the latitudinal behavior by providing for variation of the transport, radiation fields, and species concentrations with latitude, altitude, and season. These models also give an indication of hemispheric differences in atmospheric composition and in response to perturbations.

In radiative transfer research, we apply detailed models to assess the effect of perturbations in stratospheric composition on the radiation budget and the uv radiation received at the earth's surface. Also, we are developing simplified radiative transfer models for inclusion in the transport-kinetics models. This latter development is essential for assessing possible feedback mechanisms.

To assess the effects of changes in atmospheric composition on the global climate, we use a two-dimensional (latitude and vertical) climate model. The climate model includes a wide range of physical processes important in atmospheric behavior, including solar and longwave radiation, cloud cover, convective precipitation, proportional surface type, surface energy and hydrologic balances, and cryospheric annual variability. This model is unique in terms of the large number of physical processes and feedback mechanisms included.

We utilize meteorological analysis to provide guidance and support during the modeling. It allows us to make in-depth studies of atmospheric processes and phenomena. A primary responsibility in this research area is to develop test situations for validating various aspects of the numerical models.

EFFECTS OF HIGH-ALTITUDE AIRCRAFT^{*}

The effect of aircraft emissions on stratospheric composition is not dependent upon aircraft speed, but rather on flight altitude. Consequently, the delineation between supersonic transports (SST) and subsonic aircraft is artificial. Much of the long-range subsonic flight is now occurring in

^{*}This work is supported by the Federal Aviation Administration's High Altitude Pollution Program (HAPP), which began in 1975. The FAA is seeking to quantitatively determine the requirements for reduced aircraft engine emissions. The reductions will prevent unacceptable environmental effects due to stratospheric flight. A number of related activities are incorporated in HAPP: modeling, field measurements, laboratory measurements, engines and fuels, assessment, regulation, and monitoring. LLL is the major contributor in the modeling area.

the lower stratosphere. Long-range commercial aircraft such as the 747-SP now fly at altitudes up to 13 km,^[5] and small corporate jets are capable of flying at even higher altitudes. As the flight corridors become increasingly congested, more aircraft will be using the less congested air space at higher altitudes. Consequently, much larger amounts are projected for engine emissions in the lower stratosphere independent of the future trend in SST fleet sizes.

The British/French Concorde and the Soviet Tupolev-144 are the only SSTs in commercial service. These aircraft have an average cruise altitude of approximately 17 km (Fig. 6). Future advanced SSTs, if developed, will probably fly at cruise altitudes near 20 km. Consequently, studies of the environmental effects of engine effluents from SST fleets have focused on injection altitudes of 17 and 20 km.

The engine emission indices for subsonic and supersonic aircraft are shown in Table 1. The Concorde burns 19,000 kg of fuel per hour at cruise altitude. Oxides of nitrogen and water vapor are the only species of chemical significance related to ozone. SO_2 contributes to the formation of sulfuric acid aerosols in the stratosphere which affect the earth's solar and longwave radiation budgets, but the climatic effect has been assessed to be small.^[6]

The LLL transport-kinetics model used for stratospheric assessments includes 28 chemical species and 83 chemical and photochemical reactions. Species concentrations are computed at 44 levels extending from the ground to an altitude of 55 km. The model utilizes an accurate numerical method for solving stiff systems of differential equations. It accounts for multiple scattering in computing photodissociation rates, and can include

temperature coupling between changes in composition and reaction rate coefficients. Vertical transport in the one-dimensional model is parameterized using a one-dimensional diffusion formulation,^{*} which describes hemispheric (or global) average net vertical transport by an altitude dependent diffusion coefficient. The one-dimensional diffusion coefficient profile is empirically determined by a fit to actual concentration data of tracer-like species.

The chemistry is much more complex than implied by the simple catalytic cycles described above. The various catalytic cycles, rather than being independent, are coupled such that changes in one catalytic cycle may either enhance or retard ozone destruction by another catalytic cycle. The relative importance of the various cycles (and consequently, the model sensitivity to stratospheric perturbations) depends upon certain key chemical rate coefficients, which were identified by scientists at LLL.^[7] Unfortunately, several of these rate coefficients have large uncertainties. We showed that by adjusting five chemical rate coefficients, so that each minimizes the effect of an NO_x injection while remaining within uncertainty limits estimated by the National Bureau of Standards, it is possible to reverse the direction of the ozone perturbation;^[7] that is, producing ozone instead of destroying it. This condition, although within the range of possibility, was felt to be highly improbable and was studied purely for the purpose of illustrating the need for better laboratory kinetics data.

Past and current assessments of the effect on ozone of stratospheric injections of NO_x are shown in Fig. 7. This figure illustrates the potential change in total ozone at steady state due to an NO_x injection of 1.23×10^9 kg NO_x per year into a hemisphere based upon one-dimensional model results,

^{*}Eddy diffusion is a mathematical approach to representing the very complex motions of atmospheric air parcels. It should not be confused with molecular diffusion which represents the motions of molecules and is much smaller than eddy diffusion in the lowest 80 km of the atmosphere.

and it also gives some indication of the uncertainty in the calculations.

In 1974 several numerical modeling groups, including LLL, funded under the Climatic Impact Assessment Program (CIAP) of the Department of Transportation assessed the potential impact of a large fleet of SSTs. LLL's 1974 results represent the results typical of the various models at that time. In preparing the CIAP Report of Findings,^[6] the final curve was based on the average of LLL's results and results from a model used by the National Academy of Sciences.^[8]

Since 1974 there have been many changes to the numerical models. New species (mostly chlorine containing) and reactions have been added. Poorly known reaction rates have been remeasured using more accurate methods, and the photodissociation rate calculation has been improved. Temperature coupling and feedback on reaction rates has been added, and diurnal averaging has been accounted for more accurately. As these changes have been implemented, most have led to a reduction in the effect of NO_x on ozone. The most recent change, in which the reaction rate for $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$ was measured to be roughly 30 times faster than previously thought,^[9] has resulted in a reversal in the sign of the ozone change such that aircraft emissions in the lower stratosphere cause an increase in ozone. Other models not at LLL also show an ozone increase at 17 km, but results range from a slight ozone decrease to a slight ozone increase at 20 km. The models predict an ozone decrease for injection altitudes above 20 km. Most of the difference between our 1976 results and our 1977 results is due to this one change in a chemical rate measurement. It is impossible to predict the effect of future changes in the model chemistry, but until stratospheric chemistry is better understood and reaction rates are known more accurately,

there will continue to be significant uncertainty associated with the results.

There is a non-linear relationship between the magnitude of the NO_x injection and the change in total ozone. This is illustrated in Fig. 8 for 17 and 20 km injection altitudes. Doubling the rate of NO_x injection does not double the increase in total ozone. On the contrary, in the case of a 20 km injection increasing the NO_x injection rate may even cause an ozone reduction rather than an increase.

The effect of uncertainties in the parameterization of vertical transport in the one-dimensional model is also illustrated in Fig. 8. The diffusion coefficient profiles K_z-1 and K_z-2 represent significantly different yet acceptable parameterizations for the vertical transport based upon tracer studies. The profile K_z-2 allows for slower transport across the tropopause than does K_z-1 . Consequently, there is a larger increase in the NO_x burden when K_z-2 is used, which causes a larger reduction in ozone for large NO_x injection rates.

The change in the local ozone concentration is shown in Fig. 9 for NO_x injections at 20 km. Even when the change in the total ozone column is small, there may be significant changes in the local ozone concentration, which feeds back on the temperature structure and static stability of the stratosphere. The effect of these changes on vertical transport is yet to be assessed.

The increased concentrations of O_3 and NO_2 near the level of the tropopause would tend to increase the local heating due to absorption of solar and longwave radiation. Depending upon the change in tropospheric temperature, there might be an increase in the temperature of the tropical tropo-

pause, which would enable more water vapor to pass through the tropical tropopause "cold trap". The net results would be an increase in the amount of stratospheric water vapor. Past calculations showed that increasing the stratospheric water vapor abundance would decrease total ozone. [7,10] These calculations, however, only included the chemical effects of water vapor but neglected its effect on stratospheric temperature.

We have computed the effect of a change in stratospheric water vapor on total ozone first using a fixed ambient temperature profile, then including temperature feedback on reaction rates. Calculations were performed for cases with and without a simultaneous NO_x injection in order to test the sensitivity of the results to the magnitude of the NO_x injection. We considered an NO_x injection rate of 6.2×10^8 kg per year as NO_2 into a hemisphere at an altitude of 20 km. The results using the K_2 -1 profile are presented in Fig. 10, which shows the change in total ozone at steady state as a function of the change in stratospheric water vapor mixing ratio. The unperturbed stratospheric mixing ratio is assumed to be 4.3 ppmv.

The chemical effect of increased water vapor is compensated for by temperature feedback, resulting in very little net change in total ozone when water vapor is increased. Although the change in total ozone is small, changes in water vapor abundance significantly affect the local ozone concentration as shown in Fig. 11 for the case with an NO_x injection at 20 km including temperature feedback.

EFFECTS OF CHLOROFLUOROMETHANES* AND THE SPACE SHUTTLE

The two chlorofluoromethanes most widely used and about which there has been the most concern are CFCl_3 (F-11) and CF_2Cl_2 (F-12). The production data for F-11 and F-12 are shown in Figs. 12 and 13, respectively, with United States and non-United States data plotted separately. The data for F-11 show a 9%/yr growth rate in the United States and a 20%/yr growth rate abroad for the period 1965-1974. The corresponding data for F-12 show a 7%/yr growth rate in the United States and 13%/yr abroad. These data demonstrate the worldwide nature of the CFM problem since over half of the production is abroad.

CFMs were originally developed as refrigerants, but their major current use is as aerosol propellants. An estimate of the distribution of use in 1973 is shown in Table 2. The CFMs used as refrigerants eventually escape by leakage, during recharging, or after the equipment is junked. It is estimated that approximately 90% of the total production of F-11 and F-12 is released to the atmosphere.^[11]

Once the CFMs are released, relatively rapid tropospheric mixing occurs. Because there are no significant tropospheric loss mechanisms for F-11 and F-12, there is a gradual accumulation of CFMs in the troposphere. The CFMs rise slowly into the stratosphere where they are decomposed at altitudes above 25 km by the sun's ultraviolet radiation. Chlorine atoms (Cl) and chlorine oxide (ClO), which are produced directly or indirectly by this decomposition, then catalytically react to remove ozone.

*This work is supported in part by the HAPP program of the FAA and in part by the Environmental Protection Agency. The potential effect of CFMs on ozone was first pointed out by Rowland and Molina of the University of California, Irvine, in 1974.

The long-term effect of CFMs on ozone depends upon the scenario chosen for CFM production as a function of time. For purposes of assessment, it is customary to assume constant CFM production at the 1975 rate.

The National Academy of Sciences report^{*} released in 1976^[12] on the environmental effects of CFMs estimated that continued release at the 1973 level would ultimately lead to an ozone reduction of about 7%, but with an uncertainty such that there is roughly a 95 percent chance of the real value being between 2 and 20% ozone reduction. This reduction would occur gradually over many decades, taking 40-50 years to reach half of the total ozone reduction that would eventually occur at steady state.

Results of LLL calculations of the decrease in total ozone for various production scenarios are shown in Figs. 14 and 15.^[13] The shaded area shows the range of ozone reduction projections as a function of time depending on the choice of diffusion profile. Figure 14 shows the effect of constant ozone production at either the 1973 rate or one-half the 1973 rate. The model currently predicts an ozone reduction of 15% at steady state due to CFM production at the 1973 rate. This is approximately twice the value computed prior to the recent change in model chemistry.

Figure 15 shows the effect of stopping production of CFMs in either 1978 or 1983, assuming constant production at 1973 levels up until that time. The ozone reduction continues to increase following the stopping of production, reaching a peak value 7-14 years after production is halted. This is followed by a time of very slow recovery. The delay in reaching a maximum ozone reduction happens because the troposphere acts as a reservoir of F-11 and F-12, which are slowly transported upward into the stratosphere.

^{*} Dr. Julius S. Chang, a physicist at LLL, is a member of the NAS panel which prepared the report.

There is a significant difference between the vertical distributions of the change in ozone concentration for the CFM and NO_x perturbations. The change in ozone concentration versus altitude is shown in Fig. 16 for the CFM perturbation. The largest ozone reduction occurs near 40 km, and there are relatively small changes in ozone concentration below 30 km. In the case of the NO_x injection due to engine effluents (Fig. 9), there was a reduction in the local ozone concentration above 23 km and an increase in ozone concentration in the region below 23 km.

LLL scientists, through cooperation with NASA, have also studied the potential impact of the space shuttle on stratospheric chemistry. One of the major components of space shuttle engine exhaust is HCl. Assuming 60 space shuttle flights per year, the LLL calculated effect on ozone due to the additional stratospheric chlorine is a reduction of 0.27%. Other engine exhaust by-products, such as NO and H_2O , have also been studied and found to be insignificant.

EFFECTS OF ATMOSPHERIC NUCLEAR DETONATIONS^{*}

The concept of stratospheric injections of NO_x by atmospheric nuclear detonations and the possible effect on ozone was first presented by Foley and Ruderman in 1972.^[14] The major NO production mechanism is the high temperature chemical equilibrium among molecular and atomic oxygen, nitrogen

^{*}This work is supported by the Division of Military Applications of ERDA. The potential effect of a large-scale nuclear exchange was first pointed out by Dr. Julius Chang at LLL in 1973. DMA has been supporting this work since 1974.

and NO_x . In the fireball N_2 is dissociated and oxidized to form NO . The relatively fast cooling of the hot cloud leads to thermal quenching of the equilibrium state. The rates of NO production and destruction become negligibly slow when the cloud cools below 2000 K, which occurs on the order of a minute after detonation.

The NO produced is injected into the atmosphere at the cloud stabilization height, which depends upon the amount of thermal heating and the amount of ambient air that is mixed with the fireball as it rises through the atmosphere. The stabilization height also depends upon the atmospheric temperature structure, which varies significantly with latitude. Variations in the height of burst within 0-3 km of the earth's surface do not significantly affect the cloud stabilization height.

There have been several estimates of the total amount of NO produced per MT yield of the nuclear explosion, and these are summarized in Table 3. The most recent and comprehensive studies are those of Gilmore^[15] and COMESA,^[16] which agree closely with each other. The COMESA study, however, also included an estimate of the loss of NO due to disentrainment of air from the rising debris cloud. We use the COMESA value of 6.7×10^{31} molecules NO per MT yield, but note that there is a significant range of uncertainty. For ozone perturbations up to several percent, the model response varies approximately linearly with the total NO injection; thus if a readjustment of the NO production per MT should be dictated in the future, our computed ozone perturbations would scale linearly.

The cloud stabilization altitude has been parameterized as a function of MT yield by Foley and Ruderman.^[14] The cloud top height H_T and cloud base height H_B are given by:

$$H_T = 21.64 Y_{MT}^{0.2} \text{ km}$$

and

$$H_B = 13.41 Y_{MT}^{0.2} \text{ km} .$$

This parameterization is largely based upon direct observation of United States tests. [17]

Seitz et al. [18] estimated cloud top and cloud base heights from measurements of the radioactive debris a few days after the 1961-1962 atmospheric nuclear tests. Very few of the debris measurements extended above 24 km, and the tops of most of the higher yield tests were not directly measured. The parameterization of Foley and Ruderman, which we used in our earlier reports, [19,20] may overestimate the stabilization height since it is based almost exclusively on data from the tropics. However, the stabilization heights quoted by Seitz et al. probably underestimate the stabilization height. The estimates from the two different methodologies are presented in Fig. 17. Note that the yield must be greater than 1 MT in order for the cloud to significantly penetrate into the stratosphere.

Foley and Ruderman [14] suggested that an examination of the ozone measurements during the period of atmospheric nuclear testing of the 1950's and early 1960's could possibly be used to estimate the significance of NO_x catalytic destruction of ozone. There have been several analyses of the global ozone record, [16,21,22] which concluded that any ozone reductions caused by the nuclear test series must have been less than $\sim 2\%$, which is approximately the noise level of the ozone data. A gradual ozone reduction of 3-4% occurring over several years might not be inconsistent with the ozone record.

We have computed the effect of the nuclear test series on total ozone in the northern hemisphere.^[20,23] There are several published estimates of the total yield for the period 1956-1962.^[14,16,17,23] These estimates range from 429 to 451 MT, of which 303 to 340 MT were detonated in the period 1961-1962. We assume that the total yield from high-yield atmospheric detonations is 429 MT with 335 MT occurring in 1961-1962.^[23]

The computed change in total ozone for the northern hemisphere is shown in Fig. 18 as a function of time. The predicted change in total ozone is sensitive to the model chemistry and to the stabilization height prescription.

Our calculation using 1976 chemistry predicted a maximum ozone reduction which was large compared to the ~ 2% reduction estimated to be compatible with observations. With our 1977 chemistry and using the Seitz et al.^[18] stabilization height estimates, we compute ozone increases from the 1950's tests and ozone reductions less than 2% at all times. When the Foley and Ruderman^[14] stabilization height estimates are used, we compute ozone reductions throughout the testing period, and the peak ozone reduction (3% annual average for 1963 in the northern hemisphere) is larger than is easily consistent with observations. The peak ozone reduction follows a number of high-yield detonations primarily at high latitudes, and most occurred in a period of four months in late 1962. Since the one-dimensional model formulation assumes uniform horizontal mixing, this would be a poor representation for the first several months after detonation while the debris is undergoing horizontal mixing and transport in the northern hemisphere. Consequently, the model would tend to overestimate the peak ozone reduction. Our current results, therefore, may be comparable to the upper limit permitted by the observations.

The effect of varying the vertical transport coefficient profile is shown in Fig. 19. Unlike the SST calculation, the ozone change does not depend significantly upon the choice of K_z profile. The reason for this is that the NO_x perturbation is a pulse injection for the nuclear test series, and the total NO_x injected depends upon the device yield, not upon K_z . For the SST calculation, however, the increase in stratospheric NO_x depends upon the steady state injection and removal rates, since the more rapidly NO_x is transported downward out of the stratosphere, the smaller is the build-up of NO_x . The choice of K_z , however, does affect the recovery time for pulse injections of NO_x since it affects the removal rate of excess stratospheric NO_x . The recovery rate is initially also affected by the rate of vertical redistribution of NO_x within the stratosphere.

There were several assessments in 1975 of the potential effect on ozone of a very large number of nuclear detonations.^[20,24,25] LLL's modeling results^[20] were used extensively by the National Academy of Sciences in the preparation of its report.^[24] These studies estimated that a total yield of 10^4 MT, such as might occur during a large-scale nuclear exchange, would possibly cause a reduction in ozone of 30-70% in the northern hemisphere. The range represents a subjective estimate of the uncertainties as well as reflecting different assumptions regarding the distribution of individual weapon yields. LLL has continued to study the potential long-term chemical and climatic effects of a large number of nuclear detonations.

Figure 20 shows the potential effect of 1 and 5 MT devices on global ozone computed using 1976 chemistry. Because of the higher stabilization height, the 5 MT devices cause larger ozone reductions than the 1 MT devices for the same total yield. The peak ozone reduction occurs within the first

year after detonation, followed by a period of gradual recovery to near-normal ozone levels lasting 4-6 years. Similar calculations using 1977 chemistry estimating the change in ozone in the northern hemisphere are shown in Fig. 21. The recent changes in model chemistry have resulted in predictions of much smaller changes in ozone for modest NO_x injections ($\sim 10^3$ MT), but they have little effect on the changes predicted for very large NO_x injections.

The trend in nuclear weapon stockpiles is toward larger numbers of smaller yield warheads. This has been brought about primarily by two significant developments: (1) ICBM's are more accurate now, thus enabling smaller-yield weapons to be used more effectively, and (2) the development of multiple targetable reentry vehicles has reduced the individual weapon size and, consequently, the yield. Individual yields from highly fractionated weapons would likely be in the range of 250-500 kT. Detonations within this range of yield have stabilization heights very close to the tropopause (Fig. 17), so predictions of their effect on ozone are very sensitive to the method used to estimate the stabilization height. A variation in height of ± 1 km can significantly affect the amount of NO which is injected into the stratosphere.

Figure 22 shows the potential effect of 250 kT devices on ozone in the northern hemisphere computed using 1977 chemistry. According to these calculations, there may be either an increase or a decrease in total ozone depending upon the total yield. In either case, there is a very rapid recovery to near-normal ozone levels within two years after detonation.

SUMMARY

LLL is continuing to study the potential chemical and climatic effects of several anthropogenic perturbations to the stratosphere. The rapid evolution of model chemistry over the past few years has led to significant changes in the assessments. The major changes came as a result of measurements of parameters which do not affect the NO_x or ClX catalytic cycles directly. It is anticipated that there will continue to be significant changes to the model as further effort is devoted toward model validation and the reduction of uncertainties. We are in the process of developing a two-dimensional transport-kinetics model which will aid in the simulation and interpretation of the effects of high-latitude nuclear detonations. This model will also be used to predict the latitude variation of the ozone change due to aircraft flight corridors at middle latitudes.

TABLE 1. Engine emission indices assigned in CIAP to the current fleet.
Source: CIAP ROF, p. D-81.

Emission Species	Altitude (km)	Subsonic	Supersonic
Oxides of nitrogen (as NO ₂)	9-12	10 g/kg fuel	10 g/kg fuel
	12-15	7	18
	15-21	-	18
Carbon monoxide (CO)		3	3
Total hydrocarbons (THC)		0.5	0.5
Soot		0.02	0.02
H ₂ O		1.25 x 10 ³	1.25 x 10 ³
CO ₂		3.22 x 10 ³	3.22 x 10 ³
SO ₂		1	1
Total trace elements		0.01	0.01
Lubricating oil		0.1	0.1

Table 2. CFM consumption by end use.
(1973, percent of total)

Use	United States	World
Aerosol propellants	49	55
Refrigerants	28	29
Plastics and resins	4	7
Solvents	5	3
Foam blowing agents	7	4
Other	7	2

A. D. Little, 1975

TABLE 3. Estimates of NO produced per MT yield.

		10^{32} molecules/MT
Zeldovich and Razier	(1967)	0.5
Foley and Ruderman	(1972)	0.3-1.5
Johnston et al.	(1973)	0.17-1.0
Chang and Duewer	(1973)	0.5
Goldsmith et al.	(1973)	1.0
Gilmore	(1975)	0.4-1.5 (0.9)
COMESA	(1975)	0.6-1.1 (0.84)
After allowance for disentrainment		0.5-0.9 (0.67)

FIGURE 1. Temperature-height profile of the atmosphere ($1 \text{ mb} \approx 100 \text{ N}\cdot\text{m}^{-2}$).
(Source: U. S. Standard Atmosphere, 1962).

FIGURE 2. Midlatitude distributions of air density and ozone density as a function of height in the troposphere, stratosphere, and lower mesosphere. The air density distribution is from the U.S. Standard Atmosphere (1962), and the ozone density distribution is from Krueger and Minzner (1973). Note that the air density scale is 10^6 times the ozone density scale so that the ratio of the two curves at any height subjectively gives the ozone mixing ratio in ppm(v).

FIGURE 3. Vertical distributions of the rate of temperature change of the ($\text{H}_2\text{O} + \text{CO}_2 + \text{O}_3$) atmosphere in pure radiative equilibrium due to various absorbers. LH_2O , LO_3 , and LCO_2 show the rate of temperature change due to long wave radiation of water vapor, CO_2 (the effect of H_2O overlapping was included), and O_3 . SH_2O , SCO_2 , and SO_3 show the rate of temperature change due to the absorption of solar radiation by water vapor, CO_2 , and O_3 .

FIGURE 4. The latitude distribution of daily erythema dose for a receiver oriented at an angle of inclination α with respect to the horizontal ($\alpha = 0$ for a horizontal surface). The value shown is the average of many receivers randomly oriented in azimuth angle (with respect to the northerly direction).

FIGURE 5. The percent change in daily erythema dose versus latitude for ozone reductions of 10 and 20%. The percent increase in erythema dose at middle latitudes is approximately twice the percent reduction in ozone.

FIGURE 6. Flight paths for Concorde and Tupolev-144 SSTs.

Fig. 7. Ozone column change results by various models. The injection rate assumed at each altitude is 1.23×10^9 kg NO_x (as NO_2) per year into a hemisphere. The NAS and CIAP curves are based on one-dimensional model results and correspond to changes to be expected in the hemisphere.

Fig. 8. The change in the ozone column at steady state as a function of NO_x injection rate for injection altitudes of 17 and 20 km. An injection rate of $2000 \text{ molecules cm}^{-3} \text{ s}^{-1}$ in a hemispheric shell 1 km thick corresponds to an annual injection rate of $1.23 \times 10^9 \text{ kg per year}$. K_z-1 and K_z-2 are different diffusion coefficient profiles.

Fig. 9. The change in the local ozone concentration versus height at steady state due to NO_x injections at 20 km.

FIGURE 10. Change in total ozone versus the change in stratospheric water vapor mixing ratio (a) with no NO_x injection (b) with an NO_x injection of 1000 molecules cm⁻³ s⁻¹ as NO₂ over a 1 km thick layer centered at 20 km.

FIGURE 11. The percent change in ozone concentration as a function of height due to an NO_x injection at 20 km.

FIGURE 12. The past production rate of CFC1_3 (F-11) by the United States and by non-U.S. producers.

FIGURE 13. The past production rate of CF_2Cl_2 (F-12) by the United States and by non-U.S. producers.

FIGURE 14. The reduction in total ozone resulting from constant production of chlorofluoromethanes at the 1973 rate and one-half the 1973 rate. The shaded region represents the effect of using different diffusion coefficient profiles.

FIGURE 15. The reduction in total ozone computed assuming chlorofluoromethane production is stopped in 1978 or 1983.

FIGURE 16. The change in ozone concentration versus altitude due to constant production of chlorofluoromethanes at the 1973 rate.

FIGURE 17. Cloud top and cloud base vs. yield for the treatments used. The curves defining the shaded area give the cloud top and cloud base according to the parameterization of Foley and Ruderman (1972). The vertical bars extend from cloud base to cloud top for the data cited by Seitz et al. (1968) after adjustment to height above a variable tropopause as discussed in the text. The number of tests of a particular yield at high latitudes (indicated with a P) and at low latitudes (indicated with a T) is also given on the figure.

CHANGE IN O_3 VERSUS DATE, EFFECTIVE STABILIZATION PARAMETERIZATION

FIGURE 18. Calculated change in O_3 vs. date showing the effect of the treatment of cloud stabilization heights. ····· Seitz et al. (1968) stabilization height, 1977 chemistry; ---- Seitz et al. (1968) stabilization height, 1976 chemistry; — Foley and Ruderman (1972) stabilization height, 1977 chemistry; - - - - Foley and Ruderman (1972) stabilization height, 1976 chemistry. All calculations used the Chang (1976) K and diurnal averaging.

CHANGE IN O_3 VERSUS DATE FOR TWO CHEMISTRIES, INJECTION PARAMETERIZATIONS AND K_z 's

FIGURE 19. Calculated O_3 change vs. date showing the effect of choice of K_z . — Chang (1976) K_z -1; ---- Hunten (1975) K_z -2. Upper curves use the 1977 chemistry and diurnal averaging. Lower curves use the 1976 chemistry without diurnal averaging.

FIGURE 20. The change in total ozone versus time due to a large number of atmospheric nuclear explosions using devices of 1 MT or 5 MT yield. This calculation used 1976 model chemistry and corresponds to the change in global ozone.

Fig. 21(a). The change in total ozone for the northern hemisphere due to a large number of atmospheric nuclear explosions using devices of 5 MT yield. This calculation used 1977 model chemistry.

Fig. 21(b). The change in total ozone for the northern hemisphere due to a large number of atmospheric nuclear explosions using devices of 1 MT yield. This calculation used 1977 model chemistry.

Fig. 22. The change in total ozone for the northern hemisphere due to a large number of atmospheric nuclear explosions using 250 kT devices.

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***Aerosols and the Radiation Budget:
One-Wavelength Versus Full-Flux Calculations***

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Aerosols and the Radiation Budget: One-Wavelength Versus Full-Flux
Calculations

In many studies of the effects of tropospheric and stratospheric aerosols on planetary albedo, solar fluxes, and solar heating rates, it has not been uncommon for only one wavelength to be used for the calculations (e.g., $\lambda = 0.55 \mu\text{m}$). An argument often used to justify the use of only one wavelength is that the error incurred is less than that due to uncertainties in various input parameters. This argument can only be justified by comparing results from the simplified calculation with those from more complex calculations.

In this paper, one-wavelength calculations are compared with full-flux (0.285 to $2.5 \mu\text{m}$) calculations in order to assess the limitations and uncertainties of the results when only one wavelength in the visible is used. We address the questions: (1) How well do calculations at a wavelength of $0.55 \mu\text{m}$ compare with the full-flux calculations? and (2) What wavelength gives the best agreement with the full-flux calculation?

The solar radiation model used for these calculations includes molecular and Mie multiple scattering along with absorption by ozone, water vapor, carbon dioxide, oxygen, and aerosols for a plane-parallel, cloudless atmosphere. Two aerosol models were used in the calculations: a stratospheric aerosol layer ($\tau = 0.05$) and a distribution of tropospheric aerosols ($\tau = 0.25$).

The various flux components (downward direct, downward diffuse, total downward, upward diffuse, and net fluxes) are analyzed as functions of solar zenith angle, surface albedo, and altitude. Since the relative importance of molecular scattering, Mie scattering, and absorption by gases and aerosols varies with altitude, solar zenith angle, surface albedo, and aerosol properties, one wavelength cannot be expected to give the best agreement under all conditions for all flux components.

Calculations at $0.55 \mu\text{m}$ are shown to overestimate molecular scattering effects, and they slightly overestimate stratospheric gaseous absorption. Because there is only absorption by ozone at $0.55 \mu\text{m}$, calculations at this wavelength do not accurately describe tropospheric gaseous absorption. Molecular scattering effects are most accurately simulated using a wavelength of $0.57 \mu\text{m}$. Calculations in the region 0.57 - $0.60 \mu\text{m}$ give the best agreement for the stratospheric gaseous absorption for small values of surface albedo.

Calculations at $0.55\text{ }\mu\text{m}$ significantly overestimate the changes in the various flux components due to the presence of aerosols. By using a scaling factor equal to the ratio of the flux-weighted aerosol optical depth to the aerosol optical depth at $0.55\text{ }\mu\text{m}$ the one-wavelength results can be brought into reasonable agreement with the full-flux calculations. The scaled results reproduce all of the major features of the full-flux results. The error in the one-wavelength calculations can generally be reduced by using the wavelength at which the aerosol optical depth equals the flux weighted aerosol optical depth (usually between 0.6 and $0.7\text{ }\mu\text{m}$).

The change in upward flux at the top of the model atmosphere (40 km) due to the stratospheric aerosol layer is shown in Figure 1 as a function of surface albedo and solar zenith angle. The results from the full-flux calculation are indicated by the solid lines, and the results at $0.55\text{ }\mu\text{m}$ scaled by a factor of 0.749 are indicated by the broken lines. The unscaled results significantly overestimate the change in upward flux, but the scaled results generally agree to within $\pm 0.5\text{ W/m}^2$ for this particular case. Both calculations have similar features, such as the region of atmospheric warming (indicated by the decrease in upward flux).

Figure 1

*The Ozone Layer:
Assessing Man-Made Perturbations*

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The Ozone Layer: Assessing Man-Made Perturbations

Since 1972, LLL has been using numerical models to assess the potential chemical impacts on the ozone layer of engine effluents from high-altitude supersonic and subsonic aircraft and their subsequent climatic results. Since 1974, we have been assessing how nitrogen oxides from atmospheric nuclear explosions affect this layer. In addition, we are studying the potential environmental effects of chlorofluoromethanes, which are used as aerosol spray propellants, refrigerants, and foaming agents. The rapid evolution of our understanding of atmospheric chemistry and other physical processes has led to major changes in these environmental assessments.

Ozone is produced in the stratosphere through a series of photochemical reactions known as the Chapman cycle. Molecular oxygen is photolyzed by light at wavelengths less than 242 nm to yield oxygen atoms, which then combine rapidly with molecular oxygen to form ozone.

About one-fifth of the photochemical removal of ozone occurs by reaction with atomic oxygen to regenerate molecular oxygen and by photolysis of ozone at high altitude. In the middle and lower stratosphere, ozone removal occurs mainly by catalytic cycles in which a species (X) abstracts an oxygen atom from ozone and is then regenerated in a reaction with atomic oxygen:

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Such cycles have been recognized for $X = H, HO, NO, Cl, \text{ and } Br$.

Current research in stratospheric modeling deals with the complex chemical interactions involving these catalytic cycles and the impact of various man-made perturbations on their natural balances. For example, engine effluents from high-altitude aircraft are a source of additional nitrogen oxides (NO_x) and hydrogen oxides (HO_x). Atmospheric nuclear explosions produce NO in the fireball; for high-yield weapons, this NO is then injected into the stratosphere. Chlorofluoromethanes (CFMs), which are released at the ground, are slowly transported upward into the middle stratosphere where they are photolyzed, releasing chlorine. Rocket exhaust from the space shuttle will release chlorine directly into the stratosphere.

The nature and importance of the stratospheric ozone layer are discussed in the box on p. 22.

STRATOSPHERIC MODELING

The modeling effort at LLL covers five major areas of research: photochemical kinetics, coupled kinetics and transport, radiative transfer, climate modeling, and meteorological analysis. The modeling of photochemical kinetics must span gas-phase and gas-particle reaction processes, constant and varying photochemical reaction rates, a wide range of ambient temperatures and pressures, neutral and ionized species, and processes with both accurately and poorly known reaction rates.

We use numerical models that couple chemical kinetics and transport to study the structure of the atmosphere and to assess the potential stratospheric response to injections of trace species. The models currently available to us for the stratosphere are

either one-dimensional (vertical) or two-dimensional (vertical and latitude).

One-dimensional models include as complete a set of the important chemical reactions as is feasible, along with detailed photochemistry. However, they use a highly parameterized (that is, approximate) representation of vertical transport. Some models are capable of diurnal calculations, but most include some form of averaging over the day-night cycle. Our models are designed for time-dependent perturbation and sensitivity studies.

Two-dimensional models provide for variation of the transport, radiation fields, and species concentrations with latitude, altitude, and season. They also follow hemispheric differences in both atmospheric composition and response to perturbations.

In radiative transfer research, we apply detailed models to assess how changes in stratospheric composition affect both the ultraviolet radiation received at the ground and the fluxes of solar and longwave (infrared) radiation in the atmosphere. The latter effect is important because of the coupling between temperature and atmospheric composition. Changes in the concentration of radiatively active species affect atmospheric temperature; temperature changes affect chemical reaction rates; and changes in reaction rates affect species concentrations, including that of ozone.

To assess the effects of changes in atmospheric composition on the global climate, we use a two-dimensional (vertical and latitude) climate model. This model is unique in the large number of physical processes and feedback mechanisms included. Among the former are solar and longwave radiation, cloud cover, convective precipitation, proportional surface type, surface energy and hydrologic balances, and annual variability in land ice, snow, and sea ice.

Meteorological analysis provides guidance and support during modeling, enabling us to make in-depth studies of atmospheric processes and phenomena. A primary responsibility in this research is to develop test situations for validating various aspects of the numerical models.

HIGH-ALTITUDE AIRCRAFT EMISSIONS

Early concern about aircraft emissions focused on the effects of supersonic transport fleets (SSTs), expected to fly in the stratosphere. Although subsonic aircraft emit the same effluents, they fly mostly in the troposphere where these effluents are transported and removed more rapidly. As our air corridors become more crowded, however, and new subsonic aircraft are designed to fly at higher altitudes, they too will have to be considered in future assessments.

The engine emissions of concern are nitrogen oxides, water vapor, and SO_2 . Nitrogen oxides (NO and NO_2) and water vapor are the only species of chemical significance related to ozone. SO_2 contributes to the formation of sulfuric acid aerosols in the stratosphere, which affect the solar and longwave radiative fluxes, but its climatic effect is small.¹ A fleet of 100 British/French Concorde would inject approximately 6×10^7 kg NO_x /yr and 4×10^9 kg H_2O /yr at cruise altitude (about 17 km), assuming each flies an average of 4.4 hr/day at this altitude.

We have conducted studies of stratospheric pollution under funding from the Department of Transportation. The one-dimensional transport-kinetics model we use for stratospheric assessments includes 28 chemical species and 83 chemical and photochemical reactions. Species concentrations are computed at 44 levels extending from the ground to an altitude of 55 km. The model accounts for multiple scattering in computing photodissociation rates and can include temperature coupling between changes in composition and reaction-rate coefficients. Vertical transport is parameterized with a one-dimensional diffusion formulation, which describes hemispheric (or global) average net vertical transport by an altitude-dependent diffusion coefficient. The profile for this coefficient is empirically determined by a fit to actual concentration data of tracerlike species.

Ozone chemistry is more complex than implied by the simple catalytic cycles described above. Instead of being independent, these cycles are coupled such that changes in one may enhance or retard ozone destruction by another. We have shown that

the relative importance of the various cycles (and thus model sensitivity to stratospheric perturbations) depends upon certain key chemical rate coefficients, several of which have large uncertainties.²

In 1974 several numerical modeling groups, including LLL, funded under the Climatic Impact Assessment Program (CIAP) of the Department of Transportation, assessed the potential impact on total ozone of a large fleet of SSTs. The results of these studies—and of more recent LLL calculations—are shown in Fig. 1. For the sake of comparison, an injection rate of 1.23×10^9 kg NO_x/yr into a hemisphere was assumed, that is, approximately equivalent to 2000 Concorde. Our 1974 results are typical of those from the various one-dimensional models available at that time. The final CIAP curve was based on an average of our results and those from a model used by the National Academy of Sciences.

Since 1974 there have been many changes to these

Fig. 1. Ozone column change results computed by various models. The assumed injection rate is 1.23×10^9 kg NO_x (as NO_2) per year into a hemisphere. This is an arbitrary rate selected simply as a standard for purposes of comparing different models; it is not related to a particular number of aircraft. Data points represent our calculations for injections at 17 and 20 km, cruise altitudes for today's and future advanced SSTs, respectively. The curves are based on one-dimensional model results. As our 1976 and 1977 data points indicate, changes in these models have led to lower predictions of the effect of NO_x injections on ozone. Our latest results actually show a slight increase in ozone.

numerical models.³ New species (mostly containing chlorine) and reactions have been added. Poorly known reaction rates have been remeasured more accurately, and the photodissociation rate calculation has been improved. Temperature coupling and feedback on reaction rates have been added. Diurnal averaging has been accounted for more precisely. Most of these changes have led to a reduction in the computed effect of NO_x on ozone (see Fig. 1).

Most of the difference between our 1976 and 1977 results is due to a change in one key reaction rate, that of $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$, that has been measured to be many times faster than previously thought. The calculations now show a slight increase in ozone from NO_x emissions from aircraft in the lower stratosphere. Other models not at LLL also show an ozone increase for a 17-km injection altitude; for a 20-km injection altitude, however, results range from a slight ozone decrease to a slight increase. The models predict an ozone decrease for injection altitudes above 20 km. Until stratospheric chemistry is better understood and reaction rates are known more accurately, there will continue to be uncertainties associated with these results. A large uncertainty also stems from the variety of vertical transport parameterizations currently in use.

Figure 2 shows the change in local ozone concentration for NO_x injections at 20 km. The net effect of a NO_x injection on total ozone depends on the relative magnitudes of the increase in ozone concentration below 23 km and the decrease above 23 km. The increase occurs because the additional NO_x interferes with the HO_x catalytic cycle, which is the principal destruction process in this region. Although the change in total ozone is small, there are significant increases or decreases in the local ozone concentration, which relates to the stratosphere's temperature structure and stability. How these changes might affect vertical transport is yet to be assessed.

Increased concentrations of ozone and NO_2 near the level of the tropopause (around 15 km in altitude) would tend to increase the local heating due to absorption of solar and longwave radiation. It has been hypothesized that if there is an increase

Fig. 2. Change in local ozone concentration at steady state from various NO_x injections at 20 km. The net effect of an NO_x injection on total ozone depends on the relative magnitudes of the increase in ozone concentration below 23 km and the decrease above 23 km. These localized ozone concentration changes influence how temperature varies with altitude and can thus modify the stratosphere's stability. An injection rate of $6.2 \times 10^8 \text{ kg NO}_x/\text{yr}$ represents SST fleets of about 1000 aircraft.

in the temperature of the tropical tropopause, then more water vapor would be transported upward, resulting in an increase in the stratospheric water vapor concentration.

We have estimated the change in ozone concentration from this increase in water vapor concentration with calculations that consider both chemical and heat-balance effects. The chemical effect is a decrease in total ozone, but temperature feedback compensates for the chemical effect of increased water vapor, resulting in very little net change (less than 1%) in total ozone.

CHLOROFLUOROMETHANES AND THE SPACE SHUTTLE

The two chlorofluoromethanes most widely used and eliciting the greatest concern are CFCl_3 (F-11) and CF_2Cl_2 (F-12). CFMs were originally developed as refrigerants, but their major current use is as aerosol propellants. From 1965 to 1974, F-11 production grew 9%/yr in the United States and 20%/yr abroad. The corresponding growth rates for F-12 production are 7%/yr in the United States and 13%/yr abroad. Production rates have been nearly

Fig. 3. Reduction in total ozone from a constant production of chlorofluoromethanes at the 1973 rate and at one-half of that rate. The long-term effect of CFMs on ozone depends upon the production rate chosen: the 1973 rate is customarily assumed for assessment purposes. The shaded region for both rate curves represents the effect of using different diffusion coefficient profiles in the calculations. For the 1973 production rate, ozone reduction at steady state is about 15%.

Fig. 4. Change in local ozone concentration from a constant production of CFMs at the 1973 rate. In these calculations, we assumed either fixed temperature or a self-consistent temperature feedback. The results here contrast markedly with those shown in Fig. 2 for NO_x injections. In particular, CFM injections produce little or no increase in local ozone concentration in the lower stratosphere.

constant since the potential effect of CFMs on ozone was pointed out in 1974. A complete ban on the use of CFMs as aerosol propellants in the United States alone would only reduce world production by about 25%.

About 90% of the total production of F-11 and F-12 is released to the atmosphere. Once they are released, relatively rapid tropospheric mixing occurs. Because they have no significant tropospheric loss mechanisms, CFMs gradually accumulate in the troposphere and rise slowly into the stratosphere, where the sun's ultraviolet radiation decomposes them at altitudes above 25 km. The chlorine atoms and chlorine oxide produced directly or indirectly by this decomposition then catalytically react to remove ozone.

Figure 3 shows our calculations of the decrease in total ozone for two CFM production rates. Ozone is depleted gradually over many decades, taking 40 to 50 years to reach half of the total reduction that would eventually occur at steady state. The shaded area shows the range of our projections as a function of time depending on the choice of a diffusion coefficient profile. The model currently predicts about a 15% ozone reduction at steady state from

the 1973 CFM production rate.

If CFM production were stopped completely, ozone would continue to be depleted for 7 to 14 years, after which there would be a very slow recovery. This delay in reaching a maximum ozone reduction occurs because the troposphere acts as a reservoir of F-11 and F-12, which are only slowly transported upward into the stratosphere.

The vertical distributions of the ozone change resulting from CFM and NO_x perturbations vary greatly. The change in local ozone concentration from CFM injections is shown in Fig. 4. The largest ozone reduction occurs near 40 km; only relatively small changes in ozone concentration occur below 30 km. In the case of the NO_x injection due to engine effluents (Fig. 2), the local ozone concentration decreases above about 23 km but increases below this altitude.

Through cooperation with NASA, we have also studied the potential impact of the space shuttle on stratospheric chemistry. One of the major components of space-shuttle engine exhaust is HCl. Assuming 60 space shuttle flights per year, we have calculated a 0.27% ozone reduction due to the additional stratospheric chlorine. Other shuttle engine

exhaust by-products, such as NO and water, have also been studied and found to be insignificant.

ATMOSPHERIC NUCLEAR DETONATIONS

Atmospheric nuclear detonations inject NO_x into

the stratosphere. The major NO production mechanism is the high-temperature chemical equilibrium among molecular and atomic oxygen, nitrogen, and NO_x . In the fireball, N_2 is dissociated and oxidized to form NO. The relatively fast cooling of the hot cloud leads to thermal quenching of

STRATOSPHERIC OZONE: HOW IT AFFECTS US

The atmosphere is usually represented as being divided into layers whose boundaries correspond to temperature minima or maxima. The lowest layer is the troposphere, which extends from the ground to an altitude of about 16 km near the equator and 8 km near the poles. Here mean temperature decreases with height. Its upper boundary, the tropopause, is defined by the altitude at which temperature holds constant or begins to increase with height. The tropopause is an artificial boundary separating the troposphere and stratosphere. In the stratosphere, temperature increases to a maximum near 50 km, a level known as the stratopause. Because of this structure, the stratosphere is stable with respect to convective overturning, and this leads to very limited vertical motions. A tracer will remain in the stratosphere from one to several years; in the much less stable troposphere, it would mix rapidly and be subject to several removal mechanisms.

Almost all ozone is in the stratosphere. Although it is customary to speak of an ozone layer, the concentration of ozone in fact never exceeds a few parts per million. The total amount of ozone in a vertical column corresponds to only about 3 mm of pure ozone at standard temperature and pressure. Vertical profiles of ozone concentration typically show a maximum concentration near 23 km in middle latitudes.

Ozone is an effective absorber of ultraviolet radiation, essentially preventing radiation at wavelengths shorter than 290 nm from reaching the ground. It also absorbs some solar radiation in the visible region and longwave (infrared) radiation. Solar absorption by ozone is the primary warming mechanism for the stratosphere. Changes in ozone abundance are important because they affect the transport of solar and longwave radiation, which has climatic consequences, and because they affect the amount of ultraviolet radiation reaching the ground, which has biological consequences.

Perhaps the most widely discussed effect of increased ultraviolet radiation is the projected increase of skin cancer among humans. In the United States there are about 300 000 new skin cancer cases each year, of which about 2500 are fatal. The incidence rate increases toward the south: in middle latitudes (30 to 45° N), it doubles for each 10° decrease in latitude. Most of the contribution to skin cancer is believed to come from radiation in the 280- to 320-nm wavelength region. Because of the strong attenuation of solar radiation by ozone in this wavelength region, a small ozone reduction causes a much larger increase in the ultraviolet flux. For example, a 10% ozone reduction at middle latitudes leads to about a 20% increase in ultraviolet flux. In terms of the increased risk of skin cancer, this is equivalent to moving about 400 km south. Such a reduction would lead to some 60 000 new cases of skin cancer per year in the United States.

A reduction and redistribution of ozone might also lead to significant climatic effects. Based on simplified, one-dimensional, climate model calculations, the change in global mean surface temperature from supersonic aircraft and chlorofluoromethanes would be less than ± 0.2 K, but there could be much larger changes regionally, especially at high latitudes. Calculations with two- and three-dimensional models suggest that an increase in surface temperature would increase the intensity of the hydrologic cycle, thus increasing global mean precipitation. Uncertainties regarding cloud feedback processes and how climate changes will affect cloudiness, however, make it difficult at this time to quantify such climatic changes.

The accompanying article reports on LLL studies into how engine effluents from high-altitude aircraft, chlorofluoromethanes, and atmospheric nuclear explosions may affect the stratospheric ozone layer.

the equilibrium state. The rates of NO production and destruction become negligibly slow when the cloud cools below 2000 K, which occurs about a minute after detonation.

The NO produced is injected into the atmosphere at the cloud stabilization height, which depends on the amount of thermal heating and the amount of ambient air that is mixed with the fireball as it rises through the atmosphere. The stabilization height also depends on the atmospheric temperature structure, which varies with latitude. Variations in the height of burst within 0 to 3 km of the earth's surface do not significantly affect the cloud stabilization height. The device yield must be greater than 4.2 PJ (1 Mt) for the cloud to penetrate into the stratosphere.

Estimates of the total amount of NO produced per 4.2-PJ yield in a nuclear explosion vary, but we use the value of 6.7×10^{31} molecules/4.2 PJ.⁴ For ozone perturbations up to several percent, the response of our model varies approximately linearly with the total NO injection; thus, if NO production per 4.2 PJ should be readjusted in the future, our computed ozone perturbations would scale linearly.

There have been several analyses of global ozone measurements during the atmospheric nuclear test series of the 1950's and early 1960's. These have concluded that any ozone reductions caused by the nuclear tests must have been less than about 3%, which is the claimed noise level of the data. A gradual ozone reduction of 3 to 4% might not be inconsistent with the ozone record.

Under funding from the Division of Military Applications, we have computed the effect of the nuclear test series on total ozone in the Northern Hemisphere.⁵ Figure 5 shows our results with both our current model chemistry (1977) and that of a year ago. The 1977 model is preferred, but both sets of calculations are presented to show the significance of the changes in model chemistry during the past year and to give a feeling for the magnitude of the chemical uncertainties. We also use two parameterization schemes to prescribe the cloud stabilization altitude as a function of yield. Since one scheme overestimates and the other underestimates this altitude, we expect to bracket the

true values by using both.

Our calculation with 1976 chemistry predicted a maximum ozone reduction that was large compared with the 3% reduction estimated to be compatible with observations. With our 1977 chemistry and the low stabilization height estimates, we compute ozone increases from the 1950's tests and ozone reductions throughout the testing period of less than 2%.

The peak ozone reduction follows a number of high-yield detonations in late 1962. Since our one-dimensional model assumes uniform horizontal mixing, this would be a poor representation for the first several months after detonation while the debris is undergoing horizontal mixing and transport. Consequently, the model would tend to overestimate the peak ozone reduction. Our current results, therefore, may be comparable to the upper limit permitted by the ozone record.

We have also assessed the potential effect on ozone of a large number of nuclear detonations such as might occur during a large-scale nuclear exchange with individual yields of 1 to 21 PJ (250 kt to 5 Mt). Detonations within the range of 1 to 2 PJ have stabilization heights very close to the tropopause, so predictions of their effect on ozone are sensitive to the method used to estimate these heights. A variation in height of ± 1 km can significantly affect the amount of NO that is injected into the stratosphere.

Figure 6a shows the potential effect of 1-PJ (250-kt) devices on ozone in the Northern Hemisphere, computed with 1977 chemistry. According to these calculations, total ozone may increase or decrease depending upon the total yield.

Small NO_x injections due to nuclear explosions cause an increase in the ozone concentration near 16 km similar to that shown in Fig. 2. For small NO_x injections, the increase in ozone below about 20 km is greater than the reduction in ozone at higher altitudes, resulting in a net increase in total ozone. Very large NO_x injections cause the NO_x catalytic cycle to become dominant, resulting in a decrease in ozone concentration near 15 km.

Our calculations for the potential effects of 4.2- and 21-PJ (1- and 5-Mt) devices on total ozone in

the Northern Hemisphere are shown in Figs. 6b and 6c. These results are also based on our 1977 model chemistry. Because of their higher stabilization altitude (which is close to the altitude of peak ozone concentration), 21-PJ (5-Mt) devices reduce the ozone more than 4.2-PJ (1-Mt) devices for the same total yield. The peak ozone reduction occurs within the first year after detonation, followed by a period of recovery to near-normal ozone levels lasting 2 to 4 years.

In addition to changing total ozone, variations in weapon yield also affect the amount of radioactive fallout. Because of the lower stabilization height, the radioactive debris from low-yield weapons does not remain in the atmosphere so long. With less time for the debris to decay before it reaches the

ground, radiation levels are higher.

SUMMARY

We are continuing to study the potential chemical and climatic effects of several man-made perturbations to the stratosphere. In addition to our one-dimensional transport-kinetics model that has been used extensively for assessment studies, we are developing a two-dimensional version. This model will help us simulate and interpret the effects of high-yield nuclear detonations at high northern latitudes, as occurred during the 1960's. It will also be used to predict the latitude variation of ozone changes due to aircraft flight corridors at middle latitudes. We are continuing efforts to improve chemistry modeling, an area of major changes over

Fig. 5. Computed effect on total ozone in the Northern Hemisphere of atmospheric nuclear tests during 1956-1962. We assume that the total yield from high-yield detonations over this period was 1.8 EJ (429 Mt) with 1.4 EJ (335 Mt) occurring in 1961-1962. Results are shown for calculations with both our 1976 and 1977 model chemistry. The range for both sets of calculations stems from the use of two estimates of cloud stabilization heights; the upper boundaries correspond to the lower stabilization altitude estimate, the lower boundaries to the higher estimate. Our 1977 results are comparable to the upper limit permitted by ozone measurements made during the test period.

Fig. 6. Change in total ozone for the Northern Hemisphere from atmospheric nuclear explosions such as might occur during a large-scale nuclear exchange. Yields on the curves are for total yields during an exchange. All calculations were made with our 1977 model chemistry. Because of their higher cloud stabilization altitude, 21-PJ (5-Mt) devices have the greatest impact on total ozone.

the past few years. We anticipate further changes as more work is devoted to model validation and the reduction of uncertainties.

Current model calculations predict only small changes in total ozone from large fleets of high-altitude aircraft, but there may be significant changes in the local ozone concentration. CFMs are estimated to cause about a 15% reduction in total ozone at steady state, assuming a constant release rate at 1973 levels. The atmospheric detonation of a large number of nuclear devices with yields greater than 4.2 PJ (1 Mt) may cause ozone reductions much greater than 15%, returning to near-normal ozone levels after a few years.

Key Words: atmospheric nuclear explosions; chloro-fluoromethanes; ozone; ozone—chemical reactions; ozone—depletion; ozone—distribution; supersonic transport—environmental studies.

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Temperature Feedback in a Stratospheric Model

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Temperature Feedback in a Stratospheric Model

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Perturbing the stratospheric composition affects the stratospheric temperature profile via the radiation balance. Changes in temperature affect chemical reaction rates, which in turn feed back on stratospheric composition. The effect of temperature feedback on ozone concentration has been investigated for three types of perturbations: (1) stratospheric injection of NO_x , (2) release of fluorocarbons, and (3) doubling CO_2 . Temperature feedback had approximately a 10% restoring effect on ozone for small ozone reductions because of either stratospheric NO_x injection or release of fluorocarbons. Doubling CO_2 concentrations increased total ozone by 2.9%. Calculations of ozone reduction including temperature feedback were as much as 20% less than fixed temperature calculations using the U.S. Standard Atmosphere temperature profile.

INTRODUCTION

Perturbations of the stratospheric composition affect the stratospheric temperature profile via the solar and long-wave radiation balance. Changes in temperature affect chemical reaction rates, which in turn feed back on stratospheric composition. The temperature feedback mechanism has long been recognized as potentially important in mitigating perturbations to the ozone concentration, but it has only recently been included in stratospheric models.

Barnett *et al.* [1975] have investigated the temperature dependence of ozone concentration near the stratopause, and they showed that a decrease in temperature tends to increase the ozone concentration. Their theoretical analysis, considering only the basic Chapman reactions, showed that the ozone concentration is approximately proportional to $\exp(1400/T)$, or therefore $d \ln [\text{O}_3]/d(1/T) \approx 1400$. Likewise, for the HO_x and NO_x catalytic cycles they found $d \ln [\text{O}_3]/d(1/T)$ to be approximately 330–500 and 1200, respectively. In each of the cases considered, an increase in temperature tends to decrease the ozone concentration. If the change in temperature is due to a change in O_3 concentration, then this feedback mechanism tends to moderate or lessen the change in O_3 concentration; i.e., it represents a negative feedback.

The analysis above assumes that the O_3 concentration is controlled by photochemical processes alone. Consequently, this analysis is not quantitatively valid for the lower stratosphere, where atmospheric circulation (transport) is more important.

McElroy *et al.* [1974] estimated the effect of temperature feedback for stratospheric injections of NO_x , but solar absorption by NO_x , which has been shown to be important by Luther [1976a], was not included in the solar radiation calculation. Contributions on the effect of temperature feedback on ozone concentration for the atmospheric release of fluorocarbons and for doubled CO_2 have been made by Boughner and Ramanathan [1975] and Ramanathan and Boughner [1975]. Our present work expands upon these earlier investigations by using updated chemistry and including solar absorption by NO_x in the radiation balance.

MODEL DESCRIPTION

In order to investigate the effect of temperature feedback on the concentration of ozone a one-dimensional transport kinetics model was coupled to a stratospheric radiative transfer model. The transport kinetics model has been described pre-

viously [Chang, 1975; Wuebbles and Chang, 1975; Luther, 1976b], so only the main features of the model will be summarized.

The governing equation regarding the temporal variation in the number density of the i th constituent c_i is given by the continuity equation

$$\frac{\partial c_i}{\partial t} = P(c) - L(c)c_i - \frac{\partial}{\partial z} \left[K_{ip} \frac{\partial}{\partial z} \left(\frac{c_i}{\rho} \right) \right] \quad (1)$$

where $P(c)$ is the production of c_i due to photochemical interactions of the other c_j species, $L(c)c_i$ is the loss of c_i due to chemical interaction of c_i with the other c_j species, K_{ip} is the vertical transport coefficient, $\rho = \rho(z)$ is the ambient air density, and t and z are time and altitude, respectively.

The model atmosphere extends from the ground to 55 km and is divided into 44 layers. A total of 92 chemical (and photochemical) reactions are included in the model; 45 reactions describe O_x , NO_x , and HO_x chemistry, and 47 reactions describe ClO_x chemistry. These reactions are used to dynamically describe the stratospheric vertical distributions of 20 minor atmospheric species (O^1P , O_3 , NO , NO_2 , N_2O , HNO_3 , OH , HO_2 , H_2O_2 , Cl , Cl_2 , ClO , ClO_2 , OCIO , ClNO , ClNO_2 , HCl , CCl_4 , CF_2Cl_2 , and CFCl_3). ClO_x species are included only for the study involving the release of fluorocarbons. Three species (H , N , and O^1D) are assumed to be in instantaneous equilibrium, and the vertical distributions of N_2 , O_2 , H_2O , CH_4 , and H_2 are assumed to be constant throughout the calculations. The chemical rates used for six reactions important to the chlorine cycle are shown in Table I. Solar flux, absorption cross sections, and the calculation of photodissociation rates are as described by G. Linas [1974].

The vertical transport in the model is parameterized through the so-called 'eddy' mixing coefficient K_z [see Wuebbles and Chang, 1975; Chang, 1975]. The numerical technique, which is a variable order multistep implicit method, used to solve (1) is that described by Chang *et al.* [1974]. The boundary conditions, which are species dependent, are assumed to be fixed or time-varying source-dependent concentrations at the surface and flux conditions at 55 km, the upper boundary. The boundary conditions for O_3 are a fixed concentration at the earth's surface and a flux condition at 55 km. Changes in tropospheric O_3 have little effect on the computed change of total O_3 because the troposphere is relatively insensitive to change. The troposphere contains only about 5% of the total O_3 , which makes changes in stratospheric O_3 much more important than changes in the troposphere.

TABLE 1. Rates Used for Key Reactions

Reaction	Rate	Source
$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	$2.97 \times 10^{-11} \exp(-243/T)$	average of Davis <i>et al.</i> [1975] and Anderson <i>et al.</i> [1975]
$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$	5.3×10^{-11}	Watson [1974]
$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$	$5.4 \times 10^{-12} \exp(-1133/T)$	Davis <i>et al.</i> [1975]
$\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$	$2.0 \times 10^{-12} \exp(-310/T)$	Anderson <i>et al.</i> [1975]
$\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$	$2.6 \times 10^{-11} \exp(-50/T)$	Anderson <i>et al.</i> [1975]
$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	2×10^{-11}	low value quoted by Hampson and Garvin [1975]

The temperature profile above 12 km is calculated by using a stratospheric radiative transfer model, and the temperature profile below 12 km is specified. The model includes solar absorption and long-wave interaction by O_3 , H_2O , and CO_2 , along with solar absorption by NO_2 . The techniques adopted for treating long-wave radiative transfer are the same as those described by Ramanathan [1974]. This formulation was chosen because it is computationally efficient, and its accuracy has been demonstrated [Ramanathan, 1974, 1976] by comparison with much more complex models. The effects of and justification for the simplifying assumptions used in the model are discussed by Ramanathan [1976].

A band absorbance formulation is used to treat the 9.6- μm band of O_3 and the fundamental and several hot and isotopic bands of CO_2 in the 15- μm region. An emissivity formulation is used to treat long-wave radiative transfer by H_2O . Solar absorption by O_3 is treated by using the empirical formulation given by Lindzen and Will [1973]. The band absorbance formulation by Houghton [1963] is adopted for solar absorption by H_2O , and the band absorbance formulation by Ramanathan and Cess [1974] is adopted for solar absorption by CO_2 . The empirical formulation of Luther [1976c] is used for solar absorption by NO_2 . Solar absorption by O_3 and NO_2 are treated independently because absorption by these species is weak in the region where their absorption bands overlap. Solar radiation scattered from the troposphere is included by assuming an albedo of 0.3. Doppler broadening effects are included for CO_2 and O_3 as described in Appendix B of Ramanathan [1976]. The temperature dependences of the band absorbance and band intensity are included in the long-wave calculations of CO_2 and O_3 .

Fig. 1. The temperature profile derived by the model for unperturbed conditions and the U.S. Standard Atmosphere temperature profile.

A single cloud layer is included at 6.5 km with 42% cloud cover as was suggested by Cess [1974]. The lapse rate within the troposphere is assumed to be -6.5 K/km , and the temperature at the earth's surface is specified to be 288 K. The CO_2 mixing ratio is assumed to be 320 ppmv (parts per million by volume), and the stratospheric mass mixing ratio for H_2O is assumed to be 2.7 ppmm (parts per million by mass) ($= 4.3 \text{ ppmv}$). The tropospheric distribution of H_2O is based on the U.S. Standard Atmosphere (1962).

According to measurements of the H_2O distribution in the stratosphere [Harries, 1976] the mean mid-latitude northern hemisphere H_2O mixing ratio increases gradually with altitude, the mixing ratio being 2.2 ppmm at 17 km, 2.5 ppmm at 24 km, and 2.9 ppmm at 45 km. The shape of the H_2O distribution affects the computed temperature profile directly by its effect on the heating and cooling rates and indirectly by its effect on the O_3 concentration. A change in the stratospheric H_2O mixing ratio of $\pm 0.3 \text{ ppmm}$ causes a change in the computed temperature of $\pm 0.4 \text{ K}$ at 17 km, $\pm 0.2 \text{ K}$ at 26 km, $\pm 0.1 \text{ K}$ at 40 km, and $\pm 0.9 \text{ K}$ at 50 km. Changes in temperature of this magnitude have a negligible effect on the ambient ozone profile and model sensitivity.

We have chosen to specify rather than compute the H_2O profile because we believe the physical mechanisms controlling it are not sufficiently understood. The H_2O mixing ratio in the lower stratosphere is controlled by the tropical tropopause cold trap, and methane oxidation is presumably the controlling mechanism in the upper stratosphere, but computations of the H_2O profile [Liu *et al.*, 1976] predict a larger increase in H_2O mixing ratio with altitude than is observed. Changes in stratospheric H_2O due to changes in tropopause temperature may have a significant effect on the results, but this feedback mechanism has been neglected in these calculations. We do not consider the assumption of fixed H_2O and

Fig. 2. Variation of $d \ln \text{O}_3 / d(1/T)$ with height.

Fig. 3. Ozone reduction versus NO_x injection rate for 17- and 20-km injection heights.

CH_4 profiles to be serious for perturbations affecting total O_3 by only a few percent, but they may have a significant effect on the model calculations involving larger reductions in O_3 .

It should be noted that there are several differences between the radiative transfer model used here (which is the same as that of Ramanathan [1974] except that we have added solar absorption by NO_2) and the latest model of Ramanathan [1976]. His latest model computes tropospheric temperatures as well as stratospheric temperatures, whereas tropospheric temperatures are specified in our calculations. In the article by Ramanathan [1976], which was published subsequent to these calculations, an additional term was added to the equation for the long-wave flux divergence, which can affect the computed long-wave cooling rates above about 35 km depending upon the temperature gradient. These differences are discussed in detail by Ramanathan [1976].

RESULTS

The temperature profile generated by the radiative transfer model is shown in Figure 1. This profile is similar to temperature profiles observed at tropical latitudes. The temperature profile from the U.S. Standard Atmosphere (1962), which represents a mid-latitude average, is shown for comparison, since this profile is frequently assumed for transport kinetics calculations which neglect temperature feedback. The unperturbed temperature profile, which we will hereafter refer to as being 'ambient,' is similar in shape to the standard atmosphere but is a few degrees warmer above 20 km. The higher temperature is related to the model-generated ozone concentration. There is excellent agreement with the U.S. Standard Atmosphere when the mid-latitude ozone profile from the 1966 supplements is used in the temperature calculation. Large-scale dynamical processes are neglected in the determination of the temperature profile. These processes have a significant effect on the temperature profile near the tropopause at mid-latitudes. Including these effects would likely lessen the temperature gradient above the tropopause.

The model sensitivity to changes in temperature, as indicated by the quantity $d \ln [\text{O}_3] / d(1/T)$, is shown in Figure 2 as a function of altitude. The values in Figure 2 were obtained by incrementally increasing the temperature at all altitudes by an amount ΔT . The results did not depend on the choice of ΔT

for $\Delta T < 1 \text{ K}$. The model is most sensitive to changes in temperature near 42 km, where $d \ln [\text{O}_3] / d(1/T) = 1400$. The Chapman reactions attain maximum importance in this region (see model A of Duewer et al., 1977), and this value is in good agreement with the theoretical estimate. The model sensitivity to temperature decreases above this altitude as would be expected when the HO_2 reaction scheme becomes increasingly important. The NO_x reaction scheme dominates below 40 km and the HO_2 reaction scheme dominates again below about 25 km.

Transport plays an important role in affecting the O_3 profile below 25 km. Consequently, A_2 affects model sensitivity to changes in temperature in this region. In addition, the dominant mechanism in HO_2 reactions below 25 km ($\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$ and $\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$) is different from that in reactions above 40 km and is therefore expected to have a different temperature dependence. The change in the slope of $d \ln [\text{O}_3] / d(1/T)$ at 10 km is due to a large change in the value of K_2 at this level.

Changes in the thermal structure may affect the atmospheric transport, which in turn affects the O_3 concentration. This feedback effect was not included in the model, although changes in vertical flux due to changes in the gradient of the species concentrations are included. The lack of feedback on the transport introduces significant uncertainty into the results, especially for the lower stratosphere. The present analysis, however, is useful in determining the potential importance of temperature feedback as compared to other uncertainties in transport kinetics models. If temperature feedback is first shown to have a large effect, then it would be logical to extend the assessment to include feedback on the transport by using a multidimensional model.

The model was applied to three perturbations: (1) stratospheric injection of NO_x , (2) release of fluorocarbons, and (3) doubling CO_2 . Results for each of these perturbations are discussed separately in the following sections.

Stratospheric Injection of NO_x

The effect of stratospheric injections of NO_x by supersonic transports on ozone concentration was computed for four cases: (1) without temperature feedback, using the U.S. Standard Atmosphere temperature profile, (2) without temperature feedback, using the ambient temperature profile from the stratospheric radiative transfer model, (3) with temperature feedback, and (4) with temperature feedback but without including solar absorption by NO_2 . The first case is an assumption frequently made in transport kinetics calculations. The second case is the reference condition for comparison with the temperature feedback calculation, which is the third case. The fourth case is included to indicate the significance of neglecting solar absorption by NO_2 .

The reduction in the ozone column caused by the stratospheric injection of NO_x is shown in Figure 3 for the case with

TABLE 2. Ratio of Fractional Changes in NO_x and O_3 Columns

NO_x Injection Rate, kg/yr as NO_2	$-(\Delta \text{NO}_x / \text{NO}_x) / (\Delta \text{O}_3 / \text{O}_3)$	
	Temperature Feedback	U.S. Standard Atmosphere
1.2×10^0	14.1	12.0
2.4×10^0	14.0	12.1
6.4×10^0	13.4	12.4
1.2×10^1	12.2	12.1

temperature feedback. The NO_x injection rate as NO_2 represents a global average value uniformly distributed over a 1-km-thick layer centered at the indicated altitude. The ozone reduction is a steady state value obtained from a time-dependent calculation as it approached equilibrium. Relatively large levels of injection of NO_x are required to reduce the ozone column more than a few percent. The ozone reduction values in Figure 3 are smaller than those previously reported [Chang, 1975] by about a factor of 2 because of changes in the model chemistry, especially the $\text{OH} + \text{HO}_2$ reaction rate. The reaction rate presently used for $\text{OH} + \text{HO}_2$ is $2 \times 10^{-16} \text{ cm}^3/\text{s}$, whereas previously we used the upper limit $2 \times 10^{-15} \text{ cm}^3/\text{s}$ [Hampson and Garin, 1975]. See Duever *et al.* [1977] for a detailed discussion of the effects of variations in chemical reaction rates on model sensitivity.

The relative importance of changes in solar absorption by the total columns of O_3 and NO_2 depends upon the ratio $\delta = -(\Delta\text{NO}_2/\text{NO}_2)/(\Delta\text{O}_3/\text{O}_3)$ [Luther, 1976a]. Values of this ratio are listed in Table 2 for several NO_x injection rates. The ratio varies between 12 and 14, whereas previous calculations indicated values of 6–7 [Chang, 1975]. The difference is due to the changes in model chemistry previously mentioned.

In presenting our results the ratio of the ozone reduction for a given case to the ozone reduction with temperature feedback is used as a basis for comparison. These ratios are shown for each of the four cases in Figure 4 for injection altitudes of 17 and 20 km. These results demonstrate several important effects.

Sensitivity to the assumed temperature profile. The two cases without temperature feedback demonstrate the sensitivity of the calculations to the assumed temperature profile. The ozone reduction for the U.S. Standard Atmosphere temperature profile is as much as 13% greater than it is for the ambient temperature profile for small NO_x injection rates at 17 km. This larger effect is primarily due to the cooler temperatures between 10 and 20 km.

The difference in the O_3 columns is small (0.293 atm cm for the U.S. Standard Atmosphere and 0.290 atm cm for the ambient temperature), but there are significant differences in the concentration profiles, as is indicated by the ratio of O_3 concentrations shown in Figure 5 for the unperturbed atmosphere. The ozone profile is significantly changed in the region between 10 and 25 km. There is less O_3 above 25 km for the ambient temperature profile, which allows more photolysis of O_3 below 25 km; as a result, ozone below this altitude increases. In addition, increased production of $\text{O}(^1\text{D})$ from O_3 photolysis below 25 km results in an increase in the importance of the HO_x catalytic cycle for odd oxygen destruction (due to increased HO_x from $\text{O}(^1\text{D}) + \text{H}_2\text{O}$). Therefore because of interference of the HO_x cycle by the reactions $\text{HO}_x + \text{NO} \rightarrow \text{OH} + \text{NO}_2$ and $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_2 + \text{M}$, it is expected that a 17-km injection of NO_x will result in less destruction of ozone for the ambient temperature profile than for the U.S. Standard Atmosphere temperature profile. In the case of an NO_x injection rate of $1.2 \times 10^9 \text{ kg/yr}$ as NO_2 at 17 km, the ozone column is reduced 1.20% for the U.S. Standard Atmosphere profile and 1.09% for the ambient temperature profile.

Importance of temperature feedback. The importance of temperature feedback is demonstrated by comparing the results with temperature feedback to the results for the fixed ambient temperature profile. Both calculations start with the same temperature profile and the same O_3 column. For small NO_x injections, temperature feedback has a 5–10% restoring effect on the ozone column (Figure 4). The difference between

Fig. 4. The ratio of ozone reduction for a given case to ozone reduction with temperature feedback versus NO_x injection rate for a 17-km injection height and a 20-km injection height.

the temperature feedback and fixed temperature calculations decreased with increasing NO_x injection rates, the calculations eventually crossing at large NO_x injection rates (corresponding to a 9% ozone reduction for the 17-km injection case and a 14% ozone reduction for the 20-km injection case). This crossover is due to the nonlinear variation of the perturbed O_3 and NO_x concentration profiles and the resulting temperature changes.

The unperturbed O_3 and NO_2 profiles are shown in Figures 6 and 7, respectively, along with the perturbed profiles corresponding to NO_x injection rates of 2.5×10^9 and $1.2 \times 10^{10} \text{ kg/yr}$ as NO_2 at 20 km. The reduction in the O_3 concentration is spread smoothly over a broad altitude range, whereas the increase in NO_2 concentration is strongly peaked near the level of injection. These differences account for the variations in the change in temperature shown in Figure 8. Near the level of injection, which is 20 km in this case, increased solar absorption by NO_2 more than compensates for the decrease in O_3 absorption and thus leads to a temperature increase in this region. The region of temperature increase expands as the NO_x injection rate increases. The enhanced ozone destruction which occurs in the region of increased temperature eventually offsets the restoring effect of temperature feedback at higher altitudes and thus causes the ozone reduction to be less with the ambient temperature profile held fixed than with temperature feedback for large NO_x injections. Although the reduction in the ozone column may be similar for the fixed temper-

Fig. 5 The ratio of the ozone concentration for the ambient temperature profile to the ozone concentration for the U.S. Standard Atmosphere temperature profile.

ature and temperature feedback calculations, there are significant differences in the vertical distribution of the change in ozone column. The decrease in stratospheric stability above the level of injection could significantly affect stratospheric dynamics. Since dynamic feedback was not included in these calculations, the crossover between the fixed temperature and temperature feedback calculations may be artificial.

The change in ozone concentration as a function of height is shown in Figure 9 for the arbitrary case of a 20-km injection of NO_x at a rate of $2.5 \times 10^9 \text{ kg/yr}$ as NO_2 . The increase in ozone concentration in the lower stratosphere, which also occurs in the fixed temperature calculation, is attributed to NO_x interference of the HO_x induced O_3 destruction [see Duewer *et al.*, 1977] and increased photolysis of O_3 due to a decrease in the overhead ozone burden. The increase in ozone concentration is not as significant as it might appear because the ozone concentration is quite small near 15 km in comparison to the 20- to 35-km region. The maximum percent change in ozone concentration occurs near 30 km, and the maximum change in absolute concentration occurs about 2 km lower. The decrease in temperature above 22 km results in less ozone destruction in this region, and the temperature increase below 22 km results in a smaller O_3 concentration than occurs in the case with no feedback (i.e., more ozone destruction or less ozone production).

Importance of solar absorption by hO_2 . The ozone reduction in the case with temperature feedback but without solar

Fig. 6. Concentration profiles of O_3 for ambient conditions and for steady state injections of NO_x at 20 km.

Fig. 7. Concentration profiles of NO_2 for ambient conditions and for steady state injections of NO_2 at 20 km.

absorption by NO_2 is 10-15% less than it is when NO_2 solar absorption is included (Figure 4). Neglecting solar absorption by NO_2 leads to an overestimate of the stratospheric temperature change and, consequently, an overestimate of the temperature feedback effect.

The changes in temperature for the cases with temperature feedback and with feedback but without solar absorption by NO_2 are shown in Figure 10 for an NO_x injection rate of $2.5 \times 10^9 \text{ kg/yr}$ as NO_2 at 20 km. The differences between these results illustrate the relative importance of changes in solar absorption by O_3 and NO_2 . Increased solar absorption by NO_2 is sufficient in this case to cut the maximum cooling in half and to increase the magnitude and altitude range of the temperature increase in the lower stratosphere.

McElroy *et al.* [1974] estimated the effect of temperature feedback for stratospheric injections of NO_x . Their calculations, which did not include solar absorption by NO_2 , predicted values for the ratio $\Delta\text{O}_3(\text{ambient})/\Delta\text{O}_3(\text{temperature feedback})$ of 1.18 for a 10% ozone reduction and 1.11 for a 20% ozone reduction (interpolated from their Figure 16). Our calculations without solar absorption by NO_2 gave values of 1.14 and 1.12 for this ratio for the same reductions in ozone column. Thus comparable results are obtained for similar conditions, but the inclusion of solar absorption by NO_2 is important. When NO_2 absorption is included, our results are values of 1.01 and 0.98 for ozone reductions of 10 and 20%, respectively, for a 20-km injection altitude.

Release of Fluorocarbons

The assessment of the effect of temperature feedback on

Fig. 8. Change in temperature versus height for several NO_x injection rates at 20 km.

Fig. 9. Change in ozone concentration versus height for an NO_x injection rate of 2.5×10^9 kg/yr as NO_2 at 20 km.

ozone reduction due to the release of fluorocarbons differs from the NO_x calculations in that these calculations are time dependent rather than steady state. For these time-dependent calculations the temperature profile was computed at each time step by assuming radiative equilibrium conditions. To be consistent, the temperature calculations should be time dependent, taking into account the radiative time constant of the atmosphere. Because radiative equilibrium is assumed, the effect of temperature feedback is overestimated. Consequently, these calculations represent an order of magnitude assessment of the effect.

Ramanathan [1975] and Wang *et al.* [1976] have demonstrated the importance of the infrared absorption bands of fluorocarbons CFCI_3 and CF_3Cl . Since these absorption bands are not included in the stratospheric radiative transfer model, the analysis is valid only for fluorocarbon concentrations much less than 1 ppb. Fluorocarbon concentrations may reach several parts per billion by the year 2000, so we limited our calculations to estimating the reduction in ozone up to the end of 1975.

The natural atmosphere for these calculations contained HCl with an assumed mixing ratio of 10^{-9} by volume at the

Fig. 10. Change in temperature versus height for an NO_x injection rate of 2.5×10^9 kg/yr as NO_2 at 20 km (solid curve). The dashed curve indicates the change in temperature neglecting solar absorption by NO_2 .

Fig. 11. Change in ozone column due to fluorocarbon production in the period from 1950 through 1975.

earth's surface and a constant CCl_4 flux at the surface. The fluorocarbons CFCI_3 and CF_3Cl were introduced at the surface in the period from 1950 through 1975 according to world fluorocarbon production data [McCarthy, 1974]. The computed reduction in the ozone column resulting from the atmospheric release of fluorocarbons during this period of time is shown in Figure 11.

The reduction in the ozone column at the end of 1975 is 0.62% for the case with temperature feedback. The ozone reduction for the fixed temperature calculation using the ambient temperature profile is a factor of 1.09 greater than that for the case with temperature feedback. For the U.S. Standard Atmosphere temperature profile the ozone reduction is a factor of 1.18 greater. As is true in the case of NO_x injection, the results are sensitive to the temperature profile assumed for the fixed temperature calculations. Temperature feedback may significantly moderate the ozone reduction at a later time when the accumulated fluorocarbon releases are much larger.

The change in ozone concentration at the end of 1975 is shown as a function of height in Figure 12. Temperature feedback reduces the maximum percentage change in ozone, which occurs near 40 km. The maximum change in absolute concentration occurred at 28 km.

Doubling CO_2

Projections of the increase in atmospheric CO_2 resulting from the burning of fossil fuels indicate a possible doubling of CO_2 near the middle of the next century [Bacastow and Keeling, 1973; Hoffert, 1974]. Various climate models indicate a

Fig. 12. Change in ozone concentration versus height computed for January 1976.

global average surface temperature increase between 1.5 and 3 K from a doubling of CO_2 from 300 to 600 ppm [Schneider, 1975].

Boughner and Ramanathan [1975] have investigated the effect on ozone abundance of changes in stratospheric temperature due to a doubling of CO_2 . They found that doubling CO_2 increased the ozone column approximately 2%. We have repeated this calculation in order to compare model sensitivities.

For our calculations we assumed a surface temperature increase of 2 K. Doubling the CO_2 concentration from an initial value of 300 to 600 ppm caused an increase in total ozone of 2.9%. The change in ozone concentration versus altitude is shown in Figure 13. The ozone concentration increased by a maximum of 27% at 43 km, whereas Boughner and Ramanathan predicted a maximum increase of 15% at 40 km. The reason for these differences is partly attributable to differences in the predicted temperature change above 30 km.

As was mentioned above, there are differences between our radiative transfer model and that of Ramanathan [1976] which affect the long-wave cooling rates in the upper stratosphere. Our model predicts temperature changes of -5.2 K at 26 km and -11.6 K at 42.5 km, which are within 1 K of the values computed by Manabe and Wetherald [1967] but are larger than those predicted by R. E. Boughner and V. Ramanathan (private communication, 1976). The differences in the predicted temperature change are not sufficient, however, to account for the significant difference in model sensitivities. Most of the difference must therefore be attributed to model chemistry.

CONCLUSIONS

The intent of this paper has been to estimate the magnitude of the temperature feedback effect, which is an important step toward developing self-consistent calculations of changes in stratospheric composition and temperature. The effect of temperature feedback on ozone concentration was investigated for three perturbations of the atmospheric composition. Temperature feedback was found to have a similar effect for small ozone reductions for both the stratospheric injection of NO_x and the release of fluorocarbons. In both cases, temperature feedback had approximately a 10% restoring effect on the ozone column. The temperature profile used for the fixed temperature calculations has a significant effect on model sensitivity. Calculations of $\Delta\text{O}_3/\text{O}_3$ including temperature feedback were as much as 20% less than those using the U.S. Standard Atmosphere temperature profile.

The effect of temperature feedback on the reduction of total ozone decreased with increasing NO_x injection rate. Although fixed temperature and temperature feedback calculations predict similar ozone reductions, there are significant differences in the vertical distribution of the ozone change. Significant changes in stratospheric stability are also predicted which may affect atmospheric dynamics.

A region of stratospheric warming is predicted near the level of injection of NO_x . The warming is attributed to increased solar absorption by NO_x , which exceeds the decrease in solar absorption by O_3 . Calculations which neglect solar absorption by NO_x significantly overestimate the effect of temperature feedback.

The effect of changes in temperature on chemical reaction rates has been shown to be a significant feedback mechanism. The fact that different models vary in their sensitivity to perturbations of the atmospheric composition does not mask the importance of temperature feedback. As transport kinetics models improve in detail, the effects due to temperature feed-

Fig. 13. Change in ozone concentration versus height for doubled CO_2 .

back should be considered in any assessment of potential perturbations to the atmospheric composition.

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***Annual Report of Lawrence Livermore National Laboratory
to the High Altitude Pollution Program—1977***

F. M. Luther et al.

**Lawrence Livermore National Laboratory
report UCRL-50042-77, 1977
Livermore, California**

PREFACE

Since July 1, 1975, Lawrence Livermore Laboratory (LLL) has been participating in the High Altitude Pollution Program sponsored by the U.S. Department of Transportation's Federal Aviation Administration. This report describes the major accomplishments and significant findings during the fiscal year ending September 30, 1977, for work performed at LLL under Reimbursable Agreement DOT-FA76WA1-653. There are two major research areas covered by this agreement: (1) numerical modeling of the atmospheric response to stratospheric perturbations, and (2) the processing, archiving, and analysis of satellite ozone data. Each of these research areas has been divided into a number of subtasks, and the successful accomplishment of these subtasks has required contributions and cooperation from many participants. The work reported here should be considered the collective effort of all those listed below.

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ANNUAL REPORT OF LAWRENCE LIVERMORE LABORATORY TO THE HIGH ALTITUDE POLLUTION PROGRAM—1977

1. INTRODUCTION

The High Altitude Pollution Program (HAPP) was initiated by the Federal Aviation Administration to ensure that aircraft engine emissions in the stratosphere will not result in unacceptable effects on the biosphere. Lawrence Livermore Laboratory (LLL) has participated in HAPP since July 1975. The primary research emphasis at LLL is on numerical modeling of the atmospheric response to stratospheric perturbations. The modeling effort at LLL covers four major research areas: photochemical kinetics, coupled kinetics and transport, radiative transfer, and meteorological analysis.

A fundamental tool in the LLL effort has been the one-dimensional transport-kinetics model. This model, which includes as complete a set of the important chemical and photochemical reactions as is feasible, is designed for time-dependent perturbation and sensitivity studies. The model includes 28 chemical species and 83 chemical and photochemical reactions. Species concentrations are computed at 44 levels in the atmosphere, extending from the ground to an altitude of 55 km. The model uses an accurate numerical method for solving stiff systems of differential equations. Vertical transport is parameterized using a one-dimensional diffusion formulation which describes hemispheric-average net vertical transport by an altitude-dependent diffusion coefficient. The model can include temperature coupling between changes in composition and reaction rate coefficients.

During the past year we improved this one-dimensional model by adding multiple scattering effects to the photodissociation rate calculation and by developing a more accurate method for incorporating diurnal averaging. We also directed considerable attention to the problem of evaluating the effect that changes in key chemical rate coefficients (as a result of new measurements) have on the model's sensitivity.

In addition to the one-dimensional model, we are in the process of developing a two-dimensional transport-kinetics model.

Support for model development is shared between HAPP and another project at LLL involving

assessment of the chemical and climatic effects of atmospheric nuclear explosions. The latter project is funded by the Division of Military Application (DMA) of the Department of Energy. Although the same numerical models are used for both studies, the applications of the models are quite different. For example, the study of the climatic effect of nuclear explosions is primarily concerned with the time-dependent response of the atmosphere to pulse injections of NO_x , whereas the HAPP study is concerned with steady-state injections of NO_x . Work relating to model development or refinement benefits both projects, and consequently such work has been divided between the two projects. In this way each project's sponsor benefits from the participation of the other sponsor.

In August 1976, LLL's participation in HAPP was extended to include the processing, archiving, and analysis of global ozone data derived from a new series of Air Force meteorological-satellite sensors: the cross-track-scanning multifilter radiometer sensors. The Satellite Ozone Analysis Center (SOAC) was formed at LLL for the purpose of producing high-quality total-ozone data based on radiance measurements made with the new satellite sensors. The goal is to develop a capability for producing daily maps of total global ozone that can be made readily available to the scientific community. Our initial task is to demonstrate the feasibility of obtaining good ozone data from the satellite measurements. To do this we must first develop a satisfactory method for converting the satellite measurements to total ozone data. We plan to assess the quality of the resultant ozone data by comparing it in detail against corresponding Dobson ozone data obtained at selected stations in the world surface network of Dobson observatories. This feasibility study is scheduled for completion by June 1978.

In this annual report we describe LLL's major accomplishments and findings in HAPP studies since July 1, 1976. Earlier HAPP work is described in our First Annual Report (Luther et al. 1976). In the present report we emphasize the results in the atmospheric modeling area and limit our discussion

of the SOAC project to a description of the satellite multifilter radiometer sensor and a summary of the

major tasks and objectives. The results of the SOAC feasibility study will be described in a later report.

2. RESEARCH ACTIVITIES: TRANSPORT KINETICS MODELING, PHOTOCHEMICAL KINETICS, AND RADIATIVE TRANSFER

Because of the complex nature of the work, most of the research tasks represent the combined effort of several scientists rather than individual contributions. It is not possible to separate the tasks by research area or scientific discipline because of the team approach. Most of the work described below has been or is in the process of being submitted for publication in technical journals.

2.1 A Fully Diurnal-Averaged Model of the Stratosphere

An outstanding question in the formulation of stratospheric chemical kinetics models is the proper averaging procedure for photochemical reaction rates involving diurnally varying chemical species. We have developed a fully diurnal-averaged model (DAM) that is consistent with our diurnal model (DM). By definition, these two models are consistent if the average tracer concentration from the diurnal-averaged model is the same as the diurnal average of the time-dependent solution from the diurnal model, and if all the corresponding averaged photochemical reaction rates are also identical. With the DM model we can calculate relevant details and compare the results with atmospheric measurements, and with the DAM model we can study the long-term atmospheric response to any perturbation. To study this latter class of problems with the DM model would not be economical. A computation procedure has been devised to assure the total consistency between these two models under all given conditions.

Model Description

We shall limit our discussion to the one-dimensional model since this is our current development. The procedure described is directly applicable to two-dimensional models. In a one-dimensional model of the stratosphere, the continuity equation for a specific trace species i is

$$\frac{\partial n_i}{\partial t} = -\frac{\partial}{\partial z} F(n_i) + P_i - L_i n_i + S_i, \quad (1-1)$$

where n_i is the concentration of species i at time t and altitude z , $F(n_i)$ is the net vertical transport flux, P_i and $L_i n_i$ are the nonlinear chemical and photochemical production and loss rates, and S_i is the net production or loss rate due to any other process. If Eq. (1-1) is averaged over a time period T (here assumed to be 24 hours) which is very small compared to the time scale of the problem of interest, then

$$\frac{\partial \bar{n}_i}{\partial t} = -\frac{\partial}{\partial z} \bar{F}(n_i) + \bar{P}_i - \bar{L}_i \bar{n}_i + \bar{S}_i, \quad (1-2)$$

with the bar representing the following averaging process:

$$\bar{\phi} = \frac{1}{T} \int_{-T/2}^{+T/2} \phi(z, t') dt'$$

The net vertical flux $F(n_i)$ is usually represented by

$$F(n_i) = -K_z \rho \frac{\partial}{\partial z} (n_i / \rho),$$

where K_z is the one-dimensional diffusion coefficient and ρ is the air density. Because K_z and ρ are independent of n_i in this approximation,* the net vertical flux $F(n_i)$ is a linear function of n_i . Furthermore, since K_z and ρ are assumed to be independent of time, i.e., to have no variation over the averaging period, we have

$$\bar{F}(n_i) = -K_z \rho \frac{\partial}{\partial z} (\bar{n}_i / \rho) = -K_z \rho \frac{\partial}{\partial z} (\bar{n}_i / \rho) = F(\bar{n}_i).$$

The source function S_i is usually well defined, hence $\bar{S}_i$ is easily computed. Equation (1-2) will be self-consistent if we can express the nonlinear expressions in $\bar{P}_i$ and $\bar{L}_i \bar{n}_i$ in terms of $\bar{n}_i$. Fortunately, P_i and $L_i n_i$ are both linear sums of terms in the form of the typical two-body chemical kinetics reactions

*It is true that K_z may be derived from some known n_i distributions. But once it is derived the 1-D model assumes K_z as a fixed input variable.

$K_{ij}n_i n_j$ or the photodissociation reaction $J_i n_i$. The kinetics reaction rate coefficient K_{ij} may be a function of ρ but not of n_i or n_j . We define the diurnal weighting factors $\alpha_{ij}(z)$ and $\beta_i(z)$ by

$$\overline{K_{ij} n_i n_j} = \alpha_{ij} \overline{K_{ij}} \overline{n_i} \overline{n_j}$$

and

$$\overline{J_i n_i} = \beta_i \overline{J_i} \overline{n_i}.$$

Since K_{ij} is defined and is independent of time, we have

$$\alpha_{ij} = \overline{n_i n_j} / \overline{n_i} \overline{n_j}$$

and

$$\beta_i = \overline{J_i n_i} / \overline{J_i} \overline{n_i}.$$

The computation of photodissociation rates has always been an expensive part of stratospheric model calculation, hence J_i 's are expensive to evaluate in the DAM model. If we define β_i by

$$\beta_i = \overline{J_i n_i} / (J_i^{\text{noon}} \overline{n_i}),$$

then the computation in the DAM model will be significantly simplified. Using the results from a diurnal model we can determine $\overline{n_i n_j}$, $\overline{J_i n_i}$, $\overline{n_i}$, $\overline{n_j}$, J_i^{noon} so that α_{ij} and β_i can be obtained for every chemical and photochemical reaction in the model.

Using the α 's and β 's evaluated from the diurnal model, we can now write Eq. (1-2) in terms of the diurnal-averaged concentrations $\overline{n_i}$.

$$\begin{aligned} \frac{\partial \overline{n_i}}{\partial t} = & -\nabla \cdot \mathbf{F}(\overline{n_i}) + P(\alpha, \beta, \overline{n_i}, \overline{n_k}, K_{ij}, J_j^{\text{noon}}) \\ & - L_i(\alpha, \beta, K_{mi}, J_i^{\text{noon}}, \overline{n_m}) \overline{n_i} + \overline{S_i}. \end{aligned} \quad (1-3)$$

where j, k, m are taken to represent species usually different from i . Formally, Eqs. (1-1) and (1-3) are identical in form except that every reaction rate in Eq. (1-3) is multiplied by an α or β factor determined from the solutions of Eq. (1-1).

The DM consists of Eq. (1-1) and its associated boundary and initial conditions. In this model the photodissociation rate coefficients vary throughout the day and vanish at night, and the local concentrations of many trace species such as $O(^1D)$, $O(^3P)$,

NO , HO_2 , Cl , ClO , HO , HO_2 , etc. also have strong diurnal variations. For the DAM, i.e., Eq. (1-3) and the appropriate averaged initial and boundary conditions, all the photodissociation rates are constant on the diurnal time scale. All solutions of Eq. (1-3) represent averaged concentrations, i.e., they exhibit no diurnal variations. As such, solutions of Eq. (1-3) are not directly comparable to many atmospheric measurements. Most atmospheric data are taken under daytime conditions or during sunset or sunrise. For the present model it is quite simple to recover the time-dependent solution (DM model) from the averaged solution (DAM model). In the derivation of α 's and β 's a third set of variables γ_i 's can be defined,

$$n_i^{\text{noon}} = \gamma_i \overline{n_i}.$$

Consequently, given any n_i from the DAM model, the corresponding noontime concentrations can be obtained through a simple multiplication, and this n_i^{noon} can be used as the input condition to the DM model to obtain the corresponding time-dependent diurnal solution.

In this formulation of the DAM model, it is implicitly assumed that the diurnal weighting factors are essentially constant even though the individual concentrations $\overline{n_i}$, hence the corresponding n_i , may vary considerably in magnitude. This assumption is valid if the functional shapes, i.e., the periodic functions representing the individual diurnal trace-species concentrations, are not sensitive to variations in the absolute magnitude of the concentrations. This simple fact can be directly verified with the DM model through the iteration procedure outlined in Fig. 1. Given initial estimates of α 's and β 's, we can use the DAM and DA models alternatively to assure that the α 's and β 's and $\overline{n}$'s are indeed consistent for any given atmospheric condition. Since this only involves a few diurnal cycles with the DM model at a judiciously chosen juncture of the calculation, the full iteration procedure is rather economical. In fact, in the present calculations involving the study of potential NO_x and ClX perturbations in the stratosphere, we have found that two or at most three iterations are sufficient to assure constancy of better than a few percent over most of the stratosphere for every trace species. The only exceptions are NO_3 and N_2O_5 above 40 km. At this altitude these species play such an insignificant role in stratospheric chemical balances that even major errors in their local concentrations have no significant impact. Purely for the sake of theoretical consistency, a study is still proceeding to understand the interesting diurnal behavior of N_2O_5 so that a

Figure 1. Iteration procedure followed in the diurnal-averaged model (DAM).

better averaging procedure can be defined specifically for N_2O_5 to reduce this local variation in diurnal weighting factors.

Discussion of Results

The α 's and β 's calculated from the diurnal model for some of the reactions in the model are shown in Figs. 2 and 3. These reactions were selected not because they are the more important ones in the model but because they represent some of the interesting features found in the derived multipliers for kinetic rates to be used in a diurnal-averaged model.

If a reaction involves a species that does not have a diurnal variation (i.e., the concentration is essentially constant over a 24-hour period), then the α 's for that reaction will be 1.0. Therefore, if a reaction involves HNO_3 or HCl , for example, the weighting factor will not change the original reaction rate. However, if both reactants in a two-body reaction have diurnal variations, the value for α will be different from 1.0. For instance, for reactions involv-

ing two species whose diurnal variations are in phase and predominantly determined by photolysis (i.e., both having extremely small concentrations at night relative to their daytime values or vice versa), the expected values for α would be approximately 2. Thus, as shown in Fig. 2, the α 's for the reactions $\text{ClO} + \text{NO}$ and $\text{HO} + \text{HO}_2$ are both approximately 2 in the lower stratosphere. In the upper stratosphere ClO does not decrease much at night, and the value for α falls off sharply. Above 45 km ClO actually increases at night, hence it is out of phase with NO . On the other hand, the weighting factor for the ClONO_2 formation reaction $\text{ClO} + \text{NO}_2 + \text{M}$ varies exactly in the opposite manner as compared with $\text{ClO} + \text{NO}$. In the lower stratosphere ClO and NO_2 are out of phase while above 45 km they are in phase (Fig. 4). For other important reactions such as $\text{NO}_2 + \text{O}$ and $\text{NO}_2 + \text{HO} + \text{M}$, this variation in phase relation is again different. The diurnal variations of the reactants involved are very much out of phase both in the lower and upper stratosphere. These few examples show quite clearly

Figure 2. Curves relating α to altitude for some typical chemical kinetics reactions in the diurnal-averaged model.

that although the phase relationship in diurnal variations can be used as a qualitative guide in appreciating the diurnal effect on net reaction rates, it is by no means adequate. Due to the complexity of the chemical system only detailed calculations such as are used in our current procedure can provide the proper balanced evaluation. It is to be noted that when diurnally averaged concentrations are used in the rate expressions, the weighting factors (or correction factors) can have a very large effect on some of the reaction rate coefficients, increasing them by more than a factor of 2 or decreasing them by several orders of magnitude.

Figure 3 shows similar results for the photodissociation rate weighting factor β . Again there is a phase relationship between the variation of photodissociation rates and the individual trace-species concentrations. In fact from Fig. 3 it is quickly apparent that above 35 km photolysis is a dominant mechanism in determining the local concentrations of ClONO_2 , NO_2 , and N_2O_5 , although this is not the case for HO_2 . A strong out-of-phase relation with the photodissociation coefficient, J ,

shows that photolysis is the dominant loss mechanism. From this small sample of values for J , it is clear that no single averaged solar zenith angle or simple averaged photolysis rate coefficients can approximate the loss rates corresponding to even this small sample of photodissociation rates.

The computation procedure in the limit (i.e., infinite iteration) is actually the full diurnal model. Current experience indicates that a uniform local accuracy of better than a few percent deviation can be achieved with two or three iteration cycles. For such information as total ozone column or total NO_y , Cl_y , etc., one iteration would be sufficient.

2.2 Analysis of Selected Chemical Rate Data*

Our earlier work (Duewer et al. 1977b) identified several reactions for which variations in the rate coefficients have a significant effect on model sensitivity. Reduction of the uncertainties associated

*See Duewer et al. (1977c).

Figure 3. Curves relating β_i to altitude for some typical photodissociation reactions in the diurnal-averaged model.

with these rate coefficients would in turn reduce the uncertainty associated with the model assessments of the atmospheric response to stratospheric perturbations. For this reason we have carefully analyzed the chemical rate data for these reactions, taking into account recent laboratory measurements conducted at other laboratories. Our analyses for these reactions are given elsewhere.

In evaluating an experimental measurement, one normally takes the precision-based standard deviation of the measurement as a lower limit to the expected error. Historically, precision has often been a very unrealistic basis for estimating the experimental error in chemical rate data, especially when the measurements are indirect (that is, based on inferred concentrations using an assumed kinetic

Figure 4. Diurnal variation of NO_2 and ClO concentrations in the atmosphere at altitudes of 20 and 50 km.

mechanism in an often fairly complex reaction scheme). See for example the reviews of Lloyd (1974), Baulch et al. (1972, 1973), and Hampson and Garvin (1975). In cases where the concentrations of reactive species are directly measured, the precision may be a reasonable estimate of the error, although even in these cases disagreements between different workers, while usually small, are also often larger than those suggested by precision alone. (See the discussion of reaction 12 below.) In such cases the error between measurements by different workers may provide a reasonable estimate of the expected error. But for indirect measurements where the concentrations of reactive species are inferred from a multistep mechanistic model, large systematic errors are more likely, and are frequently encountered in the literature, as for example in the reviews by Dixon-Lewis et al. (1974), Baulch et al. (1972, 1973), and Lloyd (1974).

We analyzed chemical rate data for six reactions in all: reactions 18, 14, 12, 19, 26, and 20 as specified in Table 1 of our First Annual Report (Luther et al. 1976). Our analyses follow.

Reaction 18. $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$

This reaction acts as a sink for HO_x radicals, both by transforming them into the "reservoir" species H_2O_2 and through the reaction sequence

where water is unreactive. The available data and reviews are summarized in Fig. 5.

This reaction has been measured at only one temperature.* The measurements of Foner and Hudson (1962), Paukert and Johnston (1972), and Hamilton (1975) are in excellent agreement. All of these involved direct detection of HO_2 . The indirect measurement of Burgess and Robb (1957), discussed in the reviews of Baulch et al. (1972) and Lloyd (1974), is thought to be in error. The measurement by Hochanadel et al. (1972) involved a direct measurement of HO_2 , like the other measurements, but was indirect in that the value is based on modeling a fairly complex reaction system. Hochanadel's measurement was discussed by Kaufman (1975), Lloyd (1974), and Hamilton (1975). Kaufman and Lloyd point out probable errors in the data analysis, and Hamilton shows that this rate constant appears to have an anomalous dependence on water concentrations, and that this effect could have caused Hochanadel et al. to overestimate the rate by about a factor of 3.

*A preliminary unpublished measurement over a narrow temperature range has been reported by Cox (private communication, 1977) (i.e., $k = 1.4 \times 10^{-14} e^{-1681/T}$). The large negative activation energy obtained for this reaction is surprising; it may involve some of the complications responsible for the anomalous water-vapor dependence observed for this rate constant, since these incompletely understood processes might very well have a strong temperature dependence. In any case, it seems obvious that measurements of this reaction over a broad temperature range are urgently needed. If Cox's expression is even approximately valid, a novel complex mechanism is implied for this reaction. This type of mechanism had been suggested as a plausible occurrence long before experimental data supporting it were available (H. S. Johnston, private communication, 1976). At present we prefer the NASA panel's recommendation (Hudson 1977), but we believe the uncertainty to exceed a factor of 3.

Table 1. Calculated changes in total ozone due to an NO_x injection as NO_2 in a 1-km-thick layer of air for various injection altitudes, injection rates, and concentrations of ClO_x .

NO _x injection rate (molecules/cm ³ -s)	Injection altitude (km)	Percent change in total ozone calculated with following assumptions:						
		Chang (1976) K ₂ profile, ClO _x concentration of:				Huntten (1975) K ₂ profile, ClO _x concentration of:		
		0	1 ppb	2 ppb	4 ppb	0	1 ppb	2 ppb
2000	20	-4.20	-3.26	-2.61	-1.27	-10.64	-8.76	-8.06
2000	17	-1.15	-0.70	-0.40	0.23	-4.06	-2.79	-2.33
2000	13	-0.10	0.01	0.09	0.24	0.08	0.16	0.20
2000	9	0.07	0.08	0.09	0.11	-0.10	0.12	0.12
600	17	-	-0.19	-0.09	0.12	-	-0.79	-0.39
200	17	-	-0.06	-0.03	0.04	-	-0.16	-0.10

^a Thought to be unreliable; see Lloyd (1974), Baulch et al. (1972), Hamilton (1975), and Kaufman (1975).

^b From table of Baulch et al. (1972).

Experimental data (1-7) and reviews (8-15)

Symbol	Reference	T (K)	k (cm ³ /s)
1	Burgess and Robb (1957) ^{a,10}	300	1×10^{-10}
2	Hochanadel et al. (1972) ^a	300	9.5×10^{-12}
3	Paukert and Johnston (1972)	300	3.6×10^{-12}
4	Hamilton (1975)	300	3.2×10^{-12}
5	Foner and Hudson (1962)	300	3.0×10^{-12}
6	Hamilton and Liu (1976)	300	2.5×10^{-12}
7	Cox (1977)	273-338	$1.4 \times 10^{-14} e^{1651/T}$
8	Lloyd (1974)	300-1000	$1.7 \times 10^{-11} e^{-500/T}$
9	Hampson and Garvin (1974)	300-1000	$3 \times 10^{-11} e^{-500/T}$
10	Models (this work)	—	—
11	Lloyd (1971) ^b	300-800	$1.4 \times 10^{-11} e^{-500/T}$
12	Nicolet (1964)	Not given	$5 \times 10^{-12} T^{1/2} e^{-1000/T}$
13	Baulch et al. (1972)	300	$(3.3 \pm 0.3) \times 10^{-12}$
14	Hudson (1977)	200-300	2.5×10^{-12}
15	Stolarski (1977)	200-300	1×10^{-12}

Figure 5 Summary of available data for k_{18} ($\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$).

There are few data on the temperature dependence of this reaction.^a In his early review, Nicolet (1964) assumed a temperature-dependent rate coefficient of $5 \times 10^{-12} T^{1/2} e^{-1000/T}$. Lloyd (1974) assumed a temperature-dependent rate constant of $1.7 \times 10^{-11} e^{-500/T}$ based on the room-temperature measurements of Paukert and Johnston (1972) and Foner and Hudson (1962) and theoretical expectations for the high-temperature rate. Hampson and Garvin (1975) averaged the measurements of Paukert and Johnston and Hochanadel et al. and adopted Lloyd's temperature dependence in recommending the expression $k = 3 \times 10^{-11} e^{-500/T}$, uncertain by a factor of 2.

The assumed temperature dependence is arrived at by combining the room-temperature rate coefficient with a plausible theoretical estimate of the high-temperature rate coefficient. In our opinion, the room-temperature rate coefficient is fairly well

known and should be based on the average of the rate constants reported by Paukert and Johnston (1972), Foner and Hudson (1962), and Hamilton (1975) with a subjectively estimated uncertainty of a factor of 1.5. However, the temperature dependence is effectively unknown. The rate constant could be nearly independent of temperature, or its temperature dependence might be as strong as $e^{\pm 1000/T}$.

We accept the preferred value for k_{18} recommended by Lloyd (1974), but we believe the rate constant to be uncertain by roughly a factor of 4 at stratospheric temperatures.

Reaction 14. $\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$

This reaction effectively controls the efficiency of the HO_x ozone destruction cycle in the lower stratosphere and shifts the ratio $\text{OH}:\text{HO}_2$ toward OH.

This rate coefficient has never been measured directly, but there are three pertinent indirect

^aSee previous footnote.

measurements (see Fig. 6). Anderson and Kaufman (1973) determined an upper limit for k_{14} relative to k_{12} , and DeMore (1973), DeMore and Tschuikow-Roux (1974), and Simonaitis and Heicklen (1973) measured the ratio of k_{14} to the square root of k_{18} (R_1). The various measurements are all roughly consistent with each other and with the recommended rate given by Hampson and Garvin (1975).^a Indeed, as demonstrated by Johnston and Nelson (1977), at room temperature the agreement between different measurements of R_1 seems to suggest that R_1 provides an additional constraint on k_{14} more severe than the estimated error in the rate constant. However, DeMore and Tschuikow-Roux identified a systematic error (resulting from the finite optical depth of their system) that causes their ratio to be low by an amount that we estimate to be

^aIf the preliminary value for k_{18} determined by Cox (1977) is used in the estimation of k_{14} , a very different expression is obtained for k_{14} than has been used earlier. At present we do not favor an expression based on Cox (1977) but recommend that it be considered as a possibility.

Figure 6 Summary of available data for k_{14} ($\text{HO}_2 + \text{O}_3 \rightarrow \text{HO} + 2\text{O}_2$).

about a factor of 1.25 ± 0.2 (as entered on Fig. 6; Fig. 7 presents the uncorrected ratio data). Application of this correction factor reduces the agreement between DeMore and Tschuikow-Roux (1974) and Simonaitis and Heicklen (1973), and it is not the only plausible source of systematic error. When one considers that even the relative rate constants are indirect measurements derived from a fairly complex reaction system, the quoted error bounds of Hampson and Garvin seem a little large at room temperature (because of the experimental precision) but possibly too narrow for stratospheric conditions.

Reaction 12. $\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$

This reaction contributes directly to the HO_2 ozone destruction rate. However, it is also an important factor in controlling the ratio of OH to HO_2 in the models. Because these effects oppose each other, our model is only moderately sensitive to this rate constant. We include k_{12} in our discussion because some of the data for k_{14} and k_{19} are in the form of ratios involving k_{12} .

Experimental data (1-4) and reviews (5-10)

Symbol	Reference	T (K)	k (cm ³ /s)
1	Anderson and Kaufman (1973) ^a	220-450	$\leq 1.6 \times 10^{-13} e^{-1000/T}$
2	DeMore (1973) ^{b,c}	300	1.7×10^{-13}
3	Simonaitis and Heicklen (1973) ^{b,c}	225-298	$7.7 \times 10^{-14} e^{-1250/T}$
4	DeMore and Tschuikow-Roux (1974) ^{b,c,d}	273-332	$5.7 \times 10^{-13} e^{-1800/T}$
5	Garvin and Hampson (1974) ^e	225-298	$1 \times 10^{-13} e^{-1250/T}$
6	Lloyd (1974)	200-500	$1.7 \times 10^{-13} e^{-1400/T}$
7	Models (this work)	200-300	—
8	Hudson (1977)	200-300	$7.3 \times 10^{-14} e^{-1275/T}$
9	Stolarski (1977)	200-300	$1 \times 10^{-13} e^{-1525/T}$
10	Implications of Cox (1977)	—	$5.48 \times 10^{-19} e^{-449/T}$

^aUpper limit based on ratio to k_{12} .

^bRatio to $(k_{18})^{1/2}$.

^cRecalculated using k_{18} from Lloyd (1974).

^dCorrected by a factor of 1.25 to allow for a systematic error discussed by the authors.

^eUsed a higher value of k_{18} (average of Hochanadel et al. 1972 and Paukert and Johnston 1972).

Figure 7 The uncorrected ratio $R_1 = k_{14}/(k_{18})^{1/2}$. Circles are experimental data of Simonaitis and Heicklen (1974), triangles are data of DeMore and Tschuikow-Roux (1974). Our models A and A' are represented by the solid line, and models B, C, and C' by the dotted lines.

Figure 8 Summary of available data for k_{12} ($\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$).

Values for k_{12} have been independently measured by four research groups as summarized in Fig. 8. The room-temperature measurements of Davis (1974) and of Kurylo (1973) were made using the flash-photolysis resonance fluorescence technique. Accordingly they are both very direct and very precise measurements. (Both quoted values are averages of large numbers of separate determinations.) The error quoted by Kurylo (1973) was $\pm 8\%$; Davis' (1974) error was $\pm 4\%$. These two measurements differ by more than the precision bounds, although the agreement is very good by any other standard. The measurements of Anderson and Kaufman (1973) are also direct and precise, but they were made using resonance fluorescence detection in a flow system. Flow irregularities are always a potential problem in flow system measurements, and the measurement is probably slightly less accurate than the flash photolysis measurements.

The measurement of DeMore (1975) was also rather precise but was indirect, being based on a measurement of ozone in a photolysis system involving O_2 , water, and CO_2 .

We would use the average of the Davis, Kurylo, and Anderson and Kaufman measurements to establish a room-temperature rate constant and then

Experimental data (1, 3, 5, 6) and reviews (5, 6)

Symbol	Reference	T (K)	k (cm ³ /s)
1	DeMore (1973) ^a	300	8×10^{-14}
Δ	DeMore (1975) ^{a,b}	271–333	$2.4 \times 10^{-12} e^{-1230/T}$
○	Anderson and Kaufman (1973) ^c	220–450	$1.3 \times 10^{-12} e^{-956/T}$
2	Davis (1974) ^d	300	$(7.5 \pm 0.3) \times 10^{-14}$
3	Kurylo (1973) ^d	248	$(6.5 \pm 0.5) \times 10^{-14}$
4	Simonaitis and Heicklen (1973) ^a	300	$> 1.5 \times 10^{-14}$
5	Hampson (1973), quoted by Hampson and Garvin (1974), and models A, A', and C' (this work)	220–450	$1.6 \times 10^{-12} e^{-1000/T}$
6	Models B, C (this work)	—	—
(Not plotted)	Hudson (1977)	—	$1.5 \times 10^{-12} e^{-1000/T}$

^a Indirect measurement.

^b Individual determinations are plotted as triangles.

^c Individual determinations are plotted as circles.

^d Very precise measurements. Plotted points are averages of many individual determinations.

apply the activation energy measured by Anderson and Kaufman to provide a temperature-dependent rate constant. In our appraisal, an appropriate expected error would be a factor of 1.2 at room temperature, increasing to a factor of about 2.5 at 200 K. For the purposes of stratospheric modeling, our estimate is only trivially different from Hampson and Garvin's (1975) recommendation for this reaction.^a

Reaction 19. $\text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$

If the faster of the quoted rates for reaction 19 is correct, then this reaction is the major sink for stratospheric HO_x radicals. If the slower rates are correct, it is still a major sink for HO_x radicals.

^aThe NASA panel (Hudson 1977) recommends that this rate constant be lowered by 8% because of an error in the O_3 absorption coefficients used in reducing the experimental data. We would concur.

^aSeveral problems with this measurement have been discussed in the reviews of Lloyd (1974) and Kaufman (1975) and in Hamilton (1975).

^bRatio measurement. Actual measurement covered the range 273–342 K and gave a temperature-dependent rate. Slanting lines give these values for various assumed values of the other rates in the ratio.

^cHigh-temperature experiment, indirect determination.

^dIndirect determination based on an analysis of the $\text{HO}_2 + \text{NO}$ system.

^eAs quoted by Baulch et al. (1972).

This reaction is very difficult to measure, and no direct measurement has been published. (A recent direct determination does exist, 5.1×10^{-11} by Burrows et al. 1977, but it is inconsistent with upper limits estimated by others.) Clear conflicts exist between the various measurements (see Fig. 9). There are two measurements at room temperature (DeMore and Tschuikow-Roux 1974, Hochanadel et al. 1972) which lead to values in the range of 2×10^{-11} to 6×10^{-11} . The high-temperature measurements of Friswell and Sutton (1972) ($k = 2 \times 10^{-11}$), Tröe (1969) ($2 \times 10^{-12} \leq k \leq 2 \times 10^{-11}$), and Glänzer and Tröe (1975) ($k \leq 6.6 \times 10^{-11}$) and the room-temperature measurements of Hack et al. (1975) ($k \leq 3 \times 10^{-11}$) and Chang and Kaufman (1976) ($k \leq 5 \times 10^{-11}$) provide upper limits substantially below the high measurements. Semiquantitative arguments based on absolute rate theory and the rates of similar reactions lead to estimates

Experimental data (1–8) and reviews (9–14)

Symbol	Reference	T (K)	k (cm^3/s)
1	Hochanadel et al. (1972)	298	2×10^{-10}
2	DeMore and Tschuikow-Roux (1974) ^b	300	$6-16 \times 10^{-11}$
3	Friswell and Sutton (1972) ^c	2000	2×10^{-11}
4	Tröe (1969) ^d	1000	$2-20 \times 10^{-12}$
(Not plotted)	Hack et al. (1975) ^e	298	$< 3 \times 10^{-11}$
5	Glänzer and Tröe (1975) ^d	1250–1800	6.6×10^{-11}
6	Dixon-Lewis et al. (1974) ^f	1300–1800	$(3 \pm 1.5) \times 10^{-11}$
(Not plotted)	Kaufman (1964); review based on Foner and Hudson (1962)	300	$> 1 \times 10^{-11}$
7	Burrows et al. (1977)	300	5.1×10^{-11}
8	Chang and Kaufman (1977)	—	$< 3.5 \times 10^{-11}$
9	Kaufman (1975)	300	$1-3 \times 10^{-11}$
10	DeMore and Watson (1976)	200–300	$1-6 \times 10^{-11}$
11	Lloyd (1974)	300–1000	$8.3 \times 10^{-11} e^{-500/T}$
12	Nicolet (1970) ^g	—	$3 \times 10^{-12} T^{1/2} e^{-500/T}$
13	M.S. Johnston in Hampson and Garvin (1974)	200–300	$2-20 \times 10^{-11}$
14	Duwer (this work)	200–300	5×10^{-12} to 8×10^{-11}
(Not plotted)	Hudson (1977), Stolarski (1977)	—	3×10^{-11}

Figure 9 Summary of available data for k_{19} ($\text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$).

for the rate constant in the range of 3×10^{-12} to 5×10^{-11} (Kaufman 1975). Further, the observed stratospheric OH concentrations (Anderson, private communication, 1975) are very difficult to support in models using the faster rate coefficients for this reaction.

None of the above arguments is conclusive. Chemical theory has difficulty in predicting slow, nearly temperature-independent rate coefficients for simple reactions such as that for

$$(k_{21} \approx 8.9 \times 10^{-14} \text{ cm}^3/\text{s})$$

and must be used with some caution. The stratospheric models may be in error in other ways; thus they do not provide a conclusive test of the HO₂ sink rates.

We note that, as was discussed earlier, kinetic complications in the reaction system of Hohanadel et al. (1972) have been identified by Hamilton (1975) and Kaufman (1974), and the data analysis of Hohanadel used parameters at values not currently accepted (Lloyd 1974). Dixon-Lewis et al. (1974) make similar criticisms of the analysis used by Friswell and Sutton (1972). Thus, those experiments should be used with even more caution than the other indirect measurements. The data of DeMore and Tschuikow-Roux (1974) were taken in the form of the ratio

$$R_2 = \frac{k_{19} \cdot k_{14}}{k_{12} \cdot k_{18}}$$

This ratio can also be calculated from the various models. If this is done, we find that the experimental temperature dependence for the ratio has the opposite sign from the temperature dependence that can be deduced from the models unless k_{19} has a significant activation energy or there are substantial errors in the activation energies used for the other rate coefficients. None of the models agrees with this ratio over a very extended temperature range. The analysis of Johnston and Nelson (1977) indicates that heterogeneous reactions may account for much of the discrepancy in the room-temperature values for this ratio, but not for the differences in activation energy.

In our concerted variations of rate constants, where k_{18} and k_{19} were varied in the same sense, and k_{12} (which appears to be relatively well established) was either held constant or varied in the same sense as k_{14} (and oppositely to k_{18} and k_{19}), we found that models A and A' of Duewer et al. (1977b) are the extreme models, A' being in approximate agreement

with the experiment near 300 K, while B and C' are fairly close to the extrapolated data near 250 K, and A and C intercept the extrapolated experimental curve near 180–200 K.

It is troubling that the models, especially model A, are as far from this experiment as they are. However, the experimental ratio was indirectly determined and may be seriously affected by heterogeneous processes. Although, to first order, this ratio was free of the identified systematic error that appeared in the ratio of k_{14} to $(k_{18})^{1/2}$ from the same work, the data analysis was such as to potentially magnify errors in the directly determined quantities. Further, if the ratio determined by DeMore and Tschuikow-Roux (1974) is correct, then an appreciable activation energy for k_{19} , a very strong negative activation energy for k_{18} , or a large error in the ratio of k_{14} to $(k_{18})^{1/2}$ (R_1) is implied.

Finally, we note that in their recent recommendations to NASA, W. B. DeMore and K. Watson (private communication, 1976) recommended the use of values in the range of $1\text{--}6 \times 10^{-11} \text{ cm}^3/\text{s}$ for k_{19} .

Because of the indirect nature of the various experiments and the apparent incompatibility of the results of various workers, we have been guided primarily by the rates of similar reactions and by theoretical considerations and secondarily by the observed concentrations of stratospheric OH. We consider 5×10^{-12} to $8 \times 10^{-11} \text{ cm}^3/\text{s}$ to be the plausible range of values for k_{19} , with $k = 2 \times 10^{-11} \text{ cm}^3/\text{s}$ a likely value.*

Reaction 26. $\text{HO}_2 + \text{NO} \xrightarrow{\text{M}} \text{NO}_2 + \text{HO}$

This reaction couples the NO_x and HO_x cycles. It reduces the efficiency of both cycles, especially in the lower stratosphere where NO₂ is usually photolyzed.

The available data are summarized in Fig. 10. All of the data are obtained by indirect methods,† and we find no clear basis for deciding which are the most reliable measurements.

*The NASA panel recommendation (Hudson 1977) of 3×10^{-11} seems as reasonable as our use of 2×10^{-11} .

†The recent measurement of Howard and Evenson (1977), 8×10^{-12} at 300 K, was directly determined and seems substantially more plausible than any other published measurement of this quantity. Moreover, several other unpublished determinations of this rate constant have been made recently which seem to lie in the range 8×10^{-12} to 1×10^{-11} . Thus we would accept Howard and Evenson's room-temperature rate constant and speculate that the temperature dependence would be in the range $+200/T$ to $-800/T$, with $-500/T$ a plausible value.

Figure 10. Summary of available data for k_{26} ($\text{HO}_2 + \text{NO} \xrightarrow{\text{M}} \text{NO}_2 + \text{HO}$).

Experimental data (1-6) and reviews (7-12)

Symbol	Reference	T (K)	k (cm ³ /s)
Δ	Hack et al. (1975)	298-666	$2 \times 10^{-11} e^{-1200/T}$
1	Glanzer and Troe (1975)	1250-1810	$5-10 \times 10^{-12}$
2	Payne et al. (1973)	300	4×10^{-12}
3	Simonaitis and Hecklen (1973)	300	$>1.5 \times 10^{-13}$
4	Cox (1975)	298	1.6×10^{-12}
5	Simonaitis and Hecklen (1976)	298	1.0×10^{-12}
6	Howard and Evenson (1977)	298	8×10^{-12}
7	Baulch et al. (1973)	300	3×10^{-13}
8	Hampson and Garvin (1974)	300	2×10^{-13}
9	Lloyd (1974)	300	1.7×10^{-13}
10	Models (this work)	-	-
11	Hudson (1977)	200-300	9×10^{-12}
12	Stolarki (1977)	200-300	$2 \times 10^{-11} e^{-1200/T}$

We note that the newer data suggest that the room-temperature rate constant was underestimated by Hampson and Garvin, but that the reaction may have a significant temperature dependence. As a result, we believe that the uncertainty factor applied might have been increased, but that the range considered is appropriate for stratospheric conditions.

Reaction 20. $\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3$

This reaction reduces the effect of both NO_x and HO_x on ozone by tying up both species in the relatively inert species HNO_3 . Further, it catalyzes HO_x destruction through the reaction

Reaction 20 is dependent on both temperature and pressure, and the pressure dependence is a function of the identity of the third body M. As a result of this we have chosen to present the data in the form given in Fig. 11. The altitude dependence portrayed does not pertain to actual measurements at various altitudes, but rather to measurements at various temperatures and pressures interpolated or

extrapolated to the conditions of the U.S. Standard Atmosphere. There are other pertinent measurements, including recent work (e.g.: Davis 1974; P. Atkinson, private communication, 1976). However, most of that work does not cover stratospheric temperatures, is not compatible with the data presentation adopted, and is not included in Fig. 11. The data of the various workers do form a reasonably consistent set of measurements. However, as is evident in Fig. 11, for the conditions of the lower stratosphere the data of Anastasi et al. (1976) fall somewhat outside the expected error range quoted by Hampson and Garvin. In this range the curve quoted from Anastasi et al. is an interpolation from the data, but the Hampson and Garvin recommendation is based on a substantial extrapolation. The two expressions agree in the range of 30-45 km, where both are interpolating functions. In order to cover the full range of our model, 0-55 km, we fit the primary data of Anastasi et al. to the expression

$$k = \frac{2.76 \times 10^{-13} e^{880/T} \cdot \text{M}}{1.16 \times 10^{18} e^{222/T} + \text{M}}$$

Figure 11. Summary of available data for k_{20} ($\text{OH} + \text{NO}_2 \xrightarrow{M} \text{HNO}_3$).

This form is theoretically justified at moderate and low pressures but not at high pressures where it should underestimate the rate constant.* (More recent data by Anastasi and Smith (1976) indicate that this is indeed the case and suggest that our curve may underestimate the tropospheric rate constant by nearly a factor of 2.) We believe that the data of Anastasi et al. provide the best available estimate of this rate constant under stratospheric conditions and that the expression we have fitted to their data may be accurate to within a factor of 1.5 over the range where it is an interpolation, but that it may be in error by a factor of 2 to 3 for tropospheric conditions. The estimated error quoted here for interpolated values is dominated by our estimate of plausible magnitudes of systematic errors and by differences between experimenters in the low-pressure range. The fitting error is relatively small.

If we consider the five rate constants k_{14} , k_{18} , k_{19} , k_{20} , and k_{26} , two of them (k_{20} and k_{26}) seem likely to be more extreme in their difference from the value given by Hampson and Garvin than the value used in model C' of Duewer et al. (1977b), and two others (k_{18} and k_{19}) have conflicting measurements and are highly uncertain. The data suggest that the remaining one, k_{14} , may have large errors in either sense, depending on the value of k_{18} . At present our best estimates for these (and other) rate constants lead to a model-predicted ozone increase for lower stratospheric NO_x injections. However, the continuing uncertainty in chemical reaction rates leaves ample room for another reversal of the sign of the computed response to NO_x injections in the lower stratosphere.

2.3 A Reanalysis of the Effect of NO_x Injections on Ozone

Whenever there has been a significant change in the one-dimensional stratospheric model, we have reanalyzed the effect of the change on the model's sensitivity to NO_x injections. The effects of past changes in the model are discussed below in two parts. The first part updates our understanding of the effect of NO_x injections from high-altitude aircraft on stratospheric chemistry from the end of the Climatic Impact Assessment Program (CIAP) in 1974 to the end of 1976, and the second part updates these results to the present.

*The NBS group has recommended a complex expression for this rate coefficient that has been accepted by the NASA panel (Hudson 1977). At present we would accept that expression.

Changes During the Period 1974-1976

During the period 1974-1976 many changes were made in the one-dimensional stratospheric model to reflect our increased understanding of atmospheric processes, especially chemical reactions. Reaction rates were remeasured (or guesses were replaced by measurements and/or new guesses), and new reactions were added. In particular, chlorine chemistry came to play an important role in stratospheric chemical modeling, whereas chlorine was not contained in any of the NO_x injection modeling calculations done during CIAP.

The effect of changes in the LLL model chemistry (and transport) from 1974 until December 1976 is shown in Fig. 12. Only NO_x - HO_x - O_x chemistry (no ClO_x) was included in these calculations. A detailed description of the changes in each of the reaction rates is given in Appendix A. Figure 12 shows how each sequential change in the model affected model sensitivity. The largest effect came from changing the reaction rate coefficient for $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ from 2×10^{-10} to 2×10^{-11} . Changing to the new transport coefficient (Chang 1976) resulted in approximately a 10% increase in the predicted ozone reduction. Most of the changes individually had a small effect, but together they were significant. The chemical changes in the model (without changing K_2) up to December 1976 reduced the predicted change in ozone by a factor of 4.7 for a 17-km injection and by a factor of 2.9 for a 20-km injection.

Figure 12. Effects of changes in model assumptions (ordinate) on calculated change in total ozone (abscissa) for an injection of 2.46×10^8 kg/yr of NO_x at altitudes of 17 and 20 km.

Since Molina and Rowland (1974) first noted the potential effect of the chlorofluoromethanes (CFMs), CFCl_3 and CF_2Cl_2 , on the stratospheric ozone, much effort has been given to determining the effect of chlorine species such as Cl , ClO , HCl , ClONO_2 , etc. on stratospheric chemistry. The 1976 calculations predicted a background concentration of ClO_x ($\text{Cl} + \text{ClO} + \text{HCl}$) in the natural stratosphere of 1 ppb resulting from CH_3Cl and CCl_4 without any CFMs. With the addition of CFMs, we calculated approximately 1.5 ppb stratospheric ClO_x for current levels of CFCl_3 and CF_2Cl_2 , 2 ppb ClO_x for predicted 1990 levels of CFMs due to constant production beyond 1973, and 4 ppb at steady state (100–200 years).

We made a series of calculations to determine the effect of various background levels of ClO_x on the predicted ozone reduction due to NO_x injection. As an initial condition for the calculations, a background steady-state atmosphere containing various levels of ClO_x (1, 2, or 4 ppb) was derived, then the model was calculated to steady state with NO_x aircraft emissions of 2000 molecules/ $\text{cm}^3 \cdot \text{s}$ as NO_2 injected into a 1-km-thick layer centered at various altitudes (9, 13, 17, or 20 km). These calculations were carried out with the Chang (1976) and the Hunten (1975) K_z profiles. The results are summarized in Table 1.

For stratospheric injections of NO_x (at 17 and 20 km), increasing the background levels of ClO_x decreases the magnitude of the ozone reduction. The effect of the ClO_x background is substantial, even leading to a net ozone increase for a 17-km NO_x injection with a ClO_x background of about 4 ppb. The changes in total ozone are small for tropospheric injections of NO_x . The results for injections at 9 km should be considered to be within the "noise," since these changes are the net result of ozone reduction above about 20 km and ozone production below 20 km. Because the model uses fixed boundary conditions and incorporates rainout processes for NO_2 and HNO_3 , a large effect should not be expected from a 9-km injection. The change in total ozone is basically linear with NO_x injection rate using the Chang (1976) K_z profile but not with the Hunten K_z profile.

Calculations were also made for an $\text{NO}_x\text{-HO}_x\text{-O}_x$ atmosphere using an FAA estimate of 1990 aircraft emissions. The model input used is shown in Table 2. With the Chang (1976) K_z profile there was a net increase in total ozone of 0.1% after the first year, which reduced to a steady-state net increase of 0.02% after the tenth year. With the Hunten K_z profile, a 0.20% increase in total ozone after one year reduced to 0.04% at steady state.

Changes Since 1976

Since the end of 1976 there have been a number of changes to the stratospheric model including changes in chemical rate coefficients and improvements in the representation of physical processes, such as including multiple scattering in the photodissociation rate calculation. The changes in model chemistry up to June 1977 were based upon the Hudson (1977) reevaluation of chemical rate data (see Table A-1 in Appendix A). These changes led to an increase in the ozone reduction estimates due to an NO_x injection of 2000 molecules/ $\text{cm}^3 \cdot \text{s}$ as NO_2 at either 17 or 20 km. The most significant change since December 1976 was a new measurement of the reaction rate for $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$ by Howard and Evenson (1977). Using a direct measurement technique, laser magnetic resonance, they measured this reaction rate to be roughly 30 times faster than previously thought. The effect that this one change in a chemical rate measurement has on the model is shown in Table 3. With the Chang (1976) K_z profile, there is a reversal in the sign of the ozone change such that aircraft emissions in the lower stratosphere cause an increase in total ozone. With the Hunten K_z profile, there is an ozone decrease for a 20-km injection but an ozone increase for a 17-km injection.

Figures 13 and 14 show the effect the change in the $\text{HO}_2 + \text{NO}$ rate has on model-derived species concentrations. The new faster rate has a large impact on stratospheric constituents such as NO (as

Table 2. Estimated 1990 aircraft emissions used in the LLL 1-D model.

Altitude (km)	Emissions (kg NO_2/yr)
6	5.857×10^7
7	1.171×10^8
8	1.932×10^8
9	4.364×10^8
10	7.645×10^8
11	7.627×10^8
12	3.410×10^8
13	4.859×10^7
14	1.155×10^7
15	1.180×10^7
16	2.098×10^7
17	2.354×10^7
18	1.515×10^7
19	4.739×10^6

Table 3. The effect on model sensitivity of changing the rate coefficient for the reaction $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$. Old rate = 2.0×10^{-13} , new rate = $4.28 \times 10^{-11} \exp(-500/T)$ (Howard and Evenson 1977).

K _z profile	NO _x injection altitude (km)	Change in O ₃ (%)		Change in NO _x (%)	
		Old rate	New rate	Old rate	New rate
Chang (1976)	20	-4.79	0.55	46.7	47.9
	17	-1.31	1.96	27.3	27.8
Hunten (1975)	20	-10.8	-6.90	96.2	97.1
	17	-4.35	0.83	61.4	62.3

much as a factor of 3 lower concentration at 15 km) and OH (a factor of 2 larger concentration at 15 km). Other species more indirectly related to the reaction of $\text{HO}_2 + \text{NO}$, such as ClO and ClONO_2 , are also strongly affected by the new rate.

There is now a nonlinear relationship between the magnitude of the NO_x injections and the predicted change in total ozone. This is illustrated in Fig. 13 for 17- and 20-km injection altitudes. Note that doubling the rate of an NO_x injection does not result in doubling the change in ozone as was found during CIAP. Depending on the magnitude of the

injection, either a new increase or decrease of total ozone results.

The change in the local ozone concentration is shown in Fig. 16 for three different NO_x injection rates at 20 km. There is a net production of O_3 in the lower stratosphere and net destruction in the upper stratosphere. It is the summing of these two effects that determines whether a net increase or decrease in total ozone is calculated. Therefore, while there may be no net change in total ozone for a specific NO_x injection, there may be large predicted local ozone changes in the stratosphere. Such

Figure 13. Effect of the change in the $\text{HO}_2 + \text{NO}$ reaction rate on model-derived concentrations of HNO_3 , NO_2 , OH , and NO . New rate is based on Howard and Evenson (1977).

Figure 14 Effect of the change in the $\text{HO}_2 + \text{NO}$ reaction rate on model-derived concentrations of HCl, ClO, and ClONO_2 .

Figure 15. Calculated change in the ozone column at steady state as a function of NO_x injection rate (as NO_2) for injection altitudes of 17 and 20 km. An injection rate of 2000 molecules/ cm^3 .s in a hemispheric shell 1 km thick corresponds to an annual injection rate of 1.23×10^9 kg/yr.

Figure 16. Calculated change in the local ozone concentration versus height for NO_x injection rates of 500, 1000, and 1500 molecules/ cm^3 .s in a 1-km-thick layer centered at 20 km.

local changes could have important climatic considerations.

Major uncertainties still exist in our knowledge of stratospheric chemistry. It is possible, and even likely, that further significant revisions will be made in the future. Not only will reaction rates change, but it is still possible that processes not yet included may play an important contributing role.

2.4 Effect of Chlorofluoromethanes on Ozone

Five scenarios have been developed to describe possible future variations in the production rates of CFCl_3 (F-11) and CF_2Cl_2 (F-12). The scenarios are listed below:

1. Constant production of CFMs at 1975 levels. Production rate equals 347,000 tonnes/yr for F-11 and 415,000 tonnes/yr for F-12.*

2. Partial ban on the use of CFMs in the United States beginning 1 July 1978. Constant production at 1975 levels until 1 July 1978, dropping to 70% of 1975 levels thereafter.

3. Partial ban on CFMs in the United States beginning 1 July 1980. Same as scenario 2 except reduction beginning 1 July 1980.

4. Partial ban by the United States and several other countries concurrently on 1 July 1980. Constant production at 1975 levels until 1 July 1980, then dropping to 33% of 1975 levels.

5. Technical breakthrough allowing a drastic reduction in CFM production in 1984. Constant production at 1975 levels until 1 July 1984, dropping to 20% of 1975 levels thereafter.

The one-dimensional transport-kinetics model was used to assess the potential ozone reduction for each of these scenarios. The model chemistry was the same as listed in Appendix A for 1977 with the exception that the rate coefficient for the reaction $\text{NO} + \text{HO}_2$ was 6×10^{-13} . The computed change in total ozone relative to an ambient atmosphere without F-11 and F-12 is shown in Table 4 for each scenario as a function of time. Known production rates for F-11 and F-12 were used for the period before January 1976.

The effect of changing the reaction rate for $\text{NO} + \text{HO}_2$ to Howard and Evenson's (1977) recent measurement of 8×10^{-12} would be to essentially double the effect on ozone calculated in Table 4. For example, using the new rate increases the steady-state ozone reduction for scenario 1 to 15% as compared with the 7.9% shown in Table 4.

The predicted ozone reduction for a partial ban in the United States beginning in 1978 (scenario 2) differs very little from that for a partial ban beginning in 1980 (scenario 3). The ozone reduction at steady state is in direct proportion to the steady-state production rate of CFMs.

2.5 Effect of Multiple Scattering on Species Concentrations and Model Sensitivity*

Molecular multiple scattering, the earth's surface reflection, clouds, and aerosols have all been shown to have a significant effect on stratospheric and

*See Luther et al. (1977b).

Table 4. Calculated percent reduction in total ozone as a function of time for the five CFM release scenarios described in the text.

Year	CFM release scenario (see text)				
	1	2	3	4	5
1976	0.48	0.48	0.48	0.48	0.48
1977	0.58	0.58	0.58	0.58	0.58
1978	0.68	0.68	0.68	0.68	0.68
1979	0.77	0.77	0.77	0.77	0.77
1980	0.87	0.87	0.87	0.87	0.87
1981	0.96	0.95	0.96	0.96	0.96
1982	1.06	1.03	1.05	1.05	1.06
1983	1.17	1.11	1.14	1.13	1.17
1984	1.24	1.18	1.22	1.19	1.24
1985	1.33	1.24	1.29	1.24	1.33
1986	1.42	1.30	1.36	1.28	1.42
1987	1.52	1.36	1.42	1.31	1.49
1988	1.60	1.42	1.48	1.33	1.54
1989	1.69	1.48	1.54	1.36	1.58
1990	1.78	1.54	1.60	1.38	1.60
1991	1.86	1.60	1.66	1.40	1.62
1992	1.95	1.65	1.71	1.42	1.63
1993	2.04	1.71	1.76	1.44	1.63
1994	2.12	1.76	1.82	1.45	1.64
1995	2.20	1.81	1.87	1.47	1.64
1996	2.28	1.87	1.92	1.48	1.64
2001	2.68	2.12	2.17	1.56	1.64
2011	3.40	2.58	2.63	1.70	1.63
2021	4.05	2.98	3.03	1.81	1.62
2031	4.61	3.34	3.38	1.92	1.61
2041	5.11	3.65	3.69	2.01	1.61
2051	5.34	3.93	3.95	2.09	1.60
Steady state	7.94	5.55	5.55	2.55	1.53

*One tonne = 1 metric ton = 10^3 kg.

tropospheric radiative intensities at photodissociative wavelengths. The importance of molecular scattering and surface albedo and their effect on atmospheric photodissociation rates have been discussed by Luther and Gelinas (1976). Parameterizations of the effect of multiple scattering on photodissociative flux densities have been included in one-dimensional transport-kinetics models by Crutzen and Isaksen (1976), Callis et al. (1976), Ashby (1976), and Kurzeja (1976). Crutzen and Isaksen (1976) use a two-flux approximation to account for the direct and scattered radiation. Callis et al. (1976), using a detailed solar radiation model, compute correction factors which are then applied to the photodissociative rates computed assuming a purely absorbing atomic and molecular atmosphere. The correction factors vary with altitude for each photodissociative reaction, and they are assumed to be unaffected by changes in atmospheric composition.

We have assessed in detail the effect of including molecular multiple scattering and surface reflection in the transport-kinetics model on ambient species

concentration profiles and on model sensitivity to perturbations affecting stratospheric ozone. The effect of multiple scattering was incorporated into the photodissociation rate calculation by applying correction factors to the short-wave fluxes used in the pure absorption calculation (the method is described in detail below). Calculations were made with the 1977 model chemistry listed in Table A-1 of Appendix A with the exception of a few rates indicated in Table 5. Calculations were later repeated using NASA recommendations (Hudson 1977) and Howard and Evenson's (1977) new measurement of the rate for $\text{NO} + \text{HO}_2$. These changes are listed in Table 5.

The solution of the one-dimensional purely absorbing radiative transfer equation at a particular altitude z_p , solar zenith angle θ_0 , and atmospheric composition $\{N_A\}$ is given by

$$F_\lambda(z_p, \theta_0, \{N_A\}, t) = F_\lambda(\infty) \times \exp[-r_\lambda(z_p, \theta_0, \{N_A\}, t)] \quad (5-1)$$

Table 5 Reaction rate coefficients used in the latest calculations. See Table A-1 for other reactions.

Reaction	Old rate (used in first calculation)	New rate (used in second calculation)
$\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$	$2.3 \times 10^{-12} \exp(-1450/T)$	$2.1 \times 10^{-12} \exp(-1450/T)$
$\text{O}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{O}_2$	$1.6 \times 10^{-12} \exp(-1000/T)$	$1.5 \times 10^{-12} \exp(-1000/T)$
$\text{O}_3 + \text{HO}_2 \rightarrow \text{OH} + 2\text{O}_2$	$1.0 \times 10^{-13} \exp(-1250/T)$	$7.3 \times 10^{-14} \exp(-1225/T)$
$\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$	3.0×10^{-11}	3.5×10^{-11}
$\text{HO}_1 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$1.7 \times 10^{-11} \exp(-500/T)$	2.5×10^{-12}
$\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	2.0×10^{-11}	3.0×10^{-11}
$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$	$1.7 \times 10^{-11} \exp(-1000/T)$	8.0×10^{-12}
$\text{N} + \text{O}_3 \rightarrow \text{NO} + \text{O}_2$	$5.0 \times 10^{-12} \exp(-650/T)$	$2.0 \times 10^{-11} \exp(-1070/T)$
$\text{O}(\text{I}D) + \text{M} \rightarrow \text{O} + \text{M}$	$2.0 \times 10^{-11} \exp(107/T)$	$2.2 \times 10^{-11} \exp(99/T)^a$
$\text{NO} + \text{ClO} \rightarrow \text{NO}_2 + \text{Cl}$	2.2×10^{-11}	$1.0 \times 10^{-11} \exp(200/T)$
$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{OClO}$	$1.5 \times 10^{-13} \exp(-1238/T)$	$2.1 \times 10^{-12} \exp(-2200/T)$
$\text{ClO} + \text{ClO} \rightarrow 2\text{Cl} + \text{O}_2$	$4.5 \times 10^{-13} \exp(-1238/T)$	$5.0 \times 10^{-13} \exp(-1238/T)^b$
$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{ClO}_2$	$9.0 \times 10^{-13} \exp(-1238/T)$	$1.0 \times 10^{-12} \exp(-1238/T)$
$\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$	$2.8 \times 10^{-12} \exp(-400/T)$	$3.0 \times 10^{-12} \exp(-425/T)$
$\text{O} + \text{OClO} \rightarrow \text{ClO} + \text{O}_2$	5.0×10^{-13}	$2.0 \times 10^{-11} \exp(-1100/T)$
$\text{Cl} + \text{OH} \rightarrow \text{HCl} + \text{O}$	$2.0 \times 10^{-12} \exp(-1878/T)$	$1.0 \times 10^{-11} \exp(-2970/T)$
$\text{Cl} + \text{HNO}_3 \rightarrow \text{HCl} + \text{NO}_3$	6.0×10^{-15}	$1.0 \times 10^{-11} \exp(-2170/T)$
$\text{ClONO}_2 + \text{O} \rightarrow \text{ClO} + \text{NO}_3$	$5.0 \times 10^{-12} \exp(-840/T)$	$3.0 \times 10^{-12} \exp(-808/T)$
$\text{ClO} + \text{NO}_2 \xrightarrow{\text{M}} \text{ClONO}_2$	$5.1 \times 10^{-33} \exp(1030/T)$	$3.3 \times 10^{-23} T^{-3.34}$ $1 + 8.7 \times 10^{-9} T - 0.6 M^{0.5}$

^a Differs from value given by Hudson (1977).

^b No recommendation for this rate is given by Hudson (1977).

$F_\lambda d\lambda$ is the flux of photons in the wavelength interval $d\lambda$ about λ , and $F_\lambda(\infty) d\lambda$ represents the solar flux at the top of the atmosphere. The optical depth τ_λ is given by

$$\tau_\lambda(z_p, \theta_0, \{N_A\}, t) = \int_{z_p}^{\infty} \sum_A N_A(z, t) \sigma_T^\lambda[\lambda, T(z)] \sec \theta_0(t) dz \quad (5-2)$$

In Eq. (5-2) the summation on A includes all atmospheric absorbers, each having number density $N_A(z, t)$ and a total absorption cross section $\sigma_T^\lambda[\lambda, T(z)]$. Most generally, $\sigma_T^\lambda[\lambda, T(z)]$ is a function of the temperature $T(z)$.

The photodissociation rate for transforming species i to species j is denoted by

$$J_{i \rightarrow j}(z_p, \theta_0, t) N_i(z_p, t),$$

where

$$J_{i \rightarrow j}(z_p, \theta_0, t) = \int_{\text{all } \lambda} \sigma_D^i[j, \lambda, T(z_p)] F_\lambda(z_p, \theta_0, \{N_A\}, t) d\lambda \quad (5-3)$$

The microscopic photodissociation cross section $\sigma_D^i[j, \lambda, T(z_p)]$ is often written in terms of the quantum yield $Q_\lambda(i \rightarrow j)$ as

$$\sigma_D^i[j, \lambda, T(z_p)] \equiv \sigma_T^\lambda[\lambda, T(z_p)] Q_\lambda(i \rightarrow j). \quad (5-4)$$

It should be noted that significant uncertainties remain in the data used to calculate the photodissociation coefficients in the models. For example, major uncertainties remain in the branching of O_3 photolysis near 310 nm to either $O(^3P)$ or $O(^1D)$, in the branching and quantum yield for NO_2 photolysis, and in the methodology for calculating the photolysis of species having banded or line absorption-cross-section structures, such as O_2 or NO.

When molecular multiple scattering and surface albedo are included in the radiative transfer calculation, Eq. (5-1) is no longer the solution of the radiative transfer equation. However, the flux in the

direct solar beam F_λ^s is given by an equation similar to (5-1):

$$F_\lambda^s(z_p, \theta_0, \{N_A\}, t) = F_\lambda(\infty) \times \exp[-\tau_\lambda^s(z_p, \theta_0, \{N_A\}, t)] \quad (5-5)$$

where the optical depth along the slant path, τ_λ^s , is given by

$$\tau_\lambda^s(z_p, \theta_0, \{N_A\}, t) = \int_{z_p}^{\infty} \sum_A N_A(z, t) \sigma_T^\lambda[\lambda, T(z)] \sec \theta_0(t) dz + \int_{z_p}^{\infty} \sum_i N_i(z, t) \sigma_R^i(\lambda) \sec \theta_0(t) dz \quad (5-6)$$

In (5-6) the summation on i includes all atmospheric species, and σ_R^i is the Rayleigh-scattering cross section for species i. $F_\lambda^s(z_p, \theta_0, \{N_A\}, t)$ in (5-5) differs from $F_\lambda(z_p, \theta_0, \{N_A\}, t)$ as defined by (5-1) in that attenuation due to both absorption and scattering is included in (5-5), whereas only absorption is included in (5-1).

The photodissociation coefficient also depends upon the scattered (diffuse) radiation given by

$$J_{i \rightarrow j}(z_p, \theta_0, t) \equiv \int_{\text{all } \lambda} \sigma_D^i[j, \lambda, T(z_p)] \times \left[F_\lambda^s(z_p, \theta_0, \{N_A\}, t) + \int_{4\pi} I_\lambda(z_p, \omega) d\omega \right] d\lambda \quad (5-7)$$

where I_λ is the specific intensity of the diffuse radiation and ω is the solid angle. Including the effect of molecular multiple scattering and surface albedo in the calculation is simply expressed by changing the value of F_λ appearing in (5-3). For clarity we define

$$F_\lambda^{MS}(\text{multiple scattering}) \equiv F_\lambda^s(z_p, \theta_0, \{N_A\}, t) + \int_{4\pi} I_\lambda(z_p, \omega) d\omega \quad (5-8)$$

Henceforth, F_A^A (pure absorption) will refer to the flux defined by (5-1). Aside from substituting F_A^{MS} in place of F_A^A in (5-3), all other aspects of the photodissociation rate calculation are the same as for the purely absorbing molecular atmosphere.

The effect of multiple scattering was incorporated into the photodissociation rate calculation by applying correction factors to the flux F_A used in the pure absorption calculation. These correction factors, which are given by the ratio F_A^{MS}/F_A^A , were computed for the unperturbed species profiles using the same detailed solar radiation model as Luther and Gelinas (1976). A separate factor was computed for each of the 44 levels and for each of the 148 wavelength intervals between 133 and 735 nm. Different sets of correction factors were computed for each assumed value of surface albedo A_s using a solar zenith angle of 45° .

Correction factors for a solar zenith angle of 45° are qualitatively similar to, although somewhat larger than, those computed by Luther and Gelinas (1976) for $\theta = 60^\circ$. The correction factors are nearly constant with height above 20 km, but they may vary significantly with height in the region below 20 km, which is where most scattering events occur.

Including multiple scattering in the photodissociation rate calculation affects the photodissociation coefficients, the ambient species concentration profiles, and the model sensitivity to perturbations by NO_x and CIX pollutants. Each of these effects is discussed separately below.

Photodissociation Coefficients

Table 6 compares photodissociation coefficients for pure absorption and for multiple scattering computed for the same ambient model atmosphere. These coefficients were computed for a solar zenith angle of 45° and a surface albedo of 0.25. For reactions with strong absorption at wavelengths less than 290 nm, multiple scattering has the most significant effect on the photodissociation coefficients below 25 km. The coefficients are changed only slightly above 25 km. Reactions with strong absorption at wavelengths greater than 290 nm show enhancement at all altitudes due to multiple scattering. At altitudes above 10 km, including multiple scattering increases the photodissociation rates by a factor of 1.27–1.46 for O_3 , 1.56–1.64 for NO_2 , 1.23–1.67 for ClONO_2 , 1.07–1.65 for ClONO_2 , and 1.33–1.60 for OCIO . There is less than a 7% change in the photodissociation rates above 30 km for O_2 , HNO_3 , H_2O_2 , HO_2 , ClO , CF_2Cl_2 , and CFCl_3 . At lower altitudes there is significant enhancement for several of these species due to multiple scattering. For example, at 10 km the photodissociation rate is

increased by a factor of 1.59 for HNO_3 , 1.59 for H_2O_2 , and 1.46 for ClO .

Species Concentration Profiles

The concentration profiles for selected O_x , HO_x , and CIX species are shown in Figs. 17–20 for the ambient atmosphere prior to inclusion of multiple scattering. These figures define the reference conditions for assessing the fractional change in concentration caused by multiple scattering.

The changes in concentration of chemical species due to multiple scattering relative to the pure absorption calculation for a surface albedo of 0.25 are shown in Figs. 21–24. Figure 21 shows the effect of multiple scattering on O_x species concentrations. The large percentage increase in $\text{O}(^1\text{D})$ near 10 km occurs where the ambient concentration is very small; nevertheless, it has a significant effect on atmospheric chemistry. The increases in $\text{O}(^3\text{P})$ and $\text{O}(^1\text{D})$ in the 20-to-30-km region are due to increased photolysis of O_3 . Because of differences in ambient concentrations, a small percentage decrease in O_3 causes large percentage increases in the other species. The increase in $\text{O}(^3\text{P})$ near 40 km is due primarily to increased photolysis of NO_2 . Ozone at this height is increased largely as a result of the reduction in the efficiency of the NO_x catalytic destruction cycle caused by the increased rate of NO_2 photolysis. The ratio of column-integrated total O_3 computed with multiple scattering to that computed with pure absorption is 0.90.

Figure 22 shows the effect of multiple scattering on HO_x species. Increased OH below 30 km results from increased rates for the reaction $\text{HNO}_3 \xrightarrow{h\nu} \text{OH} + \text{NO}_2$ and $\text{H}_2\text{O}_2 \xrightarrow{h\nu} 2\text{OH}$. Since the concentration of H_2O_2 below 35 km is much larger than that of the other hydrogen oxide species, a small percentage decrease in H_2O_2 can cause a much larger percentage change in OH and HO_2 , as evidenced near 10 km. The increase in $\text{O}(^1\text{D})$ leads to an increase in the production rate of HO_x by $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$, yet there is actually a decrease in HO_x in the region around 10 km. This occurs because conversion of H_2O_2 to 2OH by photolysis substantially increases the HO_x destruction rate through the reactions $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ and $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$.

Figure 23 shows the effect of multiple scattering on NO_x species. Because the NO_2 photolysis rate is increased, the concentration of NO and the ratio NO/NO_2 are both increased at all altitudes. There is very little HNO_3 above 30 km, so NO_2 decreases in this region because of increased photolysis. Below 30 km, NO_2 increases because of increased photolysis of HNO_3 , which is the most plentiful NO_x species in this region.

Table 6 Comparison of photodissociation rates calculated with and without multiple scattering. The values correspond to a solar zenith angle of 45° and half-sun to account for day-night averaging.

Reaction	Altitude (km)	$J_{PA} (s^{-1})$	$J_{MS} (s^{-1})$	$J_{MS} J_{PA}$
$O_3 + h\nu \rightarrow O(^1P) + O_2$	40	2.74×10^{-4}	3.49×10^{-4}	1.27
	30	2.40×10^{-4}	3.18×10^{-4}	1.33
	20	2.06×10^{-4}	2.95×10^{-4}	1.43
	10	2.01×10^{-4}	2.94×10^{-4}	1.46
$O_3 + h\nu \rightarrow O(^1D) + O_2$	40	9.10×10^{-4}	9.09×10^{-4}	1.00
	30	5.30×10^{-5}	5.30×10^{-5}	1.01
	20	7.49×10^{-6}	9.66×10^{-6}	1.29
	10	5.44×10^{-6}	8.26×10^{-6}	1.52
$O_2 + h\nu \rightarrow O + O$	40	3.01×10^{-10}	3.01×10^{-10}	1.00
	30	1.83×10^{-11}	1.74×10^{-11}	0.95
	20	5.73×10^{-14}	4.42×10^{-14}	0.77
	10	7.64×10^{-20}	8.91×10^{-20}	1.17
$NO_2 + h\nu \rightarrow NO + O$	40	4.97×10^{-3}	7.73×10^{-3}	1.56
	30	4.85×10^{-3}	7.67×10^{-3}	1.58
	20	4.74×10^{-3}	7.74×10^{-3}	1.63
	10	4.72×10^{-3}	7.74×10^{-3}	1.64
$HNO_3 + h\nu \rightarrow OH + NO_2$	40	3.50×10^{-5}	3.51×10^{-5}	1.00
	30	4.66×10^{-6}	4.54×10^{-6}	0.97
	20	3.25×10^{-7}	4.54×10^{-7}	1.40
	10	2.61×10^{-7}	4.16×10^{-7}	1.59
$H_2O_2 + h\nu \rightarrow 2OH$	40	2.11×10^{-5}	2.14×10^{-5}	1.01
	30	3.79×10^{-6}	4.07×10^{-6}	1.07
	20	1.30×10^{-6}	1.85×10^{-6}	1.42
	10	1.10×10^{-6}	1.75×10^{-6}	1.59
$HO_2 + h\nu \rightarrow OH + O$	40	6.50×10^{-5}	6.49×10^{-5}	1.00
	30	3.35×10^{-6}	3.19×10^{-6}	0.95
	20	1.05×10^{-8}	8.08×10^{-9}	0.77
	10	1.55×10^{-14}	1.81×10^{-14}	1.17
$ClONO_2 + h\nu \rightarrow ClO + NO_2$	40	2.21×10^{-4}	2.37×10^{-4}	1.07
	30	5.09×10^{-5}	6.83×10^{-5}	1.34
	20	3.41×10^{-5}	5.46×10^{-5}	1.60
	10	3.28×10^{-5}	5.40×10^{-5}	1.65
$ClNO_2 + h\nu \rightarrow Cl + NO_2$	40	6.03×10^{-4}	7.42×10^{-4}	1.23
	30	3.41×10^{-4}	4.89×10^{-4}	1.43
	20	2.73×10^{-4}	4.46×10^{-4}	1.63
	10	2.64×10^{-4}	4.42×10^{-4}	1.67
$OCIO + h\nu \rightarrow ClO + O(^1D)$	40	2.27×10^{-3}	3.02×10^{-3}	1.33
	30	1.53×10^{-3}	2.29×10^{-3}	1.50
	20	1.40×10^{-3}	2.23×10^{-3}	1.59
	10	1.39×10^{-3}	2.23×10^{-3}	1.60
$ClO + h\nu \rightarrow Cl + O$	40	1.61×10^{-3}	1.62×10^{-3}	1.01
	30	1.77×10^{-4}	1.78×10^{-4}	1.01
	20	2.37×10^{-5}	2.86×10^{-5}	1.21
	10	1.57×10^{-5}	2.29×10^{-5}	1.46

Table 6 (continued)

Reaction	Altitude (km)	$J_{PA} \text{ (s}^{-1}\text{)}$	$J_{MS} \text{ (s}^{-1}\text{)}$	$J_{MS} J_{PA}$
$\text{CF}_2\text{Cl}_2 + h\nu \rightarrow 2\text{Cl}$	40	5.12×10^{-7}	5.14×10^{-7}	1.00
	30	6.17×10^{-8}	5.83×10^{-8}	0.94
	20	1.92×10^{-10}	1.45×10^{-10}	0.76
	10	1.09×10^{-16}	1.28×10^{-16}	1.17
$\text{CFCl}_3 + h\nu \rightarrow 2.5 \text{ Cl}$	40	4.39×10^{-6}	4.40×10^{-6}	1.00
	30	5.20×10^{-7}	4.94×10^{-7}	0.95
	20	1.79×10^{-9}	1.36×10^{-9}	0.76
	10	1.53×10^{-15}	1.78×10^{-15}	1.16

Figure 17 Calculated concentration profiles for $\text{O}(^3\text{P})$, $\text{O}(^1\text{D})$, and O_3 for the ambient atmosphere, without multiple scattering. Figure 19 Calculated concentration profiles for HNO_3 , NO_2 , and NO for the ambient atmosphere, without multiple scattering. Figure 18 Calculated concentration profiles for OH , HO_2 , and H_2O_2 for the ambient atmosphere, without multiple scattering. Figure 20 Calculated concentration profiles for Cl , ClO , ClONO_2 , and HCl for the ambient atmosphere, without multiple scattering.

Multiple scattering has a large effect on NO_2 photolysis but a negligible effect on HNO_3 above 30 km (see Table 6). The reduction in HNO_3 above 30 km, therefore, is due to a decrease in the HNO_3 production rate brought about primarily by the decrease in NO_2 . The percentage decrease in NO_2 is greater than the increase in OH , consequently there is a net decrease in the rate of the reaction $\text{OH} + \text{NO}_2 \rightleftharpoons \text{HNO}_3$. The ratio of total column abundance computed with multiple scattering to that

computed with pure absorption is 0.94 for NO_2 and 1.36 for NO .

The effect of multiple scattering on species containing chlorine is shown in Fig. 24. The concentration of ClONO_2 is reduced 35–45% between 20 and 30 km, which is the region of its maximum concentration. Photolysis of ClONO_2 affects several other chlorine-containing species through a complex chain of reactions. Certain key reactions are

Figure 21. Changes in calculated concentrations of O_3 , $\text{O}(^3\text{P})$, and $\text{O}(^1\text{D})$ when multiple scattering is included (compare Fig. 17).

Figure 23. Changes in calculated concentrations of HNO_3 , NO_2 , and NO when multiple scattering is included (compare Fig. 19).

Figure 22. Changes in calculated concentrations of H_2O_2 , HO_2 , and OH when multiple scattering is included (compare Fig. 18).

Figure 24. Changes in calculated concentrations of ClONO_2 , ClO , HCl , and Cl when multiple scattering is included (compare Fig. 20).

The peak concentration of ClONO_2 occurs near 25 km, so photolysis of ClONO_2 acts as a strong source of ClO in this region. The large increase in NO between 20 and 30 km tends to shift ClO to Cl , leading to a net decrease in ClO in this region and an increase in Cl . This leads to an increase in HCl production through reaction of Cl with CH_4 . The decrease in ClONO_2 above 40 km occurs because of the effect of decreased NO_2 on the ClONO_2 production rate ($\text{ClO} + \text{NO}_2 \xrightarrow{M} \text{ClONO}_2$).

Model Sensitivity

In addition to affecting the concentration of many species in the model, multiple scattering affects the model sensitivity to perturbations. This was tested for an NO_x perturbation and a CFM perturbation. The NO_x perturbation was an injection of NO_x at a rate of 1000 molecules/ $\text{cm}^2 \cdot \text{s}$ as NO_2 over a 1-km-thick layer centered at 20 km. The change in total ozone at steady state is shown in Table 7 for both the pure absorption and the multiple scattering calculations. The ratio of the percent change in ozone with multiple scattering to the percent change with pure absorption, $R = \text{MS/PA}$, is also presented in Table 7. Including multiple scattering has very little effect on the model sensitivity to an NO_x injection at 20 km ($R = 1.01$) in spite of significant differences in the ambient species profiles. Increasing the surface albedo from 0.25 to 0.75 also has a very small effect on the model sensitivity ($R = 1.03$). Consequently, the choice of A_s used in the photodissociation rate calculations is not a critical factor in NO_x perturbation studies which include multiple scattering where one is primarily interested in the change in total ozone. It should be noted, however, that the choice of A_s significantly affects the photodissociation rates and the ambient species profiles (see Luther and Wuebels 1976 for details).

The effect of variations in model chemistry on the above results was tested first by varying the reaction rate for $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$, then by making the changes listed in Table 5. A recent measurement by Burrows et al. (1977) gives a value of 5.1×10^{-11} for the rate coefficient of $\text{OH} + \text{HO}_2$. Chang and Kaufman (1977) report an upper limit of 5×10^{-11} for the rate coefficient, whereas their experimental results are best fitted by using a value of 2×10^{-11}

(Chang and Kaufman 1977). The calculations described above were repeated using a value of 5.1×10^{-11} , and the results are presented in Table 7. Changing this rate coefficient significantly increases the ozone reduction due to this NO_x perturbation, but there is no significant change in R (MS/PA).

When the new rate coefficients listed in Table 5 were incorporated into the model, the effect of the NO_x injection changed from a reduction to an increase in total ozone. Including multiple scattering in this case significantly enhanced the ozone increase. The change in ΔO_3 due to including multiple scattering, however, is small compared to the change in ΔO_3 resulting from changing the model chemistry.

For the CFM perturbation, we consider the steady-state ozone reduction due to CFMs at the 1975 release rate, which is assumed to be 290 kilotonnes/yr for CFCl_3 and 425 kilotonnes/yr for CF_2Cl_2 . Results for both the pure absorption and multiple scattering calculations are presented in Table 8. For the CFM perturbation, including multiple scattering increases the ozone reduction by a factor of 1.16 for a surface albedo of 0.25. As in the case of the NO_x perturbation, changing the surface albedo has little effect on the change in total ozone, e.g., the ozone reduction increases by a factor of

Table 7. Change in total ozone due to an NO_x injection of 1000 molecules/ $\text{cm}^2 \cdot \text{s}$ as NO_2 over a 1-km-thick layer centered at 20 km. R is the ratio ΔO_3 (multiple scattering)/ ΔO_3 (pure absorption).

Case	ΔO_3 (%)	R
(a) $\text{OH} + \text{HO}_2$ rate coefficient $= 2 \times 10^{-11}$:		
Pure absorption	-2.34	-
Multiple scattering, $A_s = 0.25$	-2.36	1.01
Multiple scattering, $A_s = 0.75$	-2.40	1.03
(b) $\text{OH} + \text{HO}_2$ rate coefficient $= 5.1 \times 10^{-11}$:		
Pure absorption	-3.44	-
Multiple scattering, $A_s = 0.25$	-3.50	1.02
(c) Rate changes given in Table 5:		
Pure absorption	-0.07	-
Multiple scattering, $A_s = 0.25$	0.39	1.9 ^a

^aRatio is not meaningful for such small quantities.

1.17 relative to the pure absorption calculation using a surface albedo of 0.75. When the rate coefficient for $\text{OH} + \text{HO}_2$ is increased to 5.1×10^{-11} , the ozone reduction with multiple scattering increases by a factor of 1.22 (Table 8) relative to the pure absorption calculation.

Using the rate coefficients in Table 5 approximately doubles the predicted ozone reduction due to CFMs. In this case, including multiple scattering still causes a significant increase in ΔO_3 (i.e., $R = 1.21$).

The effect of multiple scattering on species concentration profiles illustrates the importance of including multiple scattering when comparing model-derived concentration profiles with observational data. For the cases studied, the effect on model sensitivity of including multiple scattering ranged from no change in ΔO_3 compared to the pure absorption calculation to a significant increase in ΔO_3 depending upon the model chemistry. The change in ΔO_3 due to multiple scattering, however, was small compared to the change in ΔO_3 resulting from varying chemical reaction rates.

Table 8. Change in total ozone due to CFMs at the 1975 release rate. R is the ratio $\Delta\text{O}_3(\text{multiple scattering})/\Delta\text{O}_3(\text{pure absorption})$.

Case	ΔO_3 (%)	R
(a) $\text{OH} + \text{HO}_2$ rate coefficient = 2×10^{-11} :		
Pure absorption	-6.31	-
Multiple scattering, $A_s = 0.25$	-7.31	1.16
Multiple scattering, $A_s = 0.75$	-7.41	1.17
(b) $\text{OH} + \text{HO}_2$ rate coefficient = 5.1×10^{-11} :		
Pure absorption	-3.86	-
Multiple scattering, $A_s = 0.25$	-4.70	1.22
(c) Rate changes given in Table 5:		
Pure absorption	-11.95	-
Multiple scattering, $A_s = 0.25$	-14.42	1.21

2.6 Effect of Changes in Stratospheric Water Vapor on Ozone Reduction Estimates *

The potential threat to the earth's ozone layer of supersonic transports' engine effluents and chlorofluoromethanes has received a great deal of attention. Early estimates of the potential ozone reduction considered NO_x or CFM pollutants alone. However, recent assessments have also considered the possibility of a simultaneous change in stratospheric water-vapor abundance (Liu et al. 1976, Duewer et al. 1977b). Both of these studies showed that increased water vapor caused enhanced ozone reduction for the then accepted rate coefficients.

The H_2O emission index (1.3 kg/kg fuel) is much larger than the NO_x emission index (0.018 kg/kg fuel) for SSTs (Grobecker et al. 1974). An annual fuel consumption rate of 10^{11} kg/yr for a fleet of SSTs at a cruise altitude of 20 km would increase the stratospheric water-vapor burden approximately 15% (Grobecker et al. 1974, p. 52). Changes in atmospheric composition due to stratospheric perturbations might affect stratospheric water-vapor abundance indirectly by changing the temperature of the tropical tropopause. Since the saturation vapor pressure of H_2O doubles for a rise of 4 K in tropopause temperature (Ellsaesser 1974, Liu et al. 1976), this could have a larger effect than the direct injection of water vapor in the stratosphere.

The most thorough study to date of the effect of changes in water vapor abundance on the estimated ozone reduction by NO_x and CFM pollutants is that of Liu et al. (1976), who used a one-dimensional transport-kinetics model for their calculations. Imposing an increase in the water-vapor mixing ratio of 1 ppmv at the tropopause caused an additional reduction in total ozone of 0.3-1.0% (from their Fig. 12) for an NO_x perturbation and 0.4-1.4% (from their Fig. 5) for a CFM perturbation; the range cited reflects variation of the reaction rate for $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ between 2×10^{-10} and 2×10^{-11} cm^3/s . The largest sensitivity to changes in water vapor abundance was associated with the slow rate for this reaction. Although the change in stratospheric water-vapor abundance was postulated to be due to a change in tropopause temperature, the temperature profile was fixed, and the effect of changes in temperature on chemical reaction rates was not included in their calculations. We

*See Luther and Duewer (1977).

have expanded upon the work of Liu et al. (1976) by including temperature changes in our calculations.

In order to include the effect of changes in temperature, we used the one-dimensional transport-kinetics model coupled with a stratospheric radiative transfer model. The transport-kinetics model used in this study included multiple scattering in the photodissociation rate calculation assuming a surface albedo of 0.25. Calculations were made using the model chemistry listed in Table A-1 of Appendix A and the old rates listed in Table 5, then the calculations were repeated using the new rates listed in Table 5.

A stratospheric radiative transfer model (Luther et al. 1977a) is used to compute the temperature profile above 12 km. The temperature profile below 12 km is specified. The model includes solar absorption and long-wave interaction by O_3 , H_2O , and CO_2 along with solar absorption by NO_2 . The radiative transfer model is the same as Ramanathan's (1974) except that we have added solar absorption by NO_2 . There are several differences between this model and Ramanathan's latest model (Ramanathan 1976), as described in detail in his paper.

We assume that the change in surface temperature is negligible. The change in surface temperature associated with a 10% reduction in ozone due to CFMs at a tropospheric concentration of approximately 2 ppb was computed to be 0.3 K or less by Ramanathan (1975) and by Reck (1976). Ozone reductions up to 30% due to NO_x injections were computed to cause a change of less than 0.1 K in surface temperature by Ramanathan et al. (1976). Neglecting changes in surface temperature of this magnitude has no significant effect on the results.

The tropospheric distribution of H_2O is based on Mastenbrook (1974). The stratospheric mixing ratio of H_2O is assumed to be 4.3 ppmv. Liu et al. (1976) computed the stratospheric distribution of H_2O by specifying the mixing ratio at the tropopause and assuming that methane oxidation increases the water content of the upper stratosphere. Their calculations showed that changing the water-vapor mixing ratio at the tropopause by some amount ΔH_2O resulted in the same change in mixing ratio at altitudes up to 50 km. Above 50 km, the change in local H_2O mixing ratio was less than ΔH_2O at the tropopause. In our calculations, when the stratospheric water-vapor mixing ratio is changed, the same ΔH_2O is applied at all altitudes above 13 km, thus leading to a change in stratospheric water-vapor abundance similar to that of Liu et al. (1976).

Large-scale dynamical processes are neglected in the determination of the temperature profile. These

processes have a significant effect on the temperature profile near the tropopause. For our application here, the ability of the model to compute the change in temperature is more important than the particular ambient temperature profile. Since changes in atmospheric dynamics brought about by changes in temperature structure and in the radiation balance are not included in the model (or any other transport-kinetics model at the present time), there may be significant errors in the predicted temperature change in the lower stratosphere. Consequently, in discussing the results, we want to emphasize their qualitative nature rather than the quantitative details.

NO_x Injection

The effect of a change in stratospheric water vapor on total ozone was computed for cases with and without a simultaneous NO_x injection in order to test the sensitivity of the results to the magnitude of the NO_x perturbation. We consider an NO_x injection rate of 1000 molecules/cm³·s as NO_2 over a 1-km-thick layer centered at 20 km, which is a larger injection rate than that used by Liu et al. (1976). Calculations were first performed using the fixed ambient-temperature profile in order to verify qualitatively the results obtained by Liu et al. (1976), then the calculations were repeated with temperature feedback included. The results using the Chang (1976) diffusion coefficients are presented in Fig. 25, which shows the change in total ozone at steady state as a function of the change in stratospheric water vapor mixing ratio. This calculation did not include the recent changes in chemistry listed in Table 5.

With no change in H_2O , this NO_2 injection causes a reduction in total ozone of 2.25% with a fixed temperature profile and 2.03% with temperature feedback. Temperature feedback, therefore, has approximately a 10% restoring effect on the change in total ozone, which is consistent with our earlier results (Luther et al. 1977a).

The results using a fixed temperature profile are similar to those of Liu et al. (1976) for the slow reaction rate of $OH + HO_2$. The slope of ΔO_3 versus ΔH_2O is -0.42%/ppmv (at $\Delta H_2O = 0$) with the NO_x injection and -0.64%/ppmv with no NO_x injection as compared to Liu et al.'s value of -1.0%/ppmv, thus our model is less sensitive to changes in water vapor abundance. The results also demonstrate that the model sensitivity depends upon the amount of NO_x present. Since the eddy diffusion profile affects the background NO_x , the results can be expected to depend also upon the eddy diffusion profile used in the calculation.

Figure 25 Change in total ozone vs change in water-vapor mixing ratio above 13 km, computed using the Chang (1976) K_p profile with and without an NO_x injection of 1000 molecules/cm² s of NO_2 over a 1-km-thick layer centered at 20 km: (a) without NO_x injection, (b) with NO_x injection.

When temperature feedback is included, the results change dramatically. An increase in stratospheric water vapor now causes less reduction in total ozone, the slope being 0.21%/ppmv for this NO_x injection. With no NO_x injection, the model is virtually insensitive to changes in water vapor.

An analysis of the effect of changes in water vapor with fixed temperature is helpful in showing why temperature feedback has such a significant effect. Profiles of the change in ozone concentration due to the NO_x injection at 20 km are shown in Fig. 26a for various values of $\Delta\text{H}_2\text{O}$. Destruction of odd oxygen is dominated by HO_x reactions in the regions 10–20 km and 40–50 km. In the 10-to-20-km region, odd-oxygen destruction is dominated by the reactions

whereas in the 40-to-50-km region the dominant reactions are

Increasing the water-vapor mixing ratio increases the ozone destruction rate in these regions because HO_x increases (Fig. 26a). Although relatively large percentage changes occur in the ozone concentration above 40 km, these changes make a relatively small contribution to the change in total ozone because of the small O_3 concentration above 40 km.

The NO_x catalytic cycle dominates odd oxygen destruction in the middle stratosphere. Increased HO_x decreases ozone destruction in the 25-to-35-km region because of two processes. First, more NO_x is converted to HNO_3 by the reaction $\text{NO}_2 + \text{OH}$, thus inhibiting the NO_x catalytic cycle. Secondly, increased HO_x leads to interference with NO_x cycle destruction of odd oxygen through the reactions

Figure 26 Change in ozone concentration vs height due to the NO_x injection of Fig. 25, calculated for several values of $\Delta\text{H}_2\text{O}$, with and without temperature feedback.

Since the rate of destruction of odd oxygen depends upon the amount of HO_2 and NO_2 in this region, the effect of changing the water-vapor mixing ratio will depend to some extent upon the magnitude of the NO_2 injection.

Similar results for the calculation including temperature feedback are shown in Fig. 26b. Comparing Figs. 26a and 26b, we see in the latter less sensitivity to changes in water vapor above 40 km and in the region 10–20 km. However, the sensitivity is enhanced in the region 25–35 km. In order to demonstrate the effect of changes in water vapor and temperature on ozone more clearly, we introduce the quantity $\text{DO}_3(z)$ which is defined by

$$\text{DO}_3(z) = \frac{\Delta[\text{O}_3]_z}{\text{O}_3(\text{column})} \quad (6-8)$$

where $\Delta[\text{O}_3]_z$ is the change in local ozone concentration, and $\text{O}_3(\text{column})$ is the unperturbed total ozone. The function $\text{DO}_3(z)$ represents the contribution per unit altitude to the change in total ozone. The change in total ozone is therefore given by the integral

$$\Delta\text{O}_3 = \int_0^{z_{\max}} \text{DO}_3(z) dz \quad (6-9)$$

In other words, the area under the curve of $\text{DO}_3(z)$ versus z equals ΔO_3 . In order to extract the contribution to DO_3 due expressly to changes in water-vapor mixing ratio, we introduce the expression $\Delta\text{DO}_3(\text{H}_2\text{O})$, which is defined by

$$\Delta\text{DO}_3(\text{H}_2\text{O}) = \text{DO}_3(\Delta\text{H}_2\text{O}) - \text{DO}_3(\Delta\text{H}_2\text{O} = 0) \quad (6-10)$$

where $\Delta\text{DO}_3(\text{H}_2\text{O})$ is a function of altitude (z), although the z dependence is not indicated. This function is plotted for several values of $\Delta\text{H}_2\text{O}$ in Fig. 27a for the case with fixed temperature and in Fig. 27b for the case with temperature feedback.

Those regions in which changes in water vapor either increase or decrease ozone are clearly apparent. With fixed temperature the greatest contribution to the change in total ozone comes from the change in ozone concentration in the region 10–25 km, whereas with temperature feedback the greatest contribution comes from changes in the region 20–30 km. These differences are related to the sensitivity of various reaction rates to changes in temperature.

The changes in temperature due to the NO_2 injection at 20 km along with changes in water-vapor mixing ratio are shown in Fig. 28. With no change in water vapor, NO_2 injection causes a temperature increase in the vicinity of the tropopause (15 km) and a temperature decrease above 21 km. Increasing the water-vapor mixing ratio now decreases the temperature by varying amounts at all altitudes above 13 km. The ozone destruction reactions have positive activation energies, thus they are slowed when the temperature is decreased. In contrast, ozone production is a photolytic process nearly independent of temperature.

Reactions (6-1) and (6-2) have relatively high activation energies. Consequently, they are very sensitive to temperature change. As shown in Fig. 27, the ozone destruction due to enhanced water vapor in the region 10–20 km is greatly reduced due to the temperature decrease. The NO_x catalytic reactions, which dominate ozone destruction in the region 20–40 km, have moderate activation energies. Therefore, the decrease in ozone destruction in this region (which appears as enhanced ozone production in Fig. 27) is also significant, but it is not as large as in the region 10–20 km. Reactions (6-3), (6-4), and (6-5) have very low activation energies, so the region 40–50 km is least sensitive to changes in temperature.

The increase in stratospheric water vapor is postulated upon the assumption of an increase in the tropopause temperature. The calculation indeed shows (Fig. 28) an increase in temperature at the altitude of the tropopause (15 km) for $\Delta\text{H}_2\text{O} = 0$, which occurs because of increased solar absorption by NO_2 (Luther et al. 1977a). As $\Delta\text{H}_2\text{O}$ increases, the temperature at this level decreases, which is a negative feedback process limiting the change in H_2O . The tropopause temperature might also be affected by changes in surface temperature resulting from increased stratospheric water vapor, but this effect has not yet been included in the calculation. In order to accurately estimate the expected change in the temperature of the tropical tropopause and the change in the stratospheric water-vapor mixing ratio, we would need a multidimensional model

Figure 27 Calculated profiles of $\Delta O_3(H_2O)$ corresponding to various values of ΔH_2O using the Chang (1976) K_1 profile for the case of the NO_x injection of Fig. 25: (a) with fixed temperature, (b) with temperature feedback.

Figure 28 Calculated changes in temperature for the stratosphere perturbed by the NO_x injection of Fig. 25.

capable of computing changes in dynamics (transport) and temperature. This entails predicting changes in the mean and eddy components of the circulation as well as changes in the energy and moisture budgets. The one-dimensional calculation is useful in that it qualitatively demonstrates that large changes in stratospheric water vapor are unlikely.

In order to test the degree to which these results might be model-dependent, we repeated the calculations using the Hunten K_2 profile; the results are shown in Fig. 29. The model sensitivity to changes in water-vapor mixing ratio without an NO_x injection is nearly the same using the Hunten K_2 profile as it was using the Chang (1976) K_2 profile (Fig. 25). The slope of ΔO_3 versus H_2O is $-0.75\%/ppmv$ with no temperature feedback as compared with $-0.64\%/ppmv$ using the Chang K_2 profile. When temperature feedback is included, the slope is nearly zero. However, with the NO_x injection, the model sensitivity changes significantly. First, the ozone

Figure 29 Change in total ozone vs change in water-vapor mixing ratio above 13 km computed using the Hunten (1975) K_2 profile: (a) without NO_x injection, (b) with the NO_x injection of Fig. 25.

reduction with no change in H_2O using a fixed temperature profile is considerably larger with the Hunten K_2 profile: 4.66% as compared to 2.25%. Second, the slopes of the curves are changed dramatically. The amount of ozone reduction due to an increase in H_2O is reduced for the fixed-temperature calculation (the slope is $-0.07\%/ \text{ppmv}$ as compared with $-0.42\%/ \text{ppmv}$ previously). For the calculation with temperature feedback, the reduction in ΔO_3 due to increased H_2O is further enhanced (the slope is $0.63\%/ \text{ppmv}$ as compared with $0.21\%/ \text{ppmv}$ previously). Thus, the choice of the K_2 profile and the magnitude of the NO_x injection significantly affect the sensitivity to changes in H_2O .

Profiles of $\Delta\text{DO}_3(\text{H}_2\text{O})$ are shown in Figs. 30a and 30b for the calculations with fixed temperature and with temperature feedback, respectively. The results are qualitatively similar to those in Fig. 27, but there are some quantitative differences. The ozone production (or destruction, depending upon the sign of $\Delta\text{H}_2\text{O}$) in the region 20–35 km approximately balances the ozone destruction (production) in the region 10–20 km for the fixed-temperature calculation using the Hunten K_2 profile, whereas the lower region is dominant using the Chang K_2 profile. Above 35 km, the curves are virtually unchanged. The ozone production (destruction) in the region 20–35 km using the Hunten K_2 profile shows

Figure 30 Calculated profiles of $\text{DO}_3(\text{H}_2\text{O})$ corresponding to various values of $\Delta\text{H}_2\text{O}$ using the Hunten (1975) K_2 profile for the case of the NO_x injection of Fig. 25: (a) with fixed temperature, (b) with temperature feedback.

more enhancement with temperature feedback than when the Chang K_2 profile is used.

The ozone production in the region 20–35 km associated with an increase in H_2O is the net result of competing processes, some which tend to increase ozone and some which tend to destroy ozone. The net result is sensitive to the HO_x and NO_x abundances, which are affected by the diffusion coefficient profile, key reaction rates such as $OH + HO_2$ and $HO_2 + NO$, and the magnitude of the NO_x injection. Because of uncertainties in these quantities, there is a significant uncertainty in the quantitative results in the region 20–35 km of Figs. 27 and 30. These figures, however, illustrate the significant effect which changes in temperature have on the chemistry in the region below 35 km.

The computed change in total ozone due to a change in water-vapor mixing ratio using the chemical rates listed in Table 5 and the Chang K_2 profile is shown in Fig. 31. Although the model sensitivity to a stratospheric NO_x injection with $\Delta H_2O = 0$ has changed from a decrease in total ozone to an increase, the effect on ozone of changing water-vapor abundance is nearly unchanged. Compared to Fig. 25, the curves are displaced, but the slopes of the curves are changed only slightly.

Figure 31 Change in total ozone vs change in water-vapor mixing ratio above 13 km computed using the new rate coefficients in Table 5: (a) without NO_x injection, (b) with NO_x injection of Fig. 25.

Profiles of $\Delta DO_3(H_2O)$ are shown in Figs. 32a and 32b for the calculations with fixed temperature and with temperature feedback. The curves are qualitatively similar to those shown in Fig. 27, but quantitatively they are quite different. Although there are similar regions of local ozone increase or decrease, the magnitude of the change in ozone concentration has been significantly affected, particularly in the region 25–35 km.

CFM Release

The effect of changes in stratospheric water-vapor abundance on the ozone reduction due to CIX pollutants was also tested. The perturbation which we considered was a steady-state release of CFMs at the 1975 release rate, which is assumed to be 290 kilotonnes/yr for $CFCl_3$ and 425 kilotonnes/yr for CF_2Cl_2 . The long-wave effects of $CFCl_3$ and CF_2Cl_2 are not included in the radiative transfer model. These effects have been shown to be significant by Ramanathan (1976) for species concentrations of several ppb. This introduces considerable uncertainty into the temperature calculation in the region 15–25 km for the perturbed stratosphere. The effect of changes in water vapor abundance on total ozone is not altered since the incremental change in temperature due to ΔH_2O is not changed significantly. There will be an effect, however, on the ozone reduction for the temperature feedback calculation with $\Delta H_2O = 0$. The curve of ΔO_3 versus ΔH_2O will be displaced, but the slope will not be significantly affected.

The steady-state reduction in total ozone computed using the Chang K_2 profile is shown in Fig. 33 as a function of ΔH_2O . The reduction in total ozone is 6.9% for the fixed-temperature calculation with no change in water vapor. The sensitivity to changes in water vapor is enhanced by the CFM injection, unlike our findings for an NO_x injection. The slope of ΔO_3 versus ΔH_2O is $-1.2\%/ppmv$ as compared to $-0.64\%/ppmv$ with only a change in water vapor (Fig. 25a). Our results with fixed temperature agree very well with those of Liu et al. (1976), who got a value of $-1.4\%/ppmv$ with 1 ppb of CIX.

Including temperature feedback reduces the sensitivity to changes in H_2O , but not sufficiently to change the sign of the slope of ΔO_3 versus ΔH_2O as was the case with the NO_x injection. The slope with temperature feedback is $-0.6\%/ppmv$, which is half that with fixed temperature. The change in slope due to temperature feedback is approximately the same as the difference between the slopes of the curves in Fig. 25b.

Figure 34 shows the change in ozone concentration versus height for the fixed-temperature and

Figure 32. Calculated profiles of $DO_3(H_2O)$ corresponding to various values of ΔH_2O using the new rate coefficients given in Table 5, for the case of the NO_x injection of Fig. 25: (a) with fixed temperature, (b) with temperature feedback.

Figure 33. Change in total ozone at steady state vs change in water-vapor mixing ratio above 13 km, computed using the Chang (1976) K_p profile and assuming the 1975 CFM release rate.

Figure 34. Change in ozone concentration at steady state with height, computed using the 1975 CFM release rate and assuming $\Delta H_2O = 0$.

temperature-feedback calculations with $\Delta H_2O = 0$. The differences between these two calculations are attributed directly to the change in temperature (shown in Fig. 35). The temperature decreases above 30 km, thus slowing the ozone destruction reactions, resulting in less ozone destruction with temperature feedback. Below 30 km the temperature increases, which (again using an activation energy argument) results in less ozone production or more ozone destruction.

With no change in water vapor, the temperature change at the tropopause was -0.03 K. The concentration of CFMs at the tropopause was 0.7 ppb for $CFCl_3$ and 1.7 ppb for CF_2Cl_2 . Radiative transfer calculations which include the long-wave effect on CFMs at this concentration show a warming at the tropopause of about 1 K (Liu, private communication, 1977). This would enhance slightly the difference between the two curves shown in Fig. 34 in the region 10–20 km. The negative feedback between changes in water vapor and temperature discussed above for the NO_x perturbation is also apparent in Fig. 35, thus it is unlikely that the water-vapor mixing ratio will increase more than about 1 ppmv due to this CFM perturbation.

The profiles of $\Delta DO_3(H_2O)$ are presented in Fig. 36 for the CFM perturbation. The results differ

Figure 35. Calculated profiles of temperature change in the stratosphere corresponding to various values of ΔH_2O , assuming stratosphere perturbed by CFMs at the 1975 release rate.

significantly from those shown in Fig. 27 for the NO_x injection. Although there is a region of reduced sensitivity near 30 km, there is no longer a crossover region. Temperature feedback causes a shift in sensitivity similar to that for the NO_x perturbation case. For smaller CFM release rates, there is

Figure 36. Calculated profiles of $\Delta DO_3(H_2O)$ corresponding to various values of ΔH_2O using the Chang (1976) K_p profile for the case of CFMs at the 1975 release rate: (a) with fixed temperature, (b) with temperature feedback.

a crossover similar to Fig. 27, which illustrates the dependence upon the magnitude of the CFM perturbation.

The effect of changes in water vapor is somewhat different for the CFM perturbation because of the importance of the reaction

Although increased HO_x in the lower atmosphere tends to increase O_3 due to conversion of NO_x to HNO_3 and production of odd oxygen through reactions (6-6) and (6-7), it also releases more free chlorine through reaction (6-11) which tends to enhance the ozone reduction. The results depend upon the magnitude of the CFM perturbation because of its effect on the concentration of HCl . Again, we are seeing in Fig. 36 the net effect of many competing processes.

In analyzing the effect of changes in water vapor on the ozone profile, we found that the region between 10 and 35 km was most sensitive. In the 25-to-35-km region, an increase in H_2O may either increase ozone or decrease ozone depending upon the concentrations of NO_x and Cl ; the larger the NO_x perturbation, the more H_2O tends to decrease ozone.

The results depend quantitatively upon the reaction rates and the K_2 profile used for the calculation. Because of uncertainties in these quantities, the qualitative nature of the results should be emphasized rather than their quantitative nature. The change in O_3 depends upon the net effect of several competing mechanisms, particularly in the region 25–35 km. In spite of significant changes in model chemistry, the calculations still indicate that changes in stratospheric water vapor would have much less effect on total ozone than originally estimated by Liu et al. (1976).

2.7 Effect of Past Atmospheric Nuclear Tests on Ozone

It was suggested by Foley and Ruderman (1973) that the atmospheric nuclear tests of the late 1950s and early 1960s should have caused a stratospheric ozone depletion of more than 10% if then current models of the effect of NO_x on stratospheric ozone were correct. However, their analysis failed to consider the difference in effect to be expected from a pulse injection of NO_x in contrast to the effect of a

continuous NO_x source. In 1973 Chang and Duerer calculated the effect on ozone of the nuclear tests (using a production of NO_x /megaton yield about half that used by Foley and Ruderman), and obtained a calculated northern-hemisphere ozone reduction of roughly 4% for 1963. It was concluded that the calculated reduction was not inconsistent with the observed variability of atmospheric ozone as analyzed by Johnston et al. (1973).

In the intervening years, significant changes have occurred in the formulation of the model and in the experimental values of rate constants used as model input. Also, substantially more analysis of the ozone record has been carried out. We will discuss the effect several of these advances have had on the computed effect of the atmospheric nuclear test series on stratospheric ozone and some implications for models of the stratosphere.

Several workers have investigated the problem of NO_x production from a nuclear fireball (see Table 9). The most recent and comprehensive investigations are those of Gilmore (1975) and COMESA (1975). As can be seen in Table 9, these two studies are in good agreement as to their estimates for the total NO_x produced by a nuclear explosion. However, the COMESA study included an estimate of loss of NO_x from the rising debris cloud (i.e., 20%). In this work we accept the COMESA estimate of the total NO_x injection per megaton, but we note that this value should be considered uncertain by roughly $\pm 50\%$.

A related question concerns the yields of the various nuclear weapons. Table 10 gives several published estimates of the total yield for the period of active testing. In this work we have followed the procedure of taking unclassified qualitative yield descriptions and assigning them quantitative values consistent with other available data. Our integrated yield estimate for the period 1961–62 is consistent with the estimates given by COMESA (1975) and Foley and Ruderman (1973), but roughly 10% larger than those cited by Johnston et al. (1976) and Seitz et al. (1968).

A few nuclear devices were exploded in or above the stratosphere, generating clouds that stabilized in or above the mesosphere. These tests may have created more NO_x /megaton than low-altitude tests, because a low-density fireball can be expected to depart from equilibrium composition at a higher temperature than a higher density fireball. Thus, it might be argued (Hampson 1977) that these devices could have produced a very high yield of NO at altitudes of 70–200 km. However, in that altitude range NO_x has a lifetime on the order of a day (Gerard and Barth 1977), and it is unlikely that any

*See Chang et al. (1977).

significant fraction of NO_x produced at high altitudes reached the stratosphere. Further, while energetic particles escaping from a high-altitude fireball might produce NO_x in the stratosphere, it is unlikely that this process had a significant effect on the yields of NO_x summed over all tests.

The model perturbations are small enough that model response to variation of the total NO_x injection is approximately linear for most chemistries.

Table 9. Estimates of NO produced per megaton (Mt) of nuclear-explosive yield.

Source	Estimated NO production (10^{22} molecules/Mt)
Zeldovich and Razier (1967)	0.5
Foley and Ruderman (1972)	0.3-1.5
Johnston et al. (1973)	0.17-1.0
Chang and Dwyer (1973)	0.5
Goldsmith et al. (1973)	1.0
Gilmore (1975)	0.4-1.5 (0.9)
COMESA (Goldsmith et al.) (1975)	0.6-1.1 (0.84)
COMESA (after allowance for disentrainment) (1975)	0.5-0.9 (0.67)
This work uses	0.67

Thus if a readjustment of the NO_x yield should be dictated by future work, our computed ozone perturbations would, to a fair approximation, scale linearly.

A more difficult point concerns the altitude of injection. Foley and Ruderman (1972) gave a parameterization for the top and bottom of the stabilized cloud versus device yield:

$$\text{CT} = 21.64Y^{(0.2)},$$

$$\text{CB} = 13.41Y^{(0.2)},$$

where

CT = cloud top (km)

CB = cloud bottom (km)

Y = yield (megatons TNT equivalent)

This parameterization was largely based on direct observations of United States tests (Peterson 1970); it was only inferred to be valid for the Soviet tests.

Seitz et al. (1968) estimated cloud tops and bases from measurements of the radioactive debris a few days after the 1961-1962 tests. Very few of the

Table 10. Estimates of approximate total yields (in megatons (Mt)) of high-yield^a atmospheric nuclear tests by year.

	COMESA (1975)	Foley and Ruderman (1973)	Johnston et al. (1976)	Seitz et al. (1968)	This work
Pre-1956	61.6	62	-	-	-
1956	26.0	26	-	-	20
1957	13.5	} 85	-	-	16
1958	61.9		-	-	58
1959	0	0	-	-	0
1960	0	0	-	-	0
1961	120.6	} 340	99.7	97	119
1962	213.5		204	206	216
1963	-	-	-	-	-
1964	-	-	-	-	-
1965	-	-	-	-	-
1966	1.4	-	-	-	-
1967	3.5	-	-	-	-
1968	7.6	-	-	-	-
1969	3.0	-	-	-	-
1970	6.1	-	-	-	-
Total 1961-62	334	340	304	303	335
Total 1956-62	435	451	-	-	429

^aTests having a yield of 1 Mt or greater (1 Mt = 4.2×10^{15} joules).

debris measurements extended above 24 km, and the cloud tops of most of the higher yield tests were not directly measured. When samples were taken near 30 km shortly after a high yield test, the cloud top was estimated to be above 30 km; however, when no data above 24 km were available, a cloud top near 24 km was assumed (Seitz et al. 1968). From an analysis of the ratio of ^{14}C to ^{90}Sr , Telegadas and List (1969) concluded that the very large Soviet test of October 1961 probably stabilized almost entirely above the region examined by Seitz et al.

The parameterization of Foley and Ruderman (1973), which we used in earlier reports (Chang and Duewer 1973, MacCracken and Chang 1975), may overestimate the height of stabilization since it is based almost exclusively on data from the tropics. However, the stabilization heights quoted by Seitz et al. may generally underestimate the stabilization altitude of the debris from Soviet tests. Figure 37 presents the stabilization estimates from the two different methodologies.

When we used the Foley and Ruderman (1973) parameterization, we assumed the injection to result in a uniform increase in concentration between

cloud top and cloud bottom. When we used Seitz et al.'s (1968) injection altitudes we assumed that it was appropriate to adjust the injection to a constant height above the tropopause corrected to mid-latitude conditions (Johnston et al. 1976). Thus, we increased CT and CB by 4 km for polar tests and reduced them by 2 km for tropical tests. We believe that these procedures provide approximate upper and lower bounds for the stabilization altitudes of the test debris. As we will show (Fig. 38 and Table 11), the computed ozone reductions in the peak year (1963) are larger by about 1-2% (of total O_3) when we use the Foley and Ruderman (1973) expression than when we use the Seitz et al. (1968) stabilization altitudes.

In all calculations the injection was assumed to be mixed throughout the northern hemisphere, and no further dilution was considered. Mixing into the southern hemisphere might have reduced the NO_x perturbation by 15-25% in 1963-64 (Johnston et al. 1976).

Johnston et al. (1973) analyzed the global ozone record for 1960-1970 and found a statistically insignificant decrease of 2.2% for 1960-1962 followed by a statistically significant increase of 3.7% for

Figure 37 Cloud top and base elevations vs yield. The curves defining the shaded area give the cloud top and base according to the parameterization of Foley and Ruderman (1973). The vertical bars extend from cloud base to top for the data cited by Seitz et al. (1968) after adjustment to height above a variable tropopause as discussed in the text. The number of tests for a particular yield at high latitudes (P) and low latitudes (T) is also given for the data of Seitz et al.

Figure 38. Calculated change in O_3 vs year, showing the effect of the treatment of cloud stabilization height. All calculations used the Chang (1976) K_z profile and diurnal averaging.

Table 11. Effects on ozone calculated for various model inputs.

Chemistry	K_z	Stabilization parameterization	Other variations	Calculated change in ozone, ΔO_3 (%)		
				$(\Delta O_3)_{max}$	$(\Delta O_3)_{1963}$	$(\Delta O_3)_{1964}$
1973	Chang (1974)	Foley and Ruderman	0.5×10^{21} molecules NO/Mt. Bates and Hays (1967) values for N_2O , multiple scattering not included	-5.0	-4.0	-3.3
1973	Chang (1974)	Foley and Ruderman	0.5×10^{21} NO/megaton	-4.8	-3.8	-3.1
1973	Hunten (1975)	Foley and Ruderman	0.5×10^{21} NO/megaton	-5.3	-4.5	-3.9
1974	Chang (1974)	Foley and Ruderman	-	-8.2	-7.1	-6.2
1974	Chang (1976)	Foley and Ruderman	-	-	-	-
1976	Chang (1976)	Foley and Ruderman	Diurnal averaging	-6.8	-4.5	-2.7
1976	Chang (1976)	Seitz et al.	Diurnal averaging	-5.1	-4.3	-2.6
1976	Chang (1976)	Foley and Ruderman	No diurnal averaging	-6.1	-4.2	-2.6
1976	Hunten (1975)	Foley and Ruderman	No diurnal averaging	-5.0	-3.9	-2.8
1976	Chang (1976)	Seitz et al.	No diurnal averaging	-4.3	-3.8	-2.5
1977	Chang (1976)	Foley and Ruderman	Diurnal averaging	-4.2	-3.0	-1.4
1977	Chang (1976)	Seitz et al.	Diurnal averaging	-1.9	-1.5	-0.8
1977	Hunten (1975)	Seitz et al.	Diurnal averaging	-1.8	-1.4	-0.7

1963–1970. They viewed this increase as consistent with recovery from an ozone depletion of "a few percent" induced by the nuclear tests. The same data have been analyzed by several other authors (Komhyr et al. 1971, Angell and Korshover 1973, 1976, Goldsmith et al. 1973, COMESA 1975, London and Kelley 1974). Most of these more recent analyses agree in finding the observations less consistent with a nuclear test series effect. Angell and Korshover (1976) note that apparent ozone minima occurred in 1960 and 1962, whereas the major nuclear tests occurred in the autumns of 1961 and 1962 so that any predicted depletions would be expected in 1962 and 1963. When the effects of the quasi-biennial ozone variations were allowed for, Angell and Korshover (1976) concluded that any ozone reductions caused by the nuclear test series must have been less than 1–2%; this is consistent with COMESA (1975), which concluded that any nuclear test series effects were not detectable in the ozone record. In our discussion we will accept Angell and Korshover's analysis with the reservation that if an effect is calculated to have a sufficiently long time constant, the gradual increase in ozone found during the middle and late 1960s (Johnston et al. 1973, Angell and Korshover 1973, 1976) might be consistent with a slightly larger perturbation.

The model chemistry used in our 1973 calculation contained 33 reactions of HO_x , NO_x , and O_x , with rate constants based primarily on Garvin and Gevantman (1972). These are given in Table A-1 of Appendix A as 1973 chemistry.

When the CIAP calculations were carried out (1974) we incorporated the 41 reactions listed as 1974 chemistry in Table A-1. Most rate constants were taken from Garvin and Hampson (1974).

Our 1976 chemistry (Table A-1) incorporated ClO_x reactions and was nearly the same as that used in the National Academy of Sciences CFM report (National Research Council 1976). Most of the rate constants were derived from Hampson and Garvin (1975), but several had been revised to reflect 1975 or 1976 measurements (National Research Council 1976, DeMore et al. 1977). Our 1977 chemistry (Table A-1 of Appendix A) contains the same reactions as our 1976 chemistry, but several rate constants have been adjusted to reflect recent evaluations (DeMore et al. 1977, Watson 1977) and measurements (Howard and Evenson 1977, Burrows et al. 1977, Chang and Kaufman 1976). As we will show, the predicted effect of the nuclear test series is quite sensitive to model chemistry. For this study the model contained about 1.3 ppb of ClO_x from CH_3Cl and CCl_4 , but chlorofluoromethanes were neglected.

The 1973 model (Chang and Duewer 1973) did not include rainout processes. All subsequent models included rainout losses below 8 km using rates of $2.31 \times 10^{-6} \text{ s}^{-1}$ for HNO_3 , HCl , and ClO (for models including chlorine chemistry) and 1.16×10^{-6} for NO_2 . The major effect of rainout is to uncouple surface boundary conditions for NO_x and Cl_x from stratospheric and upper tropospheric concentrations. Calculated stratospheric perturbations are not strongly sensitive to the precise rainout rates chosen.

The model uses fixed concentration boundary conditions at the surface (Chang et al. 1974). For versions incorporating rainout, the model stratosphere has significant sensitivity to the boundary conditions for only N_2O , CH_4 , CH_3Cl , and CCl_4 . The 1973 model was also influenced by the surface boundary conditions for NO , NO_2 , and HNO_3 , which produced a nearly uniform 3.7 ppb NO_x mixing ratio in the troposphere. In models treating rainout processes, the NO_x mixing ratio in the upper troposphere is dependent on K_z but is smaller than 0.1 ppb.

In our 1973 calculation, we neglected multiple scattering effects and diurnal variation of species concentrations, and we used then current values for the N_2O photodissociation cross sections (Bates and Hays 1967). In all of the current calculations we used Johnston and Selwyn (1975) photodissociation cross sections for N_2O . The 1974 and 1976 models approximated diurnal variations in solar flux by using one-half the noontime photodissociation rates. The chlorine nitrate formation rate was adjusted to be consistent with a fully diurnal calculation for the 1976 model. The 1977 model averages reaction rates at each level over a diurnal cycle (Chang et al. 1977). Limited calculations were made using the 1976 chemistry and diurnal averaging. The 1976 and 1977 models included multiple scattering effects (Luther et al. 1977b).

The response of the model is little affected by the change in N_2O absorption cross sections or multiple scattering (together they resulted in a 0.2% change in total ozone for a calculated maximum depletion of roughly 5% using the 1973 chemistry). The incorporation of diurnal averaging of reaction rates increased the ozone depletion for 1977 chemistry by about 0.5 to 1% of total ozone when the Seitz injection scheme was used (see Table 10).

We considered the effects of different K_z choices by performing calculations using the Chang (1974), Chang (1976), and Hunten (1975) K_z profiles. The Chang (1974) K_z profile was used in the earlier work by Chang and Duewer (1973). Only the recovery time had a strong sensitivity to K_z (see Fig. 39 and Table 10).

Figure 39 Calculated change in O_3 vs year for two K_z profiles. Upper curves use the 1977 chemistry and diurnal averaging. Lower curves use the 1976 chemistry without diurnal averaging.

Calculations were carried out using the Foley and Ruderman stabilization parameterization for 1973, 1974, 1976, and 1977 chemistries. The Chang (1976) K_z was used with the 1974, 1976, and 1977 chemistries, the Chang (1974) K_z was used with the 1973 and 1974 chemistries, and the Hunten (1975) K_z was used with the 1973, 1976, and 1977 chemistries. The Seitz et al. (1968) stabilization estimates were considered using 1976 and 1977 chemistries with the Chang (1976) K_z and 1977 chemistry with the Hunten (1975) K_z .

In the calculation of the nuclear test series effects, the total NO_x injection is determined by the device yield and is independent of K_z . Further, most of the injection occurred over a fairly short time; therefore, unlike SST calculations, ΔNO_x is nearly independent of K_z . As Fig. 39 and Table II show, for the cases considered, the ozone depletions in 1963-64 were weakly dependent on K_z . For pre-1977 model chemistries, there is a substantial difference in recovery time, based on the effective removal rate of excess stratospheric NO_x . For the 1977 model chemistry the apparent recovery time is initially determined by the rate of vertical redistribution of the injection, although at later times recovery is controlled by the rate of removal of excess NO_x from the stratosphere. In no case

would the choice of K_z alone cause the calculation to conflict with observation.

As shown in Fig. 38 and Table II, the procedure used to estimate the stabilization altitude has a significant effect on the calculation. However, for the model chemistries studied, the differences in the effects computed using these two stabilization estimates were less dramatic than the differences between model computations using different chemistries (Fig. 40).

The estimated stabilization heights for the polar tests remain a significant source of uncertainty in the calculations. For reasons discussed above, we find the published information ambiguous and somewhat unsatisfactory. The two methods of estimation used provide a probable upper and lower bound to the true stabilization heights, but the Foley and Ruderman parameterization should be the more nearly accurate of the two. Chang (1975) and Mahlman (1977) have discussed the information available from tracer calculations based on ^{14}C and ^{90}Sr . At present, we will note that these results further strengthen the need to accept the uncertainty in cloud stabilization heights as inherent uncertainties in such analyses.

The model representation of atmospheric chemistry has evolved substantially since early 1973.

Figure 40. Calculated change in O_3 vs year for three different chemistries. All calculations used the Foley and Ruderman (1973) stabilization parameterization.

and the effect of the most recent changes has been dramatic. With our 1977 chemistry, when the Seitz et al. (1968) stabilization height estimates are used, we compute ozone increases from the 1950s tests and less than 2% ozone reductions at all times. When the Foley and Ruderman (1973) stabilization height estimates are used, we compute ozone decreases for all years during the period of active atmospheric testing, and the reductions calculated for 1963 (3% annual average ozone reduction in the northern hemisphere) are still larger than is easily consistent with observation. However, the source term consists of pulse injections primarily at high latitudes, most of them in a period of about 4 months in late 1962. Thus, at least for the several months before horizontal mixing in the northern hemisphere should have been complete, the one-dimensional approximation is expected to be poor and to overestimate the ozone depletions (Bauer and Gilmore 1975). Therefore, it would appear that our current results may be comparable to the upper limit permitted by the observations. A two-dimensional model calculation of the weapons tests would be useful in this regard.

It should be noted that the problems related to high-latitude injection of NO_x are also present in calculations of the effects of SST flight since more than half of projected SST emissions occur north of 50° (Oliver et al. 1977). Thus, many of the potential sources of error introduced by the use of one-dimensional models in the calculation of the test series effects also exist for calculations of SSTs. Two- or three-dimensional calculations of both effects are to be desired, but present multidimensional models are relatively expensive to run, and the rapid evolution of model chemistry may act to discourage extensive calculations since further substantial evolution of model chemistry seems very likely. The major changes in model chemistry—the changes that most strongly affect model sensitivities—have been in the treatment of reactions that affect HO_x species or link NO_x to minor species other than odd oxygen, rather than in the major catalytic odd-oxygen destruction cycles involving NO_x (see also Duewer et al. 1977b). Because this secondary chemistry has such a strong effect on one-dimensional model sensitivity to NO_x injection, one must closely examine the representation of the

chemistry used in multidimensional models when interpreting their results.

The calculations reported here reflect current best estimates of many input parameters, some of which (especially reaction rate constants involving HO_2) are admittedly rather uncertain (DeMore 1977, Dwyer et al. 1977b). When new measurements become available, it is likely that some model inputs and model predictions will change. Nevertheless, our current model computes ozone reductions that are not incompatible with observations.

If one accepts the analysis of Angell and Korshover (1976), then any model that predicts a response to the nuclear weapons tests of the 1950s and 1960s significantly larger than 2% (northern hemisphere annual average) must be considered to be in error, and it would be necessary to understand this apparent conflict with observation before accepting other predictions of the model.

2.8 Effect of Agriculture on Stratospheric Ozone*

In a recent comprehensive review of the possible effect of man-made fertilizer on stratospheric ozone, Johnston (1977) deduced the following simple steady-state model for the percentage decrease in ozone, $-\Delta\text{O}_3$ (%), in terms of the increment in nitrogen fixation due to man, ΔN_F (Mt of N/yr)[†]:

$$-\Delta\text{O}_3 = \alpha\beta\gamma\tau\Delta\text{N}_\text{F}/\text{N}_2\text{O}_3 \quad (8-1)$$

The remaining variables are defined as follows:

- α = the fraction of denitrified nitrogen released to the atmosphere as N_2O ,
- β = the fraction of ΔN_F that will be denitrified within a few decades, i.e., immediately or after one or more passes through living organisms, as opposed to the fraction $1-\beta$ which will be transferred to long-lived (≥ 1000 yr) oceanic or lithospheric reservoirs of fixed nitrogen,
- γ = the ratio of the percentage decrease in the O_3 column to the percentage increase in stratospheric NO_x ($\text{NO} + \text{NO}_2$),
- τ = the tropospheric lifetime of N_2O in years,
- N_2O_3 = the unperturbed atmospheric burden of N_2O (Mt of N).

*See Ellsaesser (1977c).

[†] 1 Mt = 10^6 tonnes = 10^9 kg in this usage; not to be confused with the megaton of nuclear explosive yield, which is the equivalent of the explosive energy of a million tons of chemical high explosive.

The possible ranges of values given for these parameters by Johnston (1977) are listed in Table 12. Assuming $\beta = 1$ and $\Delta\text{N}_\text{F} = 100$ Mt/yr, Johnston (1977) deduced values of 0.2% to 50% for $-\Delta\text{O}_3$, suggesting the problem was "hopelessly amorphous." Establishing limits by personal judgment, he concluded that $-\Delta\text{O}_3$ due to a continuing ΔN_F of 100 Mt/yr lay between 1 and 10%, and that if the larger figure occurred it would take hundreds of years to build up to such a steady-state ozone reduction since this required a long (~ 100 -yr) tropospheric lifetime for N_2O .

Table 13 summarizes the decreases in ozone computed by stratospheric modelers and the corresponding values used for the parameters in Eq. (8-1).

All of these estimates, whether explicitly stated or not, were based on the following additional assumptions:

1. The rate of nitrogen fixation and denitrification and the N_2O budget of the atmosphere were and would remain in a fixed steady state in the absence of man's agricultural activities.

2. Man-made changes in the nitrogen cycle are limited to increases in the nitrogen fixation rate (i.e., to making $\Delta\text{N}_\text{F} > 0$).

3. Increases in N_F ($\Delta\text{N}_\text{F} > 0$) will have no effect on the remaining parameters α , β , γ , and τ .

The available observational data tend to support the conclusion of Crutzen and Ehhalt (1977): "for millions of years the rate of denitrification must, therefore, on the average, have equalled the rate of nitrogen fixation on earth." But this leaves unconsidered man-made effects on the biosphere other than increased nitrogen fixation plus secondary changes in α , β , γ , and/or τ which may result from any disturbance of the equilibrium or steady-state natural nitrogen cycle.

Table 12. Possible ranges of parameter values as given by Johnston (1977).

Parameter	Possible range of values
α	0.025-0.1 (land) 0-1 (ocean) 0.025-0.4 (global)
β	0.01-0.75, probable average 0.1-0.15
γ	1/5 (modification to 1/3 or 1/8 considered possible)
τ	5-160 yr
N_2O_3	1300 Mt N
ΔN_F	160-650 Mt N/yr

Table 13. Summary of computed decreases in O_3 due to use of nitrogen fertilizer and values of relevant parameters used.

Computed decrease in O_3 , $-\Delta O_3$ (%)	Reference	Parameter			
		α	β	τ	ΔN_F (Mt)
19	Vupputuri (1974)	(Doubled N_2O_5)			
20 (by 2025)	McElroy (1974, 1975, 1976)	0.08	1	20	200
20 (by 2025)	McElroy et al. (1976)	0.23	1	20	200
8 (by 2100) 14 steady state	Crutzen (1975)	0.04	1	100–160	200
1.7	Crutzen (1976)	0.07	1	10	200
4.3		0.2	1	10	200
9.5		0.5	1	10	200
6.7		0.2	1	20	200
1 (by 2025) 4 (by 2050)	Liu et al. (1976)	?	1	20	40 in 1974, +6%/yr
1.6	Sze and Rice (1976)	0.26	0.1	20	200
5		0.26	0.25 (0.35 after 2000)	20	200
9		0.26	0.6	20	200
6	NRC (1976)	(Doubled N_2O_5)			
1–15 (200 yr for maximum)	Crutzen and Ehhalt (1977)	0.05–0.2	0.33	10–160	40–200

Johnston (1977) reported that the environmental conditions favoring denitrification were:

1. Saturation of soils with water.
2. Absence of oxygen.
3. Availability of organic matter for microbial consumption.

While not clarified by Johnston (1977), it appears likely that these factors favoring denitrification will lead to a larger β since a larger portion of N_F will presumably be denitrified before it has a chance to move into a long-lived reservoir, and vice versa. The environmental conditions favoring a large α were given by Johnston (1977) as:

1. Low temperature.
2. Low pH.
3. Marginal anaerobic conditions.

All three of these conditions were also cited as leading "to a low rate of denitrification." While also not addressed by Johnston (1977), it nevertheless appears likely that the latter effect may predominate, leading to a lower rate of N_2O production. That is, if the fraction $1 - \beta$ of N_F moving into long-lived oceanic and lithospheric reservoirs de-

pends on the length of time N_F remains in the soil, then these factors favoring a large α by slowing denitrification might also lead to a smaller β and to no change or even a decrease in the product, $\alpha\beta$, or fraction of ΔN_F (or $N_F + \Delta N_F$) converted to N_2O within the "short" recycle time of a few decades. According to McElroy (1976), "denitrification can take place to a significant extent only in media with pH larger than about 5.5."

While little quantitative information is available, it is well known that man, since taking up agriculture, has induced large-scale changes on the biosphere other than those resulting from the application of fertilizer. These include:

1. Increasing soil oxygen by: (a) loosening and turning the soil to produce increased aeration, (b) treatments to improve porosity and drainage, (c) reducing competitive oxygen demand from root growth through spacing of monocultured plants, elimination of competing plants or weeds, and fallowing.
2. Reducing oxygen-excluding soil moisture by: (a) increasing runoff through removal of plant

cover. (b) reducing water-retaining topsoil and humus through erosion and oxidation and non-return of plant debris. (c) measures to improve percolation and/or drainage wherever water stagnation restricts plant growth.

3. Reducing the volume of organic material or culture medium for soil bacteria as indicated in 2(b) above.

4. Increasing soil pH by: (a) loss of humus which is rich in organic acids. (b) accumulation of alkali metals through salination in most areas placed under irrigation. (c) deliberate use of lime, etc.

5. Decreasing the natural equilibrium level of N_F in the biosphere through clearing of forests and shrubs and actions in 2(b) above. For example, Soderland and Svensson (1976) estimated global soil nitrogen losses due to agricultural activities at 6,000–13,000 Mt N. (This should be compared with the estimates for N_F , or total global annual fixation rates, of 160–650 Mt N/yr (Johnston 1977) and 230–400 Mt N/yr (Crutzen and Ehhalt 1977).)

Initial appraisals of each of these anthropogenic effects suggest that, except for the increase in pH, each should have tended to decrease the rate at which N_2O is produced. Increased oxygenation, decreased organic material, and reduced water saturation all appear to operate directly to reduce the rate of denitrification and thus would appear to allow the fixed nitrogen more time to find its way into the long-lived oceanic and lithospheric reservoirs, thereby decreasing β . In addition, except insofar as they tend to increase "marginal anaerobic conditions," each of these would have tended to reduce α . Reducing the biospheric store of fixed nitrogen would not disturb any of the quantities in Johnston's (1977) simple model but would disturb the assumed steady state on which it is based. That is, the natural rate of production of N_2O can hardly remain unchanged if the accumulated fixed nitrogen in the biosphere from which it is formed is suddenly reduced. If the fixed nitrogen lost during the early years of cultivation were denitrified with no change in the preexisting steady-state product, $\alpha\beta$, then it should have caused a temporary increase in the rate of N_2O production before the decrease set in. However, it appears more likely that most of this fixed nitrogen entered the long-lived oceanic and lithospheric reservoirs and that nearly all of it (rather than the normal $1 - \beta$ fraction of it) will undergo the long-term (≥ 1000 yr) cycle of denitrification as opposed to the short-term (few decades) cycle. As indicated below, the effect of any significant increase in pH is less clear.

Another point which appears to have been overlooked in previous analyses of this problem is

the manner and locale in which man's additions of fixed nitrogen to the biosphere are made. Fertilizer is added almost exclusively to well-drained and well-aerated soils, i.e., to those which do not provide the anaerobic conditions required for denitrification until the nitrogen has moved deep enough to be below the humus or organic material which denitrifying bacteria require as a culture medium. Further, mass applications of fixed nitrogen tend to be in the reduced rather than the oxidized state. While reduced nitrogen will generally be readily oxidized by nitrifying bacteria in the soil, the fact of its being oxidized indicates soil conditions which are aerobic rather than anaerobic and thus unfavorable for denitrification, at least at that specific location and time. This suggests that most of man's additions of fixed nitrogen to the soil will be taken up by plants or move into the long-lived oceanic and lithospheric reservoirs. That portion taken up by plants may be returned to the soil, burned, or wind up as sewer sludge, feedlot manure, and/or landfill. All of these would appear to lead to lower than the natural values of the product, $\alpha\beta$. Detailed quantitative analyses will be required to reach a firm conclusion as to whether the fraction converted to N_2O is greater or less than the product $\alpha\beta$ for the assumed preindustrial steady state. Initial indications are that it is somewhat less and that, until the long-lived oceanic and lithospheric reservoirs are brought into a new equilibrium, man's effect on N_2O production will be such as to cause a decrease.

Other factors have been raised which bear on this problem, but they appear to be minor (as yet) compared with those considered above. Man is also contributing to nitrogen fixation through combustion (20 Mt N/yr), ammonia production (17 Mt N/yr), and direct output of N_2O by coal combustion (now estimated at 2.2 Mt N/yr) and auto exhaust; these latter two may become important in the future (Crutzen and Ehhalt 1977). McElroy (1976) has suggested that man's injection of sulfur and nitrogen compounds (air pollution) into the atmosphere is causing a decrease in the pH of precipitation, which in turn will cause a decrease in the environmental pH of denitrifying bacteria and thus an increase in α and N_2O production. As of now this can be considered no more than interesting speculation. Decreases in the pH of precipitation have been reported in only restricted areas of the globe, and past data for establishing trends in these areas are fragmentary at best. Soil scientists have measured pH profiles in the solums of many soils. In the podzols typical of timbered regions such as New England and Scandinavia where increasing

acidity of precipitation has been claimed, measured pH values range from 3.1 to 5.5 (Bailey 1945). The low pH's, the date of observation (1923-1935), and the fact that pH not uncommonly decreased with depth suggest that soil acidity is being controlled by factors other than the pH of precipitation. Even more critical is the fact that low pH reduces the overall rate of denitrification at the same time as it increases α . Note that all of the pH's for podzols reported by Bailey (1945) were at and below the 5.5 cutoff at which denitrification becomes insignificant according to McElroy (1976) and thus presumably unresponsive to further decrease in pH.

This admittedly qualitative analysis suggests that man's modifications of spaceship Earth may have already led to a decrease in the production of N_2O , and that this decrease, if real, is likely to continue at least until man's contributions of fixed nitrogen to the long-term oceanic and lithospheric reservoirs lead to a new global equilibrium between nitrogen fixation and denitrification. At present we have almost no information on which to estimate the rate of N_2O production that will occur when the new equilibrium is established.

Our current understanding of the chemistry of the O_3 layer suggests that any decrease in N_2O production should be followed within a few years by an increase in the depth of the O_3 layer. This should result from a decline in N_2O_x , the atmospheric burden and concentration of N_2O , causing a decrease in the rate of transport of N_2O to the stratosphere where a small fraction of it (1-5%) is oxidized to NO , a catalytic destroyer of O_3 . The recent faster rate determined by Howard and Evenson (1977) for the $NO + HO_2$ reaction is not expected to change this picture qualitatively but will, presumably, reduce γ of Eq. (8-1).

Available data on the trend in tropospheric concentrations of N_2O are very confusing (Pierotti and Rasmussen 1976, Johnston 1977, Crutzen and Ehrlert 1977) and are of little help in resolving this question at present. They suggest abrupt increases in N_2O between 1967 and 1968 and again in recent years. However, the differences in N_2O concentrations indicated by the different sets of measurements are mainly such as to cast doubt upon the accuracy of the measurements themselves. Total ozone measurements are a bit more encouraging. They suggest, if anything, an increase in total ozone since measurements were first made in the early 1920s and particularly since the significant increase in the number of observing stations which began about 1955 (Christie 1973, London and Kelley 1974, Angell and Korshover 1973, 1976).

2.9 Global Tropospheric OH Distributions *

The research for this study was first carried out using 1976 chemistry. There have subsequently been new measurements of some of the chemical rates important to tropospheric OH (see Section 2.10 for further details). Since we expect these changes to have a potentially significant effect on the magnitude and latitudinal variation of the theoretically derived OH concentrations, we are in the process of rederiving the global OH distribution. However, we do not expect the changes to have a large enough impact on the results to invalidate the qualitative features of the global OH distributions. The effect of changes in various parameters on model sensitivity is discussed later in this section under the heading "New 1-D Model Results." The methodology of the derivation as described will not be affected by these changes in model chemistry.

Global OH Distribution

The importance of the hydroxyl free radical in tropospheric photochemistry has been suggested by numerous authors (Levy 1971, Crutzen 1974, Warneck 1974, 1975, Wofsy 1976, and Davis and Klauber 1975). Among the important trace gases whose chemistry is now believed to be influenced by the hydroxyl species are carbon monoxide, methane, sulfur dioxide, nitrogen dioxide, hydrogen sulfide, and a wide variety of higher-molecular-weight hydrocarbons. On the global scale, assignment of the role of OH in defining trace gas chemistry is predicated on knowing the variability of the OH radical as a function of season, altitude, latitude, and time of day. The variability in the concentration of the OH radical is in large part a result of the nature of the formation process, i.e.,

Important loss processes include its reaction with both CO and CH_4 . For a complete listing of the key reactions used in the following model calculations see the 1976 chemistry shown in Table A-1 of Appendix A.

Assuming the hydroxyl radical has a short tropospheric chemical lifetime, we expect that the

*See Chang, Wuebbles, and Davis (1977).

tropospheric OH concentration is highly variable and is almost totally controlled by local variables such as H_2O , O_3 , CO , CH_4 , $\text{O}(^1\text{D})$, solar radiation, temperature, and others. Consequently, an accurate determination of tropospheric OH concentrations will require the detailed modeling of both tropospheric chemistry and dynamics. An alternative to this would be the utilization of many of the currently available measurements which are determined by real tropospheric dynamic transport. Insofar as the hydroxyl radicals are always in kinetic equilibrium with the governing variables listed above, and these variables are in turn based on observation, we suggest that the quasi-equilibrium hydroxyl radical concentrations represent a reasonable approximation to physical reality.

If the global distribution of species important to OH are known, then a series of local quasi-equilibrium calculations can be used to determine a global representation of the OH distribution. The model can thus account for the effect of dynamic transport through the specific concentrations of the important species at all latitudes. Vertical profiles of temperature, water vapor, carbon monoxide, ozone, and methane were specified in the model, and were varied with latitude and season according to available measurements. The temperature and water-vapor data are from Louis (1974) and Oort and Rasmussen (1971), respectively. The global CO distributions are those of Seiler (1974). The ozone latitudinal and altitudinal global distributions are from Dötsch (1969), and the surface concentrations of O_3 are assumed fixed at the values of Pruchniewicz (1973). The vertical CH_4 distribution is that reported by Ehhalt (1974).

To demonstrate the validity of the quasi-equilibrium approach, typical calculated lifetimes for OH and HO_x ($\text{OH} + \text{HO}_2 + \text{H}_2\text{O}_2$) are shown in Table 14 as a function of altitude, latitude, and season. For OH, the longest lifetime shown is 6.0 seconds, which occurs during the winter at 30°S and

10 km altitude. It should be noted, however, that near 0° latitude at 10 km, the lifetime is approximately 4–5 seconds. The small change in lifetime with latitude primarily reflects the change in CO concentration. Substantial change in lifetime would not be expected at still higher latitudes in the winter southern hemisphere where OH concentrations are decreasing rapidly (Fig. 41). The lifetime of HO_x is shown to fall in the range $1\text{--}8 \times 10^4$ seconds. These lifetimes, although considerably longer than that for OH, are still quite short when compared to those for meridional and vertical transport.

The calculation procedure used in this study was a modified version of a one-dimensional time-dependent model using the above-mentioned fixed variables. The model normally calculates the concentrations of 15 different trace species. While a number of these had fixed concentrations in this study, others important to the OH distribution have not been measured in sufficient detail. Their concentrations were calculated within the model, utilizing the variations in solar zenith angle, temperature, and concentrations of specified species to determine their distributions. Species such as N_2O , NO , NO_2 , HNO_3 , and H_2O_2 have fixed concentrations at the surface, which basically define their tropospheric profiles. These fixed boundary conditions were not varied with latitude and season in the calculations. Heterogeneous removal processes for NO_2 , HNO_3 , and H_2O_2 were included in the model by assuming a constant decay rate below 8 km with an assumed lifetime of 10 days for NO_2 and 5 days for HNO_3 and H_2O_2 . Reaction rates in the model were based on the evaluated rates as given in Hampson and Garvin (1975). Also, the chain of reactions resulting from the oxidation of methane is likely to result in the production of several HO_x molecules (Crutzen and Isaksen 1975). However, the reaction mechanism is still not fully established and needs further analysis. We have assumed in this study that each CH_3 molecule produced from CH_4 results in

Table 14. Some estimated tropospheric chemical lifetimes for HO_x ($\text{HO}_2 + \text{H}_2\text{O}_2 + \text{OH}$) and OH.

Species	Altitude (km)	Lifetime (seconds) at latitude of:		
		30°N (summer)	0°	30°S (winter)
HO_x	1	1.5×10^4	1.5×10^4	3.7×10^4
	5	3.3×10^4	3.6×10^4	6.9×10^4
	10	4.8×10^4	4.7×10^4	7.6×10^4
OH	1	1.0	1.3	3.7
	5	1.7	2.2	3.5
	10	4.6	4.7	6.0

Figure 41. Calculated global variations in tropospheric OH concentrations. Values are at local noon. heavy lines represent average tropopause altitude.

the formation of two HO_2 molecules. We have based this on the examination of a 16-step mechanism for methane oxidation. However, because of uncertainties in reaction rates, it is still not clear exactly how many HO_2 molecules result from this series of reactions.

Model sensitivity to the fixed surface concentrations of some of the less well measured species has been studied. Surface concentrations of NO_2 and NO are important in this study because of their central role in determining the OH concentration through the reactions

The relative loss rate of HO_2 through reaction (9-2) and the reaction $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ determines the effectiveness of CO as a net sink for OH through the cycle

With high NO concentration, reaction (9-3) no longer represents a major sink for OH radicals. In our calculations, we used fixed surface concentrations of 0.4 ppb for NO_2 and 0.17 ppb for NO . These concentrations were low enough that our results for OH were not very sensitive to further decreases in concentration. For example, decreasing NO and NO_2 by a factor of 20 resulted in less than a 3% change in OH concentrations. However, larger surface concentrations for NO and NO_2 would increase the sensitivity sharply. For example, increasing the NO and NO_2 concentrations by a factor of 5 (to 2.0 ppb for NO_2) resulted in approximately a 40% increase in tropospheric OH concentrations. This clearly points to the need for better NO_x measurements in the troposphere. Furthermore, insofar as the local NO_x concentration is also dependent upon the heterogeneous removal rates of HNO_3 and NO_2 , a careful quantification of global rainout would be desirable. We have also noted a high level of model sensitivity to the lower boundary condition of H_2O_2 , and this is being studied in greater detail. We would recommend strongly some measurement of tropospheric H_2O_2 in the near future.

Vertical OH distributions corresponding to local noon were computed for every ten degrees of latitude from 70°N to 70°S for the summer and winter seasons, and the results are shown in Fig. 41. The highest OH concentrations occurred in regions of high solar insolation where $\text{O}(^1\text{D})$ concentrations are highest. The lack of symmetry between the northern and southern hemispheres for the same season (Fig. 41) occurs because of the differences in CO concentrations between hemispheres (approximately a factor of 3 more CO in the northern hemisphere according to Seiler (1974)).

In order to compare these results with the autumn noon measurements of Davis et al. (1976), we averaged the summer and winter values. The resulting OH distribution is in good agreement with the available measured values. For 7 km at 32°N , Davis et al. found $(3.5 \pm 2.3) \times 10^6$ molecules/ cm^3 , whereas the model result was 3.2

$\times 10^6$. For 7 km and 11.5 km at 21°N, the observed values were respectively $(9.1 \pm 3.2) \times 10^6$ and $(4.9 \pm 2.0) \times 10^6$, whereas the model results were 4.2×10^6 and 3.2×10^6 . The concentrations corresponding to local noon in Fig. 41 were then utilized as the initial condition in a diurnal calculation of the OH distribution. Examples of the diurnal results are shown in Fig. 42. In general, OH concentrations reach a peak at local noon, when $O(^1D)$ concentration is highest, and rapidly decrease at sunset due to loss mechanisms that continue while production mechanisms have stopped.

Figure 42 Examples of the time and spatial variations in the diurnal OH distribution.

A diurnal averaging factor, α , was determined for each of the calculated diurnal variations by calculating the average 24-hour OH concentration relative to the noon value. Generally our averaging factor is somewhat larger than the value given by Warneck (1975). We believe this is due to the fact that Warneck obtained the scaling factor through averaging the photolysis rate of O_3 in forming $O(^1D)$ while ours is a direct result taking into account the diurnal variations of other trace species such as NO , NO_2 , HO_2 , etc. Values of α ranging from 0.22 to 0.50 were found depending on season and latitude, with a small dependence on altitude. Multiplying α times the noon OH concentrations gives the diurnally averaged concentrations shown in Fig. 43. Since smaller values of α occur in summer equatorial regions than in the polar regions, the diurnal-averaged distribution tends to be more uniform spatially than the distribution of local noon values.

The OH distribution averaged diurnally and seasonally is shown in Fig. 44. Approximately 75% of the tropospheric OH is contained in the band 30°S–30°N, although this band comprises only half of the global area. Therefore, a majority of the tropospheric OH will be found, in a seasonal- and diurnal-averaged sense, within the equatorial region; 97% of it is contained between 60°S and 60°N. Integrating the diurnal- and seasonal-averaged concentrations of OH in Fig. 44 results in a tropospheric average OH concentration of 1.68×10^6 molecules/cm³.

It is also interesting to note the clear presence of the tropopause in these results (Figs. 41, 43, and 44). This is expected in that the initial data such as temperature, water vapor, ozone, and carbon monoxide all exhibit distinct transitions between the troposphere and stratosphere. The preservation of such transition regions in the computed OH distribution is indirect evidence on the meaningfulness of this modeling procedure.

New 1-D Model Results

Recent remeasurements of the reaction rates for $NO + HO_2$ and $OH + CO$ (a large pressure dependence was noted) have led to significant changes in the model chemistry. The net result of these model changes is that the tropospheric average OH concentration computed with our one-dimensional model is now 1.28×10^6 molecules/cm³ as compared to the previous value of 1.7×10^6 molecules/cm³. Table 15 shows the sensitivity of the tropospheric average OH to changes in various parameters within the one-dimensional model. Note that the sensitivity to NO and NO_2 is much greater

Figure 43 Calculated diurnally averaged global OH distribution. Heavy lines represent average tropopause altitude.

than that found previously. The present values from the one-dimensional model compare very closely to those found at midlatitudes in the global distribution derivation. Therefore, although the latitudinal

Figure 44 Seasonally and diurnally averaged global OH distribution. Heavy lines represent average tropopause altitude.

distribution would be affected, a recalculation of the global OH distribution should not result in large differences in average tropospheric OH from the previous assessment.

Utilizing observational data for the key parameters to determine tropospheric OH, we have calculated a global distribution that agrees well with the available but limited measured data. We have also identified some of the major uncertainties in the determination of global OH distribution, such as the lack of measurements of H_2O_2 and HO_2 , the lack of global tropospheric data on NO_x , and the uncertainty in the production mechanisms of HO_x from hydrocarbons. In addition, it should be noted that neglected processes such as a net source or sink of HO_x from nonmethane hydrocarbons may play an important role in the determination of a global

Table 15. Sensitivity of calculated average tropospheric OH to changes in various parameters within the one-dimensional model.

Case	Average OH calculated (molecules/cm ³)
Ambient atmosphere	1.28×10^6
Change NO_x boundary conditions—less NO_x (NO from 0.1 to 0.067 ppb, NO_2 from 0.25 to 0.1 ppb)	1.05×10^6
Change NO_x boundary conditions—more NO_x (NO to 0.17 ppb, NO_2 to 0.4 ppb)	1.5×10^6
$\text{HO}_2 + \text{NO}$ rate = 6×10^{-13} rather than 8×10^{-12}	0.4×10^6
Pressure dependence of $\text{CO} + \text{OH}$ not included	1.9×10^6
Methane cycle produces 1 HO_2 rather than 2 HO_2	1.1×10^6
H_2O_2 photolysis cutoff at 254 nm rather than 315 nm	0.7×10^6

tropospheric OH distribution. Because of the emerging importance of OH in the tropospheric chemical cycles and the continuing improvements in both the laboratory kinetics data and atmospheric measurements, more detailed analyses of its temporal and spatial distribution will be required in the future.

2.10 Alternate Halocarbons: Tropospheric Lifetimes and Potential Effects on Stratospheric Ozone

Recent concern over possible regulations on the use of the halocarbons CFCl_3 and CF_2Cl_2 , because of their potential impact on stratospheric ozone (National Research Council 1976, Hudson 1977), has prompted consideration of potential replacement compounds. The prime reason for the accumulation of CFCl_3 and CF_2Cl_2 in the troposphere and eventually the stratosphere is their inertness. Consequently, in seeking alternate halocarbons, we consider it a desirable characteristic that they be degraded in the troposphere. For many of the potential substitutes, reaction with OH radicals appears to be the principal mode of degradation in the troposphere. Given a tropospheric distribution of OH, we can estimate the tropospheric chemical lifetimes.

The tropospheric chemical lifetime τ for the reaction $\text{OH} + \text{X}$ with reaction rate K can be specified by

$$\frac{1}{\tau} = \frac{\int_V K[\text{X}][\text{OH}] dV}{\int_V [\text{X}] dV}$$

where $[]$ is concentration and V is volume, indicating integration over the whole troposphere. If we assume that the species X is uniformly mixed in the troposphere, then

$$\frac{1}{\tau} = \frac{\int_V K[\text{OH}] \rho dV}{\int_V \rho dV}$$

where ρ is air density.

Assuming that the reaction with OH is the rate-determining step for the overall degradation

process, we have determined tropospheric residence times for a number of halocarbons, both natural and man-made, and these are shown in Table 16. All photochemical and kinetic evidence available indicate that both of the above assumptions are justified. These tropospheric chemical lifetimes were calculated with the diurnally and seasonally averaged OH distribution in Fig. 44. The predicted lifetime of methyl chloride, CH_3Cl , of 0.4 year is short enough that seasonal variations of this important halocarbon (~ 0.7 ppb in the troposphere, Davis (1976)) may be expected. Most of the calculated tropospheric lifetimes are very short (≤ 1 yr) and are unlikely to result in large concentrations of these compounds reaching the stratosphere. However, the long lifetimes of CF_2ClH (4.6 yr) and $\text{CH}_3\text{CF}_2\text{Cl}$ (7.1 yr), although much shorter than the lifetimes for CFCl_3 and CF_2Cl_2 , will require further analysis to determine their possible stratospheric impact.

To see how the calculated lifetimes relate to the predicted effect these halocarbons might have on stratospheric ozone, we have used the LLL one-dimensional transport-kinetics model to analyze the steady-state vertical distribution of several of these halocarbons assuming a production rate of 500,000 tonnes/yr. Table 17 shows the reaction rate assumed for each of the halocarbons reacting with OH. Temperature dependences were assigned to the rate coefficients for $\text{CF}_3\text{CH}_2\text{Cl}$, $\text{CF}_3\text{CH}_2\text{H}$, and CF_3CFCIH on the basis of a comparison with the reaction rates of similar reactions as measured by Davis (1976).

Figure 45 shows the absorption cross sections used for the five halocarbons tested. These cross

Figure 45. Absorption cross sections used for the five halocarbons tested.

Table 16 Estimated tropospheric chemical lifetimes (τ) of halocarbons.^a

Species	Designation	τ (yr)	Rate data
CH ₃ Cl	—	0.4	Davis (1976) ^b
CH ₂ Cl ₂	—	0.2	Davis (1976) ^b
CCl ₃ H	—	0.2	Davis (1976) ^b
CH ₃ Br	—	0.5	Davis (1976) ^b
C ₂ Cl ₄	—	0.2	Davis (1976) ^b
CH ₃ CCl ₃	FC-31	1.4	Howard and Evenson (1976) ^c
CH ₂ ClF	FC-31	1.5	Davis (1976)
CF ₃ Cl ₂ H	FC-123	0.6	Howard and Evenson (1976)
CCl ₂ FH	FC-21	0.6	Howard and Evenson (1976)
CCl ₂ FH	FC-21	0.7	Davis (1976)
CF ₃ CFCuH	FC-124	1.3	Howard and Evenson (1976)
CF ₃ CH ₂ Cl	FC-133a	1.5	Howard and Evenson (1976)
CF ₂ ClH	FC-22	4.5	Howard and Evenson (1976)
CF ₂ ClH	FC-22	4.6	Davis (1976)
CF ₂ ClCH ₃	FC-142b	5.4	Howard and Evenson (1976)
CF ₂ ClCH ₃	FC-142b	7.1	Davis (1976)

^aThese lifetimes are based on the 2-D OH distribution computed in Section 2.9.^bTemperature-dependent rate data.^cRoom-temperature measurements.

Table 17. The reaction rates of halocarbons with OH assumed in investigating the effects of the calculated halocarbon lifetimes (Table 16) on the predictions of stratospheric ozone (see Table 18).

Reaction	Rate coefficient	Source
CF ₃ CH ₂ Cl + OH	$5.9 \times 10^{-13} \exp(-1200/T)$	Based on Howard and Evenson (1976)
CF ₃ Cl ₂ H + OH	$1.24 \times 10^{-12} \exp(-1056/T)$	Based on Howard and Evenson (1976)
CF ₂ ClH + OH	$9.5 \times 10^{-13} \exp(-1577/T)$	Davis (1976)
CF ₃ CFCuH + OH	$5.25 \times 10^{-13} \exp(-1191/T)$	Based on Howard and Evenson (1976)
CF ₂ ClCH ₃ + OH	$1.14 \times 10^{-12} \exp(-1750/T)$	Davis (1976)

sections are based on unpublished data by Witt and Silver (private communication, 1977). All chlorine atoms in a molecule were assumed to be released when it reacted.

The change in total ozone computed at steady state is shown in Table 18 for each of the halocarbons. The predicted change in total ozone

was small for all of the halocarbons tested, ranging from -0.13% for CF₃Cl₂H to -0.40% for CF₂ClCH₃. These are to be contrasted to the -9.3% change in total ozone predicted for CF₂Cl₂ assuming the same production rate to steady state of 500,000 tonnes/yr. As shown in Table 18, changing the boundary conditions for NO and NO₂

Table 18. Calculated change in total ozone due to a steady-state release of halocarbons at a rate of 500,000 tonnes yr. Results are given for two different average tropospheric OH concentrations.

Species	Change in total ozone (%) assuming:	
	OH = $1.28 \times 10^6 \text{ cm}^{-3}$	OH = $1.05 \times 10^6 \text{ cm}^{-3}$
CF ₃ CH ₂ Cl (FC-133a)	-0.19	-0.21
CF ₃ Cl ₂ H (FC-123)	-0.13	-0.14
CF ₂ ClH (FC-22)	-0.36	-0.40
CF ₃ CFCIH (FC-124)	-0.17	-0.18
CF ₂ ClCH ₃ (FC-142b)	-0.40	-0.43

Figure 46. Calculated loss rate with altitude for CF₃CH₂Cl (FC-133). Both photochemical (*J*) and two-molecule chemical-kinetics (*k*) reactions are plotted.

Figure 48. Calculated loss rate with altitude for CF₂ClH (FC-22).

Figure 47. Calculated loss rate with altitude for CF₃Cl₂H (FC-123).

Figure 49. Calculated loss rate with altitude for CF₃CFCIH (FC-124).

Figure 50 Calculated loss rate with altitude for CF_2ClCH_3 (FC-142b).

(see Table 15) so as to reduce the average tropospheric OH to 1.05×10^6 molecules/cm³ has very little effect on the predicted ozone perturbation.

Figures 46–50 show the calculated loss rates versus altitude for each of the halocarbons. In each case, most of the loss occurs in the troposphere or lower stratosphere where very little of the released chlorine is capable of reaching altitudes important to the chlorine-ozone catalytic cycle. On the other hand, most of the CF_2Cl_2 is destroyed in the upper stratosphere, with very little being destroyed in the troposphere or lower stratosphere.

2.11 Analysis of Global Budgets of Halocarbons

A two-box model provides a framework within which one may examine the consistency of atmospheric data concerning the abundance and hemispheric ratio of man-made halocarbons and their release rate data. The continuity equations that constitute the model relate the hemispheric abundances (north and south) to the anthropogenic release rates, the chemical removal rates, and the interhemispheric transport time. Given the usually representative exponentially increasing release rates, the solutions of the two-box model are no more complicated than those of the simple one-box model, but they add considerable insight into the adequacy and deficiencies of these simple analysis

techniques. By accounting for the two hemispheric abundances separately, it is possible to check the internal consistency of hemispheric data and global averages.

The continuity equations for the abundance of a given trace species in each hemisphere may be written

$$\frac{dM_N}{dt} = S_N - \frac{1}{\tau_N} M_N - \frac{1}{\tau_T} (M_N - M_S) \quad (11-1)$$

$$\frac{dM_S}{dt} = S_S - \frac{1}{\tau_S} M_S + \frac{1}{\tau_T} (M_N - M_S) \quad (11-2)$$

where

M_N, M_S = the total hemispheric abundances (north and south),

S_N, S_S = the hemispheric release rates,

τ_N, τ_S = the chemical removal rates,

τ_T = the interhemispheric mixing time.

Following the pattern of historical release data, the release rate in the northern hemisphere is taken to be equal to a simple exponential function,

$$S_N = ae^{bt} \quad (11-3)$$

and the southern hemispheric release rate is assumed to equal zero. The solutions for (11-1) and (11-2) are

$$M_N(t) = \alpha_0 e^{bt} + \alpha_1 \exp(-\lambda_1 t) + \alpha_2 \exp(-\lambda_2 t) \quad (11-4)$$

$$M_S(t) = \beta_0 e^{bt} + \beta_1 \exp(-\lambda_1 t) + \beta_2 \exp(-\lambda_2 t) \quad (11-5)$$

where

$$\alpha_0 = \frac{a\tau_T(1 + b\tau_T + \tau_T/\tau_S)}{(1 + b\tau_T + \tau_T/\tau_S)(1 + b\tau_T + \tau_T/\tau_N) - 1}$$

$$\alpha_1 = -\alpha_0 - \alpha_2$$

$$\alpha_2 = \frac{\alpha_0(1/\tau_N + 1/\tau_T - \lambda_1) - \beta_0/\tau_T}{\lambda_1 - \lambda_2}$$

$$\beta_0 = \frac{a\tau_T}{(1 + b\tau_T + \tau_T/\tau_S)(1 + b\tau_T + \tau_T/\tau_N) - 1}$$

$$\beta_1 = \alpha_1 \tau_T (1/\tau_N + 1/\tau_T - \lambda_1)$$

$$\beta_2 = \alpha_2 \tau_T (1/\tau_N + 1/\tau_T - \lambda_2)$$

$$\lambda_{1,2} = \frac{1}{2} \left[(1/\tau_S + 1/\tau_N + 2/\tau_T) \pm \left[(1/\tau_N - 1/\tau_S)^2 + 4/\tau_T^2 \right]^{1/2} \right] \quad (11-6)$$

and we have assumed $M_N = M_S = 0$ at $t = 0$. A similar solution may be found for the case in which S_N varies exponentially, as in (11-3), with different rates, b , over different time periods.

The total cumulative amount of gas released into the atmosphere at any given time t is

$$M_T = \frac{a}{b} (e^{bt} - 1) \quad (11-7)$$

For sufficiently long times ($bt \gg 1$), the ratio of the total atmospheric abundance, $M = M_S + M_N$, to the total released is approximately constant.

$$\frac{M}{M_T} = \frac{b\tau_S}{1 + b\tau_S - \frac{1}{1+R} (1 - \tau_S/\tau_N)} \quad (11-8)$$

where R is the hemispheric ratio of abundances, M_S/M_N . This formula reduces to the formula derived for the one-box model in the case $\tau_S = \tau_N$ (compare Singh 1977). To the same order of approximation, the ratio R is further related to the parameters τ_S and τ_T according to

$$R = \frac{M_S}{M_N} = \frac{1}{1 + b\tau_T + \tau_T/\tau_S} \quad (11-9)$$

from which τ_T may be easily deduced from a knowledge of the hemispheric abundance ratio for a gas with a fairly long lifetime (see next subsection). For our further discussion we introduce the

northern hemispheric total abundance ratio, M_N/M_T , which is given by

$$\frac{M_N}{M_T} = \frac{b\tau_T}{(1 + b\tau_T + \tau_T/\tau_N) - R} \quad (11-10)$$

and the global average lifetime, τ , given by

$$\frac{1}{\tau} = \left(\frac{M_S}{\tau_S} + \frac{M_N}{\tau_N} \right) \frac{1}{M} \quad (11-11)$$

We also find

$$\tau = \tau_S \frac{1 + R}{R + \tau_S/\tau_N} \quad (11-12)$$

If $\tau = \tau_S = \tau_N$ (e.g., F-11 and F-12), we have from Eq. (11-8)

$$\frac{\Delta\tau}{\tau} = -\frac{\Delta b}{b} = \frac{\Delta(M/M_T)}{(M/M_T)} \left[1 + \frac{M/M_T}{(1 - M/M_T)} \right]$$

Consequently, if one deduces the atmospheric lifetime from the real release rate coefficient b and the measured global abundance ratio, M/M_T , the percent variation in τ is only directly proportional to the percent variation in b but may have a very strong dependence on the variations in M/M_T . If M/M_T is in the range of 0.8 to 0.9 as is observed for the long-lived halocarbons, the amplification factor on the variation of the atmospheric lifetime is in the range of 5 to 10. Thus, a 5% uncertainty in the global abundance ratio M/M_T for F-11 or F-12 will lead to 25% to 50% error in the deduced lifetime for these trace species. A large number of very accurate measurements with good global coverage would be required to establish the abundance ratio M/M_T to better than 5%. Thus it is nearly impossible to conclusively detect the existence or nonexistence of the so-called "hidden tropospheric sinks" for long-lived halocarbons through global budget analysis (see the second subsection following for further discussion).

For shorter-lived species we may hope to derive a more meaningful lifetime from a budget analysis. It is important, however, in this case to use the two-box model to check the atmospheric data for consistency with the analysis. If τ_T and b are known, Eqs. (11-9) and (11-10) provide a clear test for this

purpose. While the lifetime analysis for shorter-lived species is still highly sensitive to uncertainties in R and M_N/M_T if varied separately, the field of possible variations is reduced with the two-box model since both R and M_N/M_T must be consistent with a single interhemispheric mixing time, τ_T .

We have framed our two-box model discussion in terms of the parameters M_N/M_T and R because we believe that their determination from atmospheric data should be relatively more accurate than the determination of either hemispheric abundance separately. The determination of R should be less sensitive than that of either M_N or M_S to any possible systematic instrumental bias present in the measurements. The use of M_N/M_T is preferable to the use of M_S/M_T because the relative error for M_N should be smaller than the relative error for M_S . This follows because of the better latitudinal coverage in the northern hemisphere and the larger magnitude of local concentrations. For the gases discussed below, R and M_N/M_T were calculated assuming a constant mixing ratio equal to that obtained for a particular observation above 20° latitude in the northern hemisphere and below 30° latitude in the southern hemisphere (Rasmussen 1977), and assuming a linearly decreasing concentration from 20°N to 30°S . The mixing ratio was constant throughout the troposphere, whose vertical extent was taken equal to 16 km from 30°N to 30°S , and decreased linearly from a value equal to 13 km at 30°N and 30°S to 8 km at the poles. The concentration in the stratosphere was taken equal to zero, except for the species with known long tropospheric lifetimes.

Application to Freon-11

As shown in Fig. 51, we obtain a good fit to the release rate data for F-11 using the exponential function given in Eq. (11-3), for the periods 1958–1965, 1965–1973, 1973–1974, and 1974–1977, with the following parameters:

a	b	Period
28.0	0.19	1958–1965
106	0.13	1965–1973
314	0.032	1973–1974
324	-0.025	1974–1977

The formulas (11-9) and (11-10) relating M_N/M_T and R to τ_N , τ_S , and τ_T should be applicable for data obtained before 1975 if we use $b = 0.13$. Data obtained after early 1975 must be analyzed using the full time-dependent solution given by (11-4) and (11-5), since a new steady state for M_N/M_T and R would take several years to develop (see Fig. 54).

Unfortunately, as discussed below, not many measurements for F-11 are available for the period before 1975.

Figure 52 shows how the solutions for the interhemispheric mixing time, τ_T , and atmospheric lifetime, τ , depend on the parameters M_N/M_T and R in the case $\tau_S = \tau_N$. Large values for the ratio R are consistent with short mixing times; large values for M_N/M_T are consistent with long atmospheric lifetimes. The dependence of the lifetime on M_N/M_T is quite sensitive to values of M_N/M_T near the physical upper limit.

$$M_N/M_T = \frac{1}{1+R} \quad (\text{as } \tau_S = \tau_N \rightarrow \infty)$$

This is illustrated further in Fig. 53, and we may conclude that, as already mentioned, a very high level of accuracy in the data for the hemispheric abundance is required in order to derive a reliable estimate for the lifetime of long-lived species (i.e., F-11 and F-12). For example, Fig. 53 shows that M_N/M_T would need to be known to better than 6% in order to conclusively show that the lifetime for

Figure 51. Release rate of F-11 (Freon 11). Data points were taken from Hudson (1977) and Van Horn (1977). The straight lines correspond to the fit obtained using the parameters for Eq. (11-3) given in the text.

Figure 52. Relationship between the F-11 hemispheric ratio of abundances, $R = M_S/M_N$, the northern hemispheric abundance ratio, M_N/M_T , the interhemispheric mixing time, τ_T , and the chemical removal time, τ , for the two-box model with $\tau = \tau_S = \tau_N$. The units for τ and τ_T are years.

Figure 53. Sensitivity of the derived atmospheric lifetime of F-11 to changes in the abundance ratio M_N/M_T for the case $\tau = \tau_S = \tau_N$ for two values of the interhemispheric mixing time τ_T (in years).

F-11 was equal to 30 ± 10 years. It is clear from the scatter of points shown in Fig. 52, however, that the data obtained before 1975 cannot be used to establish a short lifetime for F-11. The data points displayed in Fig. 52 were calculated from measurements of F-11 taken before 1975 (see Table 19). The derived values for R range from 0.65 to 0.82. They

are consistent with transport times in the range from 0.94 to 3.0 years. The measured total abundance ratios, M_N/M_T , are also widely scattered and range from 0.31 to 0.49. The concentrations reported by Rasmussen (1977) appear to be most consistent with the 60-year lifetime for F-11 determined from atmospheric models (National Research

Table 19. Measurements of CFC_{11} used to calculate data points of Fig. 52.

F-11 mixing ratio (ppt) ^a	Latitude	Date	R	M_N/M_T	Reference
70	50°N	Nov.-Dec. 1971	0.640	0.417	Lovelock et al. (1973)
38	60°S				
79.8	52°N	Sept.-Dec. 1974	0.824	0.313	Cox et al. (1976)
61.7	33°S				
125	43°N	Jan. 1975	0.782	0.489	Rasmussen (1977)
90	90°S				
138	43°N	Jan. 1976	0.860	0.489	Rasmussen (1977)
113	90°S				
143	43°N	June 1976	0.903	0.483	Rasmussen (1977)
125	43°S				
154	43°N	Jan. 1977	0.822	0.493	Rasmussen (1977)
127	90°S				

^aParts per trillion (10^{12}).

Council 1976). His measured interhemispheric ratio, 0.78, would imply an interhemispheric mixing time of 1.9 years.

Since 1975 the value for R derived from atmospheric measurements has apparently increased. As shown in Fig. 54 the growth in R is consistent with the decreasing rate for the release of F-11 (Fig. 51). A very rapid growth of R , as suggested by the data shown in Fig. 54, is not consistent with the two-box time-dependent model. As shown in Fig. 54 the calculated rise in R after 1975 increases more rapidly for longer interhemispheric mixing times. If the interhemispheric transport time were longer than two years, a rapid rise could be explained, but then the calculated absolute value of R would be substantially less than that required by the data. Since there were very few measurements taken before 1975, conclusions based on the rate of growth for R are risky. We therefore take $1 \text{ yr} < \tau_T < 2 \text{ yr}$ as an acceptable range for the interhemispheric transport time (compare Czeplak and Junge 1973).

Application to CH_3CCl_3

The time history for the release of methylchloroform is shown in Fig. 55 along with the exponential release rate we used for Eq. (11-3). The data shown in Fig. 55 do not correspond precisely to the single exponential growth rate chosen, but the solutions for R and M_N/M_T are very stable to changes in the parameter b used in Eq. (11-3). We have verified numerically that the change in b could

be as large as 50% lasting over 3-year periods without causing the solution for R and M_N/M_T to change by more than 5%.^{*} We may therefore use Eqs. (11-9) and (11-10) in what follows.

Table 20 presents the data for CH_3CCl_3 and the calculated values for R and M_N/M_T . In order to compare these values with the two-box theory, we must specify one of the three parameters τ_S , τ_N , or τ_T , or introduce another relationship. CH_3CCl_3 is removed in the troposphere by reaction with OH, and the average abundance of OH in each hemisphere is not expected to be the same since higher concentrations of CO in the north should cause a lower OH concentration (Wofsy 1976). Current models suggest there should be about a 25% variation in the average concentration for OH between the hemispheres. In what follows we therefore assume $\tau_S = 0.75\tau_N$, although the conclusions drawn are not very sensitive to the precise value used for the ratio of the removal rates.

Figure 56 shows the values for R and M_N/M_T from Table 20 plotted on a graph which relates these parameters for several values of τ_T , with $\tau_S = 0.75\tau_N$. Also shown are the values derived using a constant tropospheric mixing ratio in each

^{*}This conclusion was based on the use of $\tau_T = 1.5$ years.

Figure 54 Growth in the F-11 hemispheric abundance ratio, $R = M_N/M_T$, for the release data shown in Fig. 51, for four values of the interhemispheric mixing time τ_T (in years). Data points are taken from Table 19 and refer to the measurements of Lovelock et al. (1973), Cox et al. (1976), and Rasmussen (1977).

Figure 55 Release rate of CH_3CCl_3 . Data points were taken from Neely and Plonka (1977). The straight line corresponds to the fit obtained with $b = 0.17$ in Eq. (11-3).

Table 20. Measurements of CH_3CCl_3 mixing ratios.

CH_3CCl_3 mixing ratio (ppt) ^a	Latitude	Date	R	M_N/M_T	Reference
64.8	52°N	Sept.-Dec. 1974	0.503	0.285	Cox et al. (1976)
24.4	35°S				
90	47°N	Jan. 1975	0.686	0.403	Rasmussen (1977)
52	90°S				
98	47°N	Jan. 1976	0.672	0.376	Rasmussen (1977)
57	78°S				
109	43°N	June 1976	0.743	0.389	Rasmussen (1977)
73	43°S				
110	47°N	Jan. 1977	0.716	0.364	Rasmussen (1977)
70	90°S				

^aParts per trillion (10¹²).

hemisphere equal to the value measured in each hemisphere. For Rasmussen's (1977) data, the more carefully derived hemispherical abundances are consistent with an average interhemispheric transport time of 1.5 years. This is easily within the range of acceptable values for τ_T derived from the budget for the more extensively measured F-11. The interhemispheric transport time derived from the raw abundance data is 2.11 years, somewhat longer than that considered appropriate.

Figure 56. Relationship between the CH_3CCl_3 northern hemispheric abundance ratio, M_N/M_T , and the hemispheric ratio, $R = M_S/M_N$, for the case $\tau_S/\tau_N = 0.75$, for four values of the interhemispheric mixing time τ_T (years). The circle data points are measurements by Cox et al. (1976), the square points by Rasmussen (1977) (see Table 20).

Even for the adjusted values, the earliest measurements (Cox et al. 1976) appear not to be consistent with interhemispheric mixing times that are less than about two years. This conclusion remains true unless the removal rate in the southern hemisphere is more than two times faster than that in the north, a condition that is not presently supported by two-dimensional models for the tropospheric OH abundance (Wofsy 1976, Chang et al. 1977). Using the data measured by Cox et al. (1976) and assuming the northern hemispheric removal rate is 25% slower than that in the south, we derive a transport time equal to 2.3 years and an average atmospheric lifetime for CH_3CCl_3 equal to about 4.5 years. This same analysis applied to the measurements made by Rasmussen (1977) leads to a rather different conclusion. Rasmussen's measurements for CH_3CCl_3 are consistent with transport times ranging from 1.3 to 1.8 years and with average lifetimes ranging from 10.0 to 12.8 years. If we average his data, we obtain a lifetime for CH_3CCl_3 of about 11.3 years.

As illustrated in Figs. 57a and 57b, the derived lifetime for CH_3CCl_3 is rather sensitive to the values for R and M_N/M_T , although not as sensitive as the derived lifetimes for F-11 and F-12. If we decrease the derived value for the total abundance obtained from Rasmussen's data by 10%, from 0.38 to 0.34, the average lifetime decreases to 8.6 years. If, in addition, the hemispheric abundance ratio is lowered from the derived value of 0.7 to 0.62, the value obtained from an average of Rasmussen's (1977) raw data for each hemisphere, the lifetime would decrease to 7.6 years. This again illustrates the high level of sensitivity to uncertainties in the atmospheric data.

Figure 57 (a) Sensitivity of the CH_3CCl_3 derived southern hemispheric lifetime, τ_S , to the hemispheric abundance ratio, $R = M_S/M_N$, for the case $\tau_S/\tau_N = 0.75$, for four values of the interhemispheric mixing time τ_T (years). (b) Sensitivity of τ_S to the northern hemispheric abundance ratio, M_N/M_T , for the same conditions as in (a).

The 11.3-year average lifetime for CH_3CCl_3 derived above is not consistent with the lifetime derived using the OH concentrations from a one-dimensional chemical model. In order to obtain a lifetime for CH_3CCl_3 consistent with the values derived from the two-box model, the diurnally and vertically averaged tropospheric OH concentration in the one dimensional model would have to be

lowered from the current value of 8.0×10^5 molecules/cm³ to 2.5×10^5 .

It is not likely that the entire tropospheric OH concentration from the one-dimensional model is a factor of 3 too high since the calculated noontime OH concentrations near 7 km and 11 km are already somewhat lower than the values measured by Davis et al. (1976). If the entire tropospheric OH column were adjusted downward in order to calculate a longer lifetime for CH_3CCl_3 , the concentrations near 7 km and 11 km would be at least a factor of 5 smaller than those measured by Davis et al. (1976). While Davis's measurements might be somewhat higher than the appropriate noontime global background values at those altitudes, it is difficult to imagine local perturbations which might increase OH by a factor of 5. The model results for OH above 7 km are therefore probably fairly reliable. In any case, any adjustment for OH above 5 km has very little effect on the calculated lifetime for CH_3CCl_3 , since the concentration for CH_3CCl_3 decreases exponentially with the air density. The major contribution to the chemical removal of CH_3CCl_3 comes from the OH molecules near the earth's surface. This is also the region where complex processes that are not accounted for by current models may cause large variations in the density of OH. In order to increase the calculated lifetime for CH_3CCl_3 from the one-dimensional model by a factor of 3, the OH concentrations below 4 km would have to decrease by about a factor of 3.

The requirement for a large change in the concentration of OH near the surface would be reduced somewhat if the global abundance for CH_3CCl_3 were actually smaller than the values derived above. It is clear that a better understanding of the chemical balances in the lower troposphere is needed. More latitudinal coverage in the measurements of CH_3CCl_3 and more measurements of the OH concentration in the lower troposphere are highly desirable.

2.12 A Review of Ozone Theory and Observational Data*

Until recently, attempts to validate ozone models have been restricted to comparisons within the stratosphere and primarily to total column depths and vertical profiles of measurable species. For 1-D

*With the cross sections for photolysis of H_2O_2 of Molina and Molina (private communication, 1977) the average OH concentration in our model increases to 1.25×10^6 molecules/cm³. Compare Section 2.9.

*See Ellisasser (1976b).

(one-dimensional) models such comparisons have been ambiguous at best due to the large seasonal and latitudinal variations and the paucity of observational data even for ozone and particularly so for all other trace species. Duewer et al. (1977b) demonstrated that comparison of computed and observed species profiles within the stratosphere is currently inadequate to determine a choice between ensembles of reaction rates producing drastically different sensitivities to stratospheric injection of oxides of nitrogen. In addition, with the recent development of several 2-D stratosphere models, it has become apparent that by a judicious choice of transport prescription it is possible to match latitudinal and seasonal variations in total ozone with various representations of stratospheric chemistry. Accordingly, it now appears that validation of the chemistry of the stratospheric ozone layer can best be done outside the stratosphere, or at least outside the middle and lower stratosphere where species concentrations depend more on transport than on photochemical equilibrium. That is, the most sensitive regions for validating ozone chemistry by comparison with observations appear to be above 35 km, where photochemical equilibrium is believed to be least disturbed by transport, and in the troposphere where we have the most observational data.

A review of comparisons which have been made in these regions indicates some remaining flaws or uncertainties in our current understanding of the chemistry of the ozone layer. Prechlorine models typically computed a maximum ozone mixing ratio exceeding that observed and a decrease in ozone concentration with height ($-d[O_3]/dz$) above this altitude more rapid than observed. This in turn led to computation of lower ozone concentrations than observed in the upper stratosphere and lower mesosphere.

Theory vs Observation Above Ozone Maximum

Dütsch and Ginsburg (1969) and Dütsch (1971) pointed out that with a pure oxygen atmosphere and Chapman chemistry, $-d[O_3]/dz$ is determined by the temperature dependence (or activation energy) of the ratio of the reaction rate k_2 for ozone formation ($O + O_2 + M \rightarrow O_3 + M$) to the rate k_3 for ozone destruction ($O + O_3 \rightarrow 2O_2$) and the temperature lapse rate in the stratosphere. They obtained the best fit to available ozone observations by assuming no temperature dependence for this ratio, a surprising result since 1800 K (i.e., $k_2/k_3 \approx e^{1800/T}$) was the smallest value they ever found reported from laboratory results at that time. (The currently accepted temperature dependence for this ratio is $e^{2810/T}$ (Hampson and Garvin 1975).)

While the introduction of hydrogen, nitrogen, and chlorine chemistry would be expected to have reduced the computed ozone mixing ratio at the level of the maximum and the rate of decrease with height above this level, the above discrepancy with observation appears to have persisted. Including hydrogen and nitrogen chemistry, Kurzeja (1975) computed up to 25% higher ozone concentrations over the equator at 35 to 45 km than observed. Both the ozone excess and the decrease with height, $-d[O_3]/dz$, were greater when the more accurate fully diurnal integration was used. Kurzeja (1975) concluded that his diurnally computed ozone "exceed[ed] observed values by amounts too large to be attributed solely to observational error." The ozone excess above 26 km amounted to as much as $30 \text{ m} \cdot \text{atm} \cdot \text{cm}$ or 9% of the ozone column density. Both Frederick and Hays (1977) and Liu and Cicerone (1977) state that some recent measurements indicate two to three times more ozone in the 50-to-60-km region than computed from current models. However, they disagree on the situation at 40 km: Frederick and Hays (1977) appear to find agreement between computed and observed amounts while Liu and Cicerone (1977) claim that the observed ozone concentration exceeds that computed even for odd chlorine mixing ratios as low as 2.3 ppb. Both sets of authors suggested that the most likely source of these discrepancies was in our present imperfect understanding of ozone chemistry.

Theory vs Observation in the Troposphere

The most obvious and most discussed disagreements between our current understandings of ozone theory and observation occur with respect to tropospheric ozone. While suggestions that tropospheric ozone was not simply a tracer and that photochemistry might be important to tropospheric (nonurban) levels of ozone were made by Frenkiel (1955) and Ripperton et al. (1971), pioneer development of the photochemistry of tropospheric ozone and particularly of the methane cycle is generally attributed to Crutzen (1973) and Johnston and Quitevis (1974). Papers by Levy (1972, 1973), Wofsy et al. (1972), and Chameides and Walker (1973, 1976) are also relevant.

Crutzen's (1972, 1973) early work in this area led to estimates of tropospheric ozone production which exceeded the estimates of stratospheric injection and boundary-layer destruction rates of $(5.6 \pm 1.8) \times 10^{10} \text{ molecules/cm}^2 \cdot \text{s}$ (Fabian and Pruciniewicz 1977) by more than 10-fold. Crutzen (1973) cautioned against accepting his results because of their apparent conflict with the observational evidence. Using more recent reaction rates

and lower concentrations of odd nitrogen. Crutzen (1974b) calculated net tropospheric (lowest 2 km) ozone production rates of $(-1.2 \text{ to } +2.6) \times 10^{11}$ molecules/cm²-s for the reaction schemes considered. While inferring that tropospheric ozone was not chemically inert, he could not decide whether there is net destruction or production, "due to insufficient knowledge of some essential chemical processes" (Crutzen 1974b). In a still later study Fishman and Crutzen (1976), using 0.2 ppb of NO₂, arrived at a net ozone column production rate of 5×10^{10} molecules/cm²-s, a rate regarded as "significant compared with...estimates of downward ozone flux from the stratosphere and photochemical column destruction rates." They concluded that it is "difficult to explain the observed tropospheric ozone profiles" and hypothesized "therefore, that catalytic ozone-producing mechanisms are operative in the troposphere in addition to those...considered" or "that the rate coefficients which govern ozone production are substantially larger than assumed."

Johnston and Quitevis (1974), using Crutzen's (1973) photochemistry, determined the crossover altitude as 13 km at which the "standard" NO_x profile switches from net destruction of ozone in the stratosphere to net production of ozone at lower levels via the "methane smog cycle." Their Fig. 13 indicates a net ozone column production below 13 km of about 10^{11} molecules/cm²-s. Since then the crossover altitude for NO_x net production of ozone has been pushed above 13 km by Hidalgo and Crutzen (1976), Duewer et al. (1976), and Widhopf et al. (1977).

From their calculations Chameides and Walker (1973, 1976) concluded that tropospheric ozone is near a state of photochemical equilibrium (i.e., not transport-dominated). Serious conflicts between their results and observational data were cited by Fabian (1974), Chatfield and Harrison (1976), and Fabian and Pruchniewicz (1977). A reexamination of the tropospheric ozone budget by Chameides and Stedman (1977), in the light of revised reaction rates and lower observed concentrations of odd nitrogen, concluded "that at mid-latitudes photochemistry acts primarily as an ozone sink."

A recent more complete tropospheric model by Stewart et al. (1977), using more recent reaction rates, obtained results differing from previous models in several respects. One of their more interesting findings was that ozone did not increase monotonically with NO_x but rather exhibited a maximum for [NO_x] $\approx$ 0.5 ppb. Although they could choose an NO_x concentration that would produce an ozone level near that observed, over

most of the range of likely NO_x amounts the computed ozone concentration was much less than that observed. They concluded that "photochemical activity alone cannot account for observed [tropospheric] values of ozone and many other important species."

In addition to the dramatic evolution in model results reviewed above, all recent investigators have concluded that tropospheric ozone is photochemically active: except for very specific profiles of NO_x, they compute ozone production or destruction rates which exceed or are a significant fraction of the rates (generally considered to be identical) at which ozone enters the troposphere from the stratosphere and at which it is destroyed at the earth's surface. Thus, unless the observational data have been misinterpreted, there appear to be serious errors in our understanding of ozone chemistry in the troposphere. It appears unlikely that correction of such errors would leave our computations of stratospheric ozone unchanged.

The Importance of Transport

Transport has long been recognized to be the overriding controlling mechanism for many types of variations revealed by the ozone data. The list of variations begun by Chamberlain and Leovy (1975) has been expanded upon and now includes:

1. Seasonal variation. Total ozone has long been known to have a seasonal variation with maxima occurring in winter to spring and minima in summer to fall. Photochemistry alone would predict a maximum in summer and a minimum in winter.

2. Latitudinal variation. Minima in total ozone occur near the equator and maxima occur poleward of 55° latitude.

3. Biennial oscillation. Ozone observations generally reveal an oscillation with an amplitude of about 5% which in low latitudes is in phase with the quasi-biennial oscillation in the 50-mbar zonal wind over Panama. The oscillation shows an increasing phase lag with latitude but little change in the percentage amplitudes (Wilcox et al. 1977).

4. Day-to-day local variations. Day-to-day variations of total ozone correlated with the passage of synoptic systems have long been recognized.

5. Longitudinal variations. As with synoptic variations, changes in vertical motion patterns and heights of the tropopause induced by the semistationary long-wave patterns of the general circulation are accompanied by primarily longitudinal variations in total O₃. In addition, longitudinal variations in total ozone in the tropics have been ascribed to large-scale cells of ascending and descending motion induced by continent and

ocean contrasts in surface heating and topographic uplift.

6. Northern hemisphere total ozone increase of 5 to 11% from 1957 to 1970. Unless this change can be related to the parallel increase in stratospheric water vapor (Harries 1976), this increase, which is apparently restricted to the northern hemisphere (London and Kelley 1974), cannot be explained by photochemistry alone. Ellsaesser (1976c) proposed that this increase was due to a progressive weakening of Hadley-cell-driven exchange between stratosphere and troposphere evidenced by the weakening and virtual disappearance of the Junge layer in 1971, the Sahelian drought, and the lowering and warming of the tropical tropopause reported by Angell and Korshover (1974).

7. Hemispheric variation. Most investigators have concluded that mean annual total O_3 is less over the southern hemisphere than over the northern. London (1975), for the period July 1957 to June 1970, reported values of 282 and 292 m·atm·cm, respectively. From IRIS data for April through July 1969, Lovill (private communication, 1977) obtained 303 and 318 m·atm·cm, and from Nimbus BUUV* data for April 1970 through April 1971, Heath (1974) reported mean hemispheric values of 301 and 314 m·atm·cm.

Stratospheric Odd-Nitrogen Budgets

Tables 21 and 22 summarize a review of stratospheric odd-nitrogen budgets determined from theoretical work and from observational data. It is apparent that the theoretical work reveals an uncertain consensus that N_2O produces approximately 80% of the odd nitrogen in the stratosphere and cosmic rays account for most of the remainder. While the N_2O production rate shows a fairly strong mode near 9×10^7 molecules/cm²·s, the range is 20-fold, extending from 2×10^7 to 40×10^7 . Additional sources that have been proposed (other than cosmic rays) include:

1. Downward transport from the thermosphere, particularly during the polar night.
2. Oxidation of NH_3 .
3. Upward transport of NO_2 from the troposphere.
4. Other hypothesized but unidentified sources.

On the other hand, estimates of odd-nitrogen turnover rates in the range $4.4\text{--}50 \times 10^7$

molecules/cm²·s have been obtained using the same types of vertical transport used in models and basing the results at least partially on observational data such as the stratospheric profiles of HNO_3 and N_2O . Only estimates made using stratospheric profiles based on the filter collections of HNO_3 by Lazrus and Gandrud (1974) provide numbers ($4.4\text{--}12.4 \times 10^7$) close to the mode of the theoretical estimates (11×10^7). All other estimates derived from observed profiles of HNO_3 and N_2O are 2-to-5-fold larger than the theoretical estimates. Since there are reasons to believe that the filter collections by Lazrus and Gandrud (1974) are underestimates, this seems to suggest rather strongly that current models are underestimating the odd-nitrogen budget of the stratosphere. This is a conclusion also reached by Ackerman (1975) and COMESA (1975).

2.13 Effect of Receiver Orientation on Erythema Dose

Because reductions in total ozone would permit greater amounts of ultraviolet (uv) radiation to reach the surface of the earth (Cutchis 1974, Halpern et al. 1974), a number of studies have been performed with the goal of assessing biological sensitivity to ozone-induced changes in uv radiation (National Research Council 1973). One branch of these studies has been concerned with the impact of increased uv radiation on human beings, the principal effects being increased occurrence of skin cancer (Urbach 1969, Giese 1968) and increased vitamin D production (Leach et al. 1976). One approach has been to correlate skin cancer incidence data directly with ozone layer thickness. The possible influence of such factors as duration of sunlight, clothing and exposure habits, and optical path length have been considered (McDonald 1971, van der Leun and Daniels 1975). Another approach has been to explicitly consider the dose of uv radiation received as a function of ozone amount and other climatic variables (Green and Mo 1975). The radiation dose is then related to cancer incidence after weighting by a wavelength-dependent function accounting for variation in radiation efficacy. This second approach, though less direct, is appealing because the mechanism of cancer production is more fully represented in it, and it allows for experimentation with combinations of independent variables outside the rather narrow range of reliable observation.

As the first step in this approach, Green and co-workers developed a semiempirical model for

*BUUV is the abbreviation for the backscatter ultraviolet sensor carried on the Nimbus satellite.

Table 21 Estimates of production rates for exotic sources of stratospheric NO_x .

Source	Reference	Production rates		Remarks
		10^{15} molecules cm^{-2} per event or year	10^{32} molecules per event or year	
Solar-proton PCAs (latitude 65° or higher)	Zinn and Sutherland (1975)	20	96	Four equal events of 11 May–17 July 1959, computed by E. M. Jones.
	Crutzen et al. (1975)	2	14	12–16 Nov. 1960 event.
		0.6	4	2–5 Sept. 1966 event.
		6	40	2–10 Aug. 1972 event.
Galactic cosmic rays (GCRs), mean and solar-cycle amplitude	Warneck (1972)	0.22	11	Reported as global mean of $0.07 \times 10^8 \text{ cm}^{-2} \cdot \text{s}$, 0.33 NO per ion pair.
	Nicolet and Peetermans (1972)	0.16–1.6	—	Reported as latitudinal range of 0.05 – 0.5 $\times 10^8 \text{ cm}^{-2} \cdot \text{s}$.
	Johnston (1974a)	—	(?) :4	Reported as solar-cycle double amplitude of 8×10^{32} , approx 17 SSTs or 50 Concorde.
	Ruderman and Chamberlain (1975)	1.4 ± 0.21	9.8 ± 1.5	Reported as 0.45 $\times 10^8 \text{ cm}^{-2} \cdot \text{s} \pm 15\%$ for high latitudes.
	Nicolet (1975a)	1.57 ± 0.31	10.8 ± 2.2	Reported as solar-cycle min and max of 0.4 and $0.6 \times 10^8 \text{ cm}^{-2} \cdot \text{s}$ for lat. $>60^\circ$.
		0.6 ± 0.13	30 ± 6.5	Global means from integrals of his Fig. 10.
	Crutzen et al. (1975)	1.5 ± 0.3	10.3 ± 2.6	Reported as 1.2 – 1.8 $\times 10^{15} \text{ cm}^{-2} \cdot \text{s}$ at lat. $>60^\circ$.
Nuclear explosions (per Mt yield)	Bauer and Gilmore (1975)		0.17–2.5	Range of estimates in literature.
Oxidation of N_2O	Crutzen et al. (1975)	0.75–7.5	38–380	Range of estimates in literature.
Relativistic-electron- precipitation (REP) bremsstrahlung	Thorne (1977)	0.075	1.8	Columnar production given as $3 \times 10^9 \text{ cm}^{-2} \cdot \text{s}$ "typically having a duration of a few hours," about half in stratosphere.

calculating uv radiation at the surface of the earth in the spectral region 280–340 nm (Green et al. 1974a,b, Mo and Green 1974). They have calculated erythema (sunburn) dose as a function of total ozone, solar zenith angle, latitude, season, and cloud amount. Their model was also used in the Climatic Impact Assessment Program's analysis of ozone depletion (Green et al. 1975).

One feature of this model, and of uv dosimetry in general (Berger et al. 1975), is that the receiver is assumed to be horizontal. The geometry of humans, however, is such that the majority of exposed skin

would normally be in a nonhorizontal position. In fact, the horizontal projection of an upright person amounts to only a few percent of total surface area (Fanger 1970). This suggests that receiver orientation should be considered in the study of uv doses.

The effect of receiver orientation on incident solar radiation is routinely included in studies of building heating load (e.g., Kasuda 1973) and human comfort (Morgan 1972, Burt 1976). Orientation has also been investigated directly in connection with south-facing plane areas (Dave et al. 1975) and human beings (Terjung and Louie 1970) using

Table 22. Available estimates of continuous natural stratospheric sources and sinks of odd nitrogen (10^8 molecules $\text{cm}^{-2}\cdot\text{s}$ averaged over the globe unless otherwise stated). Positive numbers imply sources; negative numbers, sinks.

Source or sink	Reference	Magnitude	Remarks
Oxidation of N_2O by $\text{O}(^1\text{D})$ in the stratosphere	Crutzen (1971)	0.29-1.5	Per Johnston (1972), not stated in report.
	McElroy and McConnell (1971)	0.2, 0.24, 0.63	Tropopause values (15 km) read from their Fig. 1b. Abstract cites ~0.2. Due to different diffusion profiles.
	Nicolet and Peetermans (1972)	0.5-2.5	Reported as 1.5 ± 1 . Due to different diffusion and $\text{O}(^1\text{D})$ profiles and zenith angles.
	Isaksen (1973a)	0.7, 1.0, 1.4	Winter, annual, and summer averages computed from his Fig. 4. Quoted by Johnston (1974a) as 0.8-1.0.
	Isaksen (1973b)	1.2	
	Brasseur and Cieslik (1973)	1.5, 4.0	Integrals computed from their Fig. 6 for two different diffusion profiles.
	McConnell and McElroy (1973)	0.3, 0.9	For two different diffusion profiles.
	McConnell (1973)	0.3, 0.9	Integrals computed from his Fig. 4 for two different diffusion profiles.
	Brasseur and Nicolet (1973)	0.5, 0.9, 1.4, 1.9	Integrals computed from their Table 1. Due to different diffusion and $\text{O}(^1\text{D})$ profiles.
	McElroy et al. (1974)	0.819, 0.889	Due to reduced and normal O_3 profiles.
	Johnston (1974b)	~1	Based on first three estimates above.
	Crutzen et al. (1975)	0.25-2.5	Cited as range of first four estimates above.
	Duewer et al. (1976)	0.64, 0.98, 1.00, 1.53	Models B, A, A' and C', and C respectively. Due partly to rate for $\text{N}_2\text{O} + \text{O}(^1\text{D})$ reaction.
	Duewer (1976)	0.92	Current LLL 1-D model with new Chang K_2 profile and 20% increase in $\text{O}(^1\text{D})$ quenching rate.
	Schmelttekopf et al. (1977a)	4.5	Observed N_2O profiles and Crutzen's (1973) 2-D model.
	Schmelttekopf et al. (1977b)	5.1	Observed N_2O profiles and Crutzen's (1973) 2-D model.
Oxidation of NH_3	McConnell and McElroy (1973)	-0.9, -0.5, 1.0	Source considered more likely.
	McConnell (1973)	-0.6, 0.6	—
	McElroy et al. (1974)	2.0	Integral computed from their Fig. 11.
Flux through stratopause	Crutzen (1971)	1.0	Tested in model.
	Nicolet and Peetermans (1972)	0.5	For $8 \times 10^8/\text{cm}^3$ (40 ppb) of NO at 80 km and maximum diffusion.
	McConnell and McElroy (1973)	0.15	Prescribed to model the possibility of significant high-latitude winter transport.
	McConnell and McElroy (1973)	-0.4, -0.2	Upward fluxes at 50 km from their Fig. 11.
	Brasseur and Nicolet (1973)	-0.1 to -0.02	Peak upward fluxes on their Fig. 24.

Table 22. (continued)

Source or sink	Reference	Magnitude	Remarks
Flux through stratopause (contd.)	Crutzen (1974a)	>0	Obtained from diffusion profile of Wofsy and McElroy (1973).
	Hessvedt (1974)	>0	Downward-directed gradient in NO _y in high latitudes in winter.
	Johnston (1974b)	~0.1	Provided it is a source at all.
	Nicolet (1975b)	0	—
	Duewer et al. (1976)	-0.23	Model-computed photodissociation of NO in upper stratosphere.
	Zinn and Sutherland (1975)	<0	Upward gradient in model-computed mixing ratio at stratopause.
Flux through tropopause	Lazrus and Gandrud (1974)	-1.24 to -0.44	As HNO ₃ , based on measured HNO ₃ and Krey and Krajewski's (1970) model.
	Ackerman (1975)	-0.8, -3, -5	As HNO ₃ ; larger values would require NO source in addition to N ₂ O.
	Ackerman (1975)	>0	As NO ₂ , particularly in summer.
Galactic cosmic rays (GCRs)	Nicolet (1975a)	0.16, 0.24	Global mean solar cycle min and max, from integrals of his Fig. 10.
Net of all sources	Johnston (1974b)	1.0-2.0	Given as net effect of all natural sources.

the entire solar spectrum. The purpose of this work is to determine the significance of receiver orientation in the wavelength region responsible for sunburn and skin cancer. The effects on erythema dose are considered for different latitudes and seasons, and variations in total ozone and the erythema weighting curve are also included.

The procedure employed here involves using the Green model (Green et al. 1974a) to obtain total uv radiation ($Q_h + q_h$) as a function of wavelength λ and solar zenith angle θ . Valid for clear sky conditions, it is essentially a Beer-Bouguer formulation for both direct beam (Q_h) and diffuse (q_h) radiation. The latter is assumed to be isotropically distributed. These fluxes are determined using the relationships

$$Q_h(\theta, \lambda) = H(\lambda) V^2 \exp[-A_i(\theta, \lambda)] \cos \theta \quad (13-1)$$

and

$$q_h(\theta, \lambda) = H(\lambda) V^2 \exp[-D_i(\theta, \lambda)] \quad (13-2)$$

where $H(\lambda)$ is the extraterrestrial solar irradiance at the mean earth-sun distance (taken from Howard et al. 1960). The symbol V , which does not appear in the Green model, is the ratio of the mean earth-sun

distance to the earth-sun distance on a particular day. It thus allows for eccentricity in the earth's orbit, which causes variations in the extraterrestrial flux of about $\pm 3.5\%$.

The terms A_i and D_i are optical thickness functions accounting for the presence of ozone (oz), air (a), and particulate matter (p); they are given by Green et al. (1974a):

$$A_i(\theta, \lambda) = w_{oz} k_{oz} \exp[-(\lambda - \lambda_0)/d] \text{seq}(\theta, y_{oz}) \\ + w_a k_a \left(\frac{\lambda_0}{\lambda}\right)^{v_a} \text{seq}(\theta, y_a) + w_p k_p \left(\frac{\lambda_0}{\lambda}\right)^{v_p} \text{seq}(\theta, y_p) \quad (13-3)$$

and

$$D_i(\theta, \lambda) = K_{oz} \text{seq}(\theta, q_1) \\ \times \exp \left\{ K k_{oz} w_{oz} - \frac{(\lambda - \lambda_0)}{[\delta \cdot \text{seq}(\theta)]} \right\} \\ + K_{ap} \text{seq}(\theta, q_2) \quad (13-4)$$

where

$$\text{speq}(\theta) = \left(1 - \frac{\sin^2 \theta}{1.148}\right)^{-1/4} \quad (13-5)$$

and

$$\text{seq}(\theta, y) = \left[1 - \frac{\sin^2 \theta}{q}\right]^{-1/2} \cdot q = [1 + (y/R)]^2 \quad (13-6)$$

Values for the parameters appearing in (13-3) through (13-6) are the same as those published in the study by Green et al. (1974a). For the spectral region considered here, the total ozone optical depth w_{02} is of special interest.

To calculate the direct-beam radiation incident on an inclined surface Q_p , it is necessary to replace θ in Eq. (13-1) with the angle between the position of the sun and a line normal to the surface (i):

$$Q_p(\theta, \lambda) = H(\lambda) V^2 \exp[-A_i(\theta, \lambda)] \cos i \quad (13-7)$$

where

$$\cos i = \cos \alpha \cos \theta + \sin \alpha \sin \theta \cos(a - a') \quad (13-8)$$

Here a' is the solar azimuth (relative to north), a is the azimuth of the receiver, and α is the angle of the receiver's inclination (relative to horizontal). For a horizontal receiver, $\alpha = 0$. Equations required to find θ and a' as a function of latitude, season, and time of day may be found in Dave et al. (1970), Sellers (1965), or the Smithsonian Meteorological Tables (List 1958). The last reference also contains tabulated values of V .

Diffuse radiation incident on an inclined surface has two components: that arriving from the sky as scattered radiation, q_s , and that reflected from the surface, q_r . Under the assumption of isotropic reflection and the earlier assumption of isotropic atmospheric scattering, these quantities are given by (Dave et al. 1970):

$$q_s(\theta, \lambda) = \frac{1}{2} q_h(\theta, \lambda)(1 + \cos \alpha) \quad (13-9)$$

and

$$q_r(\theta, \lambda) = \frac{1}{2} [Q_\lambda(\theta, \lambda) + q_h(\theta, \lambda)] \times (1 - \cos \alpha) \quad (13-10)$$

The ground reflectivity r is small for surfaces other than snow and ice at uv wavelengths (Kondratyev 1973). A value of 0.1 was chosen here for r .

The sum $Q_p + q_s + q_r$ represents the total radiation incident per unit area on a plane inclined at an angle α and with azimuth a . Because radiation is not equally efficient at all wavelengths in producing a biologic response, one cannot integrate incident radiation directly over wavelength and obtain a meaningful measure of skin tissue insult. One must know the relative response of skin to uv radiation as a function of wavelength. In the case of sunburn the so-called action spectrum (or erythema efficiency) has been studied using uv lamps (e.g., Coblenz and Stair 1934, Magnus 1964, Cripps and Ramsay 1970) and can be represented by (Green et al. 1974b):

$$\epsilon(\lambda) = \left[4 \exp\left(\frac{\lambda - 297}{3.21}\right)\right] \times \left[1 + \exp\left(\frac{\lambda - 297}{3.21}\right)\right]^{-2} \quad (13-11)$$

The action spectrum for skin cancer in humans is not known; it is usually assumed to be the same as for erythema or similar to the DNA action spectrum (Setlow 1974).

Equations (13-8) through (13-11) may be used to calculate the instantaneous erythema dose for any time of day, date, latitude, ozone amount, and receiver position. In analyzing the effects of receiver orientation, we have numerically integrated over wavelength and time to produce daily erythema doses for northern hemisphere latitudes, assuming the receiver is stationary. Integrations were performed for the 15th day of each month using a time step of approximately 20 minutes. The total ozone was specified as a function of latitude for each month based on data from the Nimbus 3 satellite reported by Lovill (1972). Ozone reductions of 10 and 20% were also considered in the calculations.

To estimate the average dose for a population where there is random orientation (i.e., no preferred orientation), we made calculations while allowing the receiver to rotate 360° at each time step. Doses were computed at 20° intervals in the azimuth angle, and the average of these was used for integration. The inclination angle α was held fixed at values of 0, 45, and 90 degrees.

Figure 58 shows the daily total erythema dose for a rotated surface as a function of latitude for different ozone amounts and receiver inclinations for the 15th days of June, September, and December. Following the seasonal migration of solar declination, the peak daily erythema dose occurs in the latitude region $30-45^\circ\text{N}$ in June and moves

southward to 0–20°N in September and to the southern hemisphere in December.

The relationship between dose magnitude and inclination is such that inclined surfaces generally receive less daily integrated dose than a horizontal surface at the same latitude. Exceptions to this occur in some low sun situations (large θ) where the dose on the inclined surface (e.g., $\alpha = 45^\circ$) slightly exceeds that on the horizontal surface. This result is in contrast to the study of Dave et al. (1970) using the full solar spectrum where radiation on south-facing surfaces was shown to grow larger than that received by a horizontal surface near the poles. At the wavelengths contributing to erythema, the radiation is predominantly diffuse. Consequently, the angle of incidence does not exert as strong an influence as it would when the radiation is predominantly in the direct beam. For the isotropic model used here, the diffuse radiation flux incident on an inclined surface decreases with increasing angle of inclination (Eq. (13-9)) because as α increases less sky is visible to the inclined surface (e.g., the ratio is 1/2 for $\alpha = 90^\circ$).

Figure 58 also indicates that daily erythema dose does not change uniformly with inclination angle. For example, at middle latitudes (30–50°N) for $\alpha = 45^\circ$, the daily erythema dose ranges from 75 to 80% of the dose received by a horizontal surface depending upon month and latitude. For a vertical surface ($\alpha = 90^\circ$), the daily erythema dose ranges from 25 to 50% of the dose received by a horizontal surface.

Variations in α also affect the latitudinal gradient of erythema dose. In June the largest changes in the latitudinal gradient occur at middle and low latitudes (Fig. 58a), with the smallest changes occurring poleward of 60°N. Increasing α decreases the latitudinal gradient poleward of the peak dose. In September the latitudinal gradient is almost unchanged at latitudes poleward of 50°N for $\alpha \leq 45^\circ$, but the gradient is reduced by approximately a factor of 2 for $\alpha = 90^\circ$. In December the latitudinal gradient is reduced only slightly for $\alpha \leq 45^\circ$ in northern latitudes.

Figure 59 shows the percent change in erythema dose as a function of latitude for the rotated surface for reductions in total ozone of 10 and 20%. The maximum percent increase in daily erythema dose due to ozone reduction occurs at high latitudes where the average solar zenith angle is largest. The amplification factor on erythema dose ($\Delta \text{dose} / \Delta O_3$) ranges from about 1.4 at low latitudes to over 3 at high latitudes (where the dose is small), the maximum value depending on season. Increasing α decreases the amplification factor at middle and low

Figure 58 Daily total erythema dose in the northern hemisphere for a rotated surface: (a) June 15, (b) September 15, (c) December 15.

Figure 59. Change in daily erythema dose for a rotated surface due to reductions in total ozone of 10 and 20%: (a) June 15, (b) September 15, (c) December 15.

Figure 60. Change in daily erythema dose for a rotated surface with the peak in the action spectrum shifted to 270 nm: (a) June 15, (b) September 15, (c) December 15.

latitudes. This occurs because a change in ozone amount changes the partitioning of energy between the direct and diffuse flux components (see Eqs. (13-3) and (13-4)). In order for a change in partitioning to have an effect on the amplification factor, the direct and diffuse components must be roughly comparable in magnitude, which is only true for small zenith angles. Consequently, the greatest variation in amplification factor occurs at the latitude corresponding to solar declination.

As mentioned earlier, the action spectrum for skin cancer is an unknown function. However, van der Leun and Daniels (1975) argue that the peak in the action spectrum should occur near 270 nm. This is shifted considerably in wavelength from the location of the peak in the erythema action spectrum described by Eq. (13-11), which occurs at 297 nm. In order to test the sensitivity of dose to action spectrum position, the above calculations were repeated

substituting 270 nm for 297 nm in Eq. (13-11). Aside from the expected decrease in dose magnitude, very little changed from the results obtained above. An important exception concerns the fractional change in dose produced by changing ozone amount, which is shown in Fig. 60. Dose amplification factors are significantly higher at middle and low latitudes where the dose is already highest for the action spectrum centered at the shorter wavelength. The minimum amplification factor is now about 2.0 compared with 1.4 for the results shown in Fig. 59. The reason for this increase is related to the ozone absorption cross section, which in the region near 300 nm is a rapidly decreasing function of wavelength. Shifting the action spectrum to shorter wavelengths, where the uv fluxes are more sensitive to variations in ozone amount, leads to larger amplification factors.

3. SATELLITE OZONE DATA: PROCESSING, ARCHIVING, AND ANALYSIS

3.1 Overview

Atmospheric total ozone has considerable temporal variability over a wide variety of geographical scales ranging from as large as the planetary scale to as small as the mesoscale (see e.g. Bojkov and Lovill 1969, Dobson et al. 1927, Dütsch 1969, Heath 1974, London 1963, Lovill 1969, 1970, Lovill and Miller 1968, Miller et al. 1976, Pittcock 1971, and Reinking and Lovill 1971). These variations are postulated to be produced by a number of external as well as internal forcing functions. The effect of external mechanisms (such as sunspot intensity, solar proton events, and solar sector crossings) and internal mechanisms (for example, CFMs, aircraft effluents, volcanic effluents, and transport phenomena) are not well understood presently, due principally to the small total-ozone data set available since the establishment of the world total ozone surface network of Dobson observatories two decades ago. This surface network consists of fewer than 100 presently active total-ozone observatories, principally located in the northern hemisphere and on land masses. Clearly large voids remain in this "Dobson data" network over oceanic areas and in the southern hemisphere.

The advent of the meteorological satellite sensor in the early 1960s brought to the atmospheric sciences the first satellite ozone measurements in 1969. The measurements were taken by the Nimbus 3 and 4 spacecrafts' Infrared Interferometer Spectrometer (IRIS) and Backscatter Ultraviolet (BUV) sensors. Two years' worth of data taken by these sensors has been processed at the present time (Heath 1974, Lovill 1974, Prabhakara et al. 1971). The satellite IRIS sensor provided approximately 30 times as many total ozone observations in a day as the entire surface network could produce in the same time period. Moreover, the satellite data had none of the regional bias inherent in the surface network data (Reiter and Lovill 1974). The analysis of this satellite ozone data has given additional insight into the external and internal mechanisms mentioned earlier.

A new series of meteorological satellite sensors with ozone measurement capability was authorized for deployment in 1976 by the Department of Defense. The first of these sensors (termed a Multifilter Radiometer (MFR)) was launched in September 1976 and began transmission of meteorological data in March 1977.

The Satellite Ozone Analysis Center (SOAC) at Lawrence Livermore Laboratory was formed in August 1976. Its purpose is to produce total ozone data of high quality from measurements taken by the unique cross-track-scanning MFR sensor. This sensor permits areas as small as 39 km in diameter to be resolved for the first time with pole-to-pole coverage (Lovill et al. 1976). The increased data rate of this sensor enables 20 to 30 times as much ozone data to be obtained per day as was obtained by earlier satellite sensors. The initial SOAC effort is directed toward an analysis of the feasibility of obtaining useful data from the MFR ozone sensor. This feasibility study is scheduled for completion by June 1978.

The feasibility study will include a demonstration of the data-conversion technique, which is now being developed, and an assessment of the quality of the ozone data that results. To assess the quality of this satellite ozone data, we will compare it in detail with corresponding Dobson ozone data. We will also analyze the satellite ozone data to determine if it can be assimilated with other atmospheric data for a more complete understanding of the atmospheric general circulation and the delineation of anthropogenic and nonanthropogenic perturbations in the earth's atmosphere.

Data analysis beyond the feasibility study will be needed to show to what extent the SOAC MFR ozone sensor data are of use in (1) initializing numerical models, (2) long-term monitoring of global total ozone for trend analysis, (3) analysis of ozone variation at the meso-scale (which may be possible with the higher resolution of the MFR sensor), (4) analysis of the diurnal variability of total ozone (with a two-satellite ozone sensor system), and (5) integrating with studies under way by the World Meteorological Organization's Global Ozone Monitoring and Research Project (GORMP) and the United Nations Environmental Program's Global Environmental Monitoring (GEM).

The Defense Meteorological Satellite Program (DMSP) spacecraft with the MFR sensors are designed to provide water-vapor and temperature information to the Air Force Global Weather Central (AFGWC) for operational DOD meteorological commitments. After a storage period of less than 24 hours, these data are overwritten in the AFGWC data-base system by new data, and the old data would be lost if they were not archived by SOAC.

A memorandum of agreement was signed in 1976 between Lawrence Livermore Laboratory and the Department of Commerce's Environmental Data Service. Under this agreement the U.S. Air Force will furnish all available MFR data to SOAC. The data provided will be raw spectral radiance values with time and location identification. In addition to converting this raw data to ozone data, SOAC will also transmit the unchanged raw data to the National Climatic Center where it will be archived. From the derived ozone data SOAC will produce daily global total-ozone maps for the Air Force and NOAA.

The ultimate use of the data is to permit the national and international scientific communities to perform research directed toward a more complete understanding of the variability of the ozonosphere. The SOAC study contributes to this end by the integration of several tasks, described separately in the following sections. The SOAC operational plan, which describes the data flow beginning with the initial satellite sensor observation and terminating with the data dissemination and research objectives, is indicated in Fig. 61.

3.2 The Satellite Multifilter Radiometer (MFR) Sensor

SOAC receives spectral radiance data from the MFR sensors via a communication link that allows the satellite data to be telemetered to earth stations in the United States and then retransmitted to a telecommunication geosynchronous satellite, which in turn transmits to the Air Force Global Weather Central in Omaha, Nebraska. These data are then mailed to SOAC (Fig. 61) on magnetic tape.

The cross-track-scanning MFR returns 16 spectral radiance values: one radiance is located at $9.8\text{ }\mu\text{m}$ for ozone absorption, six are located in the $13\text{-to-}15\text{-}\mu\text{m}$ CO_2 band (selected for vertical temperature structure delineation), eight are located between 18 and $29\text{ }\mu\text{m}$ (selected for vertical and total water-vapor distribution), and one channel is at $12\text{ }\mu\text{m}$ for determination of the surface radiance. The channel spectral centers, widths, and noise equivalences are indicated in Table 23. Note that the noise-equivalent spectral radiance (NESR) for the $9.8\text{-}\mu\text{m}$ ozone measurement is only $0.05\text{ erg/sec}\cdot\text{cm}^2\cdot\text{sr}\cdot\text{cm}^{-1}$ (Nichols 1975).

Figure 61. Operational diagram for the Satellite Ozone Analysis Center (SOAC).

Table 23. The cross-track-scanning MFR sensor provides 16 channels of spectral radiance data: one channel for ozone (O_3) at 9.8 μm , one channel for the window at 12.0 μm , six CO_2 channels at 13.4 to 15.0 μm for delineation of the vertical temperature structure, and eight water-vapor channels at 18.7 to 28.3 μm . Tabulated below are the spectral centers, widths, and noise-equivalent spectral radiances (NESRs) for the 16 data channels.

Channel No.	Species detected	Spectral center		Spectral width (cm^{-1})	NESR (10^{-7} $W/cm^2 \cdot sr \cdot cm^{-1}$)
		(μm)	(cm^{-1})		
1	O_3	9.8	1022	12.5	0.05
2	(Window)	12.0	835	8	0.11
3	CO_2	13.4	747	10	0.12
4	CO_2	13.8	725	10	0.11
5	CO_2	14.1	708	10	0.11
6	CO_2	14.4	695	10	0.10
7	CO_2	14.8	676	10	0.09
8	CO_2	15.0	668.5	3.5	0.30
9	H_2O	18.7	535 ^a	16	0.15
10	H_2O	24.5	408.5	12	0.14
11	H_2O	22.7	441.5	18	0.09
12	H_2O	23.9	420	20	0.12
13	H_2O	26.7	374	12	0.18
14	H_2O	25.2	397.5	10	0.16
15	H_2O	28.2	355	15	0.25
16	H_2O	28.3	353.5	11	0.33

^aThis channel is not on the F1 MFR sensor.

The AFGWC provides the 16-channel digitized, calibrated, and earth-located data in an eight-computer-word (36 bits per word) packet for each sensor sample point. There are 25 sample points per cross-track scan, 190 cross-track scans per orbit, and 14.4 orbits per day, giving a total of 67,500 ozone, temperature, and water-vapor measurements each day. The scan geometry of the sensor is given in Fig. 62 (Nichols 1975). At the suborbit point note that the field of view resolved is 39.3 km. This is bet-

ter earth resolution by factors of 3.8 and 2.4, respectively, than given by the IRIS sensors on Nimbus 3 and 4. The instrument data return of 67,500 ozone values per day is 20-30 times that of any previous ozone sensor.

The first of the new series of Air Force meteorological satellite sensors was placed into an 835-km-altitude polar orbit on September 10, 1976. The satellite flight model 1 (F1) was delayed from its originally scheduled launch date until difficulties

Figure 62. Scan geometry for the multifilter radiometer (MFR) cross-track-scanning sensor used to obtain the satellite data from which SOAC will derive global ozone data. Earth projection of the scan is shown (F.O.V. means field of view). All dimensions are in kilometres.

with the on-board computer and upper stage were alleviated. Prelaunch solar panel abnormalities during vibrational testing produced additional delay. The F1 vehicle achieved the predicted near-noon ascending orbit on September 10, but due to malfunction of an attitude-control gas valve within minutes after launch, the spacecraft began to spin about its vertical axis. The combined efforts of a USAF and industry team during the period from September 1976 to March 1977 produced a software telemetry command sequence that eventually permitted stabilization of the spacecraft and allowed data transmission on March 26, 1977. The F1 MFR sensor transmitted CO_2 , H_2O , and O_3 data until September 1977, but postanalysis of the data stream indicated sensor degradation and CO_2 channel failure during the period July 15–29, 1977.

The F2 MFR sensor achieved an 835-km-altitude orbit on June 5, 1977. This sensor orbits with a view near the day-night terminator and a local early-morning ascending orbit. The first MFR data were transmitted from the sensor on July 11, 1977. An F3 MFR sensor will be launched in early 1978. It will be identical to those on the F1 and F2 satellites.

Figure 63 indicates the location of all cross-track-scan total ozone observations over the northern hemisphere taken by the F1 MFR on June 20, 1977. On this date approximately 31,000 observations were made over the northern hemisphere. This is 10% fewer observations than the theoretical maximum of 33,750 over a hemisphere. Note the high density of data over the polar region. It is

theoretically possible to obtain 14 total ozone observations every 24 hours at the highest polar latitudes (an ozone observational rate of once per 1.7 hours). Figures 64 and 65 indicate the optical schematic of the sensor and the data flow, respectively (Nichols 1975). Note that the ozone channel at 1022 cm^{-1} makes six times as many observations as any of the other channels during a given atmospheric sounding.

3.3 Data Quality Control

A SOAC Satellite/Dobson Calibration Program to relate the SOAC satellite ozone data to the Dobson ozone data has been established to provide quality control for the satellite total-ozone observations. SOAC has carefully analyzed the data from the approximately 100 active Dobson stations in the world ozone network and from them has selected a high quality subset to participate in the quality control program. Thirty-three selected Dobson observatories have agreed to participate in the SOAC program (see Fig. 66). These stations were not selected for their geographical location, but on the basis of quality of observation. The Dobson-observatory geographical coverage extends from 90°S to 75°N (Fig. 66). The greatest data density is over North America, Europe, and in the Australian-New Zealand area. As many as five additional observatories may be added to our program

Figure 63 Locations of total ozone observations in the northern hemisphere taken by the MFR on DMSP Satellite F1 on June 20, 1977.

Figure 64 Optical schematic of the ozone, temperature, and water-vapor detectors in the MFR sensor (Nichols 1975).

in 1978, pending the results of the 1977 Boulder Dobson Intercomparison program.

SOAC has obtained NASA/NOAA software for satellite orbit prediction and has modified the coding for specific use. SOAC has an agreement with the NORAD (Colorado Springs) satellite-tracking facility to provide orbital elements of the DMSP satellites. These parameters are used with modified prediction software to produce a prediction of the daily passage of the MFR sensor over each of the Dobson stations participating in the SOAC program. An example of the prediction sent to the participating stations is shown in Fig. 67, indicating the overhead passage time of the MFR sensor for each day of the month for the Dobson observatory in Hohenpeissenberg, Germany.

All observatories in the SOAC Satellite/Dobson Calibration Program network receive the satellite

prediction times at monthly intervals. These observatories have agreed to transmit their total ozone observations at weekly intervals by either telex or air mail. An example of the type of observation taken at a typical observatory by the Dobson spectrophotometer can be seen in Fig. 68. Information from the Hohenpeissenberg observatory includes the total ozone amount (in units of $\text{m} \cdot \text{atm} \cdot \text{cm}$), the background against which the observation was taken, the specific uv wavelength, and the optical air mass. These data from the global SOAC Dobson network are integrated into the SOAC data base continually.

A communique was begun in August 1977 initiating a dialogue between SOAC and the participating Dobson observatories. The communique, referred to as the SOAC Bulletin, is issued at monthly intervals and provides a frequent update to

Figure 65 Flow diagram for data from the ozone, temperature, and water-vapor detectors in the MFR sensor (Nichols 1975).

those in the ozone community interested in learning of research at SOAC and those individuals outside of SOAC interested in communicating their recent results or comments on programs. As an example, the September 1977 SOAC Bulletin was used in part by the World Meteorological Organization (WMO) to communicate to the community the stations that participated in the Dobson intercomparison tests. These instruments were designated in August 1977 as area secondary-standard instruments by the In-

ternational Ozone Commission (IOC), and the WMO in the SOAC Bulletin urged that all Dobson spectrophotometers not participating in the intercomparison should calibrate against the secondary instruments as soon as possible.

In addition to the special Dobson observations taken at the participating observatories, a smaller set of observatories has agreed to launch ozonesondes simultaneous with the passage of the MFR sensor. The first of these simultaneous

Figure 66 Locations of the 33 Dobson observatories that have agreed to participate in the SOAC Satellite/Dobson Calibration Program.

SATELLITE OZONE ANALYSIS CENTER (SOAC)							
ORBITAL PREDICTION TIMES FOR SATELLITE OZONE SENSOR (F2)							
HOHENPEISSENBERG (47 08N - 11 01E)							
TIMES: GREENWICH MEAN TIME							
OCT 1977							
TIME 1				TIME 2			
DATE	HR	MIN	SEC	DATE	HR	MIN	SEC
1	4	41	21.86	1	6	20	0.79
2	6	4	5.69	2	0	0	0.
3	5	47	10.97	3	0	0	0.
4	5	31	16.04	4	0	0	0.
5	5	14	21.08	5	0	0	0.
6	4	57	26.10	6	0	0	0.
7	4	41	31.11	7	20	10	04
8	4	4	15.03	8	0	0	0.
9	4	47	19.98	9	0	0	0.
10	5	30	24.94	10	0	0	0.
11	5	14	29.88	11	0	0	0.
12	4	57	34.79	12	0	0	0.
13	4	41	39.68	13	6	20	18.60
14	6	4	23.48	14	0	0	0.
15	5	47	28.33	15	0	0	0.
16	5	30	33.17	16	0	0	0.
17	5	14	37.99	17	0	0	0.
18	4	57	42.78	18	0	0	0.
19	4	41	47.57	19	6	20	28.49
20	6	4	31.25	20	0	0	0.
21	5	47	35.99	21	0	0	0.
22	5	30	40.72	22	0	0	0.
23	5	14	45.43	23	0	0	0.
24	4	57	50.11	24	0	0	0.
25	4	41	54.79	25	20	30	69
26	6	4	38.34	26	0	0	0.
27	5	47	42.97	27	0	0	0.
28	5	30	47.58	28	0	0	0.
29	5	14	52.18	29	0	0	0.
30	4	57	56.76	30	0	0	0.
31	4	42	1.31	31	6	20	40.21

Figure 67 Example of the predictions supplied to each participating Dobson observatory of the times when the satellite will be overheard. This printout shows the predicted passage times for DMSP Satellite F1 over the Dobson observatory in Hohenpeissenberg, Germany, for the month of October 1977.

results is shown in Fig. 69. This is for a high-altitude, low-pressure case. Smoothing has been achieved using a triangular slit function. This phase of development determined which spectral intervals could be processed using the band model and which required the line-by-line integration technique.

The second stage of technique development was focused toward the selection of high-quality vertical ozone data, well distributed both by latitude and season. The selection was made, for example, from 12 ozonesonde soundings in Antarctica and 12 from Northern Canada (high-latitude cases), 12 ozonesonde soundings from Panama (tropical set),

and 12 ozonesonde soundings from Hohenpeissenberg (middle-latitude location). These soundings are assimilated together and run against the band model and line-by-line calculations to produce a variety of multilevel, multilatitude models.

Approximately 6000 ozonesondes are archived in the SOAC data base. These consist of data from numerous observatories around the world that began taking vertical ozone soundings in the early 1960s. A large number of these soundings are utilized to generate statistics for regression and eigenvector analyses with various seasonally and latitudinally dependent distributions.

Figure 70. The SOAC global ozone data will be presented in a form similar to the above plot, which shows the average distribution of total ozone from April 19 to July 21, 1969, for the northern hemisphere. Shading represents total ozone values less than 240 m-atm-cm (Lovill 1974).

The final stage of the technique development will involve generation of large samples of simulated measurements for the desired MFR channels through the use of transmittances for individual profiles of atmospheric gases and temperature, and the development of the statistical regression equations relating the measurements to total ozone.

3.5 Data Analysis

A computer spline analysis will be performed on the approximately 68,000 final processed total-

ozone values obtained daily. The data will be displayed in a graphical form similar to that shown in Fig. 70 and will also be tabulated in a global 2° grid. Processed ozone values with spatial and temporal locations will be available on tape to all interested agencies. A master software program is being written which will sequentially run the six programs involved in the data calibration, processing, quality control, and spline analyses in a production mode.

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APPENDIX A

CHANGES TO THE 1-D TRANSPORT-KINETICS MODELS

In the past year a number of changes have occurred in the series of theoretical models used at LLL to study tropospheric and stratospheric chemistry. These changes are discussed below.

1. Code Development

The 1-D transport-kinetics models for diurnal and time-dependent calculations have been redesigned to increase user efficiency. Whereas we formerly had to choose from one of three different codes to calculate an atmosphere, selecting the code according to the assumed level of chlorine in the atmosphere—zero chlorine, or background chlorine (due to CH_3Cl and CCl_4), or levels of chlorine predicted on the basis of prescribed growth rates for F-11 and F-12—we now have a single code that handles all three cases. The user decides at the beginning of a run which case to be used. I/O (input/output) efficiency was also improved in the redesigned code. These improvements have decreased the amount of user and computer time necessary to set up and perform a calculation.

In addition, a new code was developed which takes chemical equations and puts them into the forms required by the model. This code makes future changes to model chemistry much simpler.

2. Chemistry Changes

Table A-1 shows kinetic rate changes that have occurred in the past year as well as a comparison with the chemistry used in 1973 and 1974 (as discussed in Section 2.7 on the effect of past nuclear tests). One reaction presently included in recent model calculations (i.e., Section 2.9) is the pressure-dependent rate for $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$, 7.3×10^{-33} . In addition, the absorption cross sections for H_2O_2 and HCl were modified to the recommended values in Hudson (1977).

3. Boundary Conditions

Due to changes in model chemistry (especially changes in rate coefficients for $\text{HO}_2 + \text{NO}$ and $\text{CO} + \text{OH}$), the lower boundary conditions for some of the species in the model have changed. New surface values (in molecules/ cm^3) for some of the more important species are listed below:

NO_2	2.3×10^9 (<0.1 ppb)
NO	9.0×10^8
OH	1.5×10^6
O_3	9.7×10^{11}
H_2O_2	7.0×10^{10}
HO_2	2.7×10^8
N_2O	8.2×10^{12}
HNO_3	1.6×10^{10}
CH_4	3.34×10^{13}
HCl	2.55×10^{10}

Heterogeneous removal of H_2O_2 at altitudes from the surface to 8 km with a lifetime of five days is now included in the model. Previously, such removal processes were included for only NO_2 , HNO_3 , and HCl .

4. Physical Improvements

Multiple scattering is now an integral part of the model and is included in all calculations. Diurnal averaging is also now included in the model as standard procedure for future calculations.

Table A-1. Changes from 1973 through 1977 in chemical rate constants used in LLL computer simulations to study tropospheric and stratospheric chemistry. Asterisk (*) indicates multiple scattering effects are included, N.I. indicates the reaction is not included in the model. QJ's are photodissociation rate coefficients.

Reaction	Rate 1977	Rate 1976	Rate 1974	Rate 1973
$O_2 + h\nu \rightarrow O + O$	QJ(1)*	QJ(1)	Same	QJ(1) $\times$ 2
$O_3 + h\nu \rightarrow O + O_2$	QJ(2)*	QJ(2)	Same	QJ(2) $\times$ 2
$O_3 + h\nu \rightarrow O(^1D) + O_2$	QJ(3)*	QJ(3)	Same	QJ(3) $\times$ 2
$O + O_2 + M \rightarrow O_3 + M$	$1.10 \times 10^{-34} \exp(510/T)$	$1.07 \times 10^{-34} \exp(510/T)$	Same	Same
$O + O_3 \rightarrow 2O_2$	$1.9 \times 10^{-11} \exp(-2300/T)$	Same	Same	Same
$NO_2 + h\nu \rightarrow NO + O$	QJ(4)*	QJ(4)	Same	QJ(4) $\times$ 2
$O_3 + NO \rightarrow NO_2 + O_2$	$2.1 \times 10^{-12} \exp(-1450/T)$	$9.0 \times 10^{-13} \exp(-1200/T)$	Same	Same
$O + NO_2 \rightarrow NO + O_2$	9.4×10^{-12}	Same	Same	Same
$N_2O + h\nu \rightarrow N_2 + O(^1D)$	QJ(5)*	QJ(5)	Cross sections were larger	QJ(5) $\times$ 2 (larger cross sections)
$N_2O + O(^1D) \rightarrow N_2 + O_2$	5.5×10^{-11}	7×10^{-11}	1.1×10^{-10}	6.6×10^{-11}
$N_2O + O(^1D) \rightarrow 2NO$	5.5×10^{-11}	7×10^{-11}	1.1×10^{-10}	6.6×10^{-11}
$NO + h\nu \rightarrow N + O$	QJ(6)	QJ(6)	Same	QJ(6) $\times$ 2
$N + O_2 \rightarrow NO + O$	$5.5 \times 10^{-12} \exp(-3220/T)$	$1.1 \times 10^{-14} T \exp(-3150/T)$	Same	$1.02 \times 10^{-14} T \exp(-3130/T)$
$N + NO \rightarrow N_2 + O$	$8.2 \times 10^{-11} \exp(-410/T)$	2.7×10^{-11}	Same	$5.1 \times 10^{-11} \exp(-170/T)$
$O(^1D) + H_2O \rightarrow 2OH$	2.3×10^{-10}	2.1×10^{-10}	3.5×10^{-10}	2.8×10^{-10}
$O(^1D) + CH_4 \rightarrow OH + CH_3$	1.3×10^{-10}	Same	4.0×10^{-10}	2.4×10^{-10}
$HNO_3 + h\nu \rightarrow OH + NO_2$	QJ(7)*	QJ(7)	Same	QJ(7) $\times$ 2
$O_3 + OH \rightarrow HO_2 + O_2$	$1.5 \times 10^{-12} \exp(-1000/T)$	$1.6 \times 10^{-12} \exp(-1000/T)$	Same	$1.3 \times 10^{-12} \exp(-956/T)$
$O + OH \rightarrow O_2 + H$	4.2×10^{-11}	Same	Same	Same
$O_3 + HO_2 \rightarrow OH + 2O_2$	$1.0 \times 10^{-13} \exp(-1250/T)$	Same	Same	$1.0 \times 10^{-12} \exp(-1875/T)$
$O + HO_2 \rightarrow OH + O_2$	3×10^{-11}	Same	$8 \times 10^{-11} \exp(-500/T)$	1.0×10^{-11}
$H + O_2 + M \rightarrow HO_2 + M$	$2.08 \times 10^{-32} \exp(+290/T)$	Same	Same	$1.1 \times 10^{-32} \exp(407/T)$
$O_3 + H \rightarrow OH + O_2$	$1.23 \times 10^{-10} \exp(-562/T)$	Same	2.6×10^{-11}	2.6×10^{-11}
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$1.7 \times 10^{-11} \exp(-500/T)$	Same	$3 \times 10^{-11} \exp(-500/T)$	$3 \times 10^{-11} \exp(-500/T)$
$HO_2 + OH \rightarrow H_2O + O_2$	2×10^{-11}	Same	2×10^{-10}	2×10^{-10}
$OH + NO_2 + M \rightarrow HNO_3 + M$	Parameterization of Tsang et al. (1971)	$2.76 \times 10^{-13} \exp(880/T)$ $1.166 \times 10^{18} \exp(222/T) + M$	4×10^{-11} $1.12 \times 10^{18} + M$	10^{-11} $1.5 \times 10^{20} \exp(-750/T) + M$
$OH + HNO_3 \rightarrow H_2O + NO_3$	8.9×10^{-14}	Same	1.3×10^{-13}	1.3×10^{-13}
$H_2O_2 + h\nu \rightarrow 2OH$	QJ(8)*	QJ(8)	Same	Same
$H_2O_2 + OH \rightarrow H_2O + HO_2$	$1.0 \times 10^{-11} \exp(-750/T)$	$1.7 \times 10^{-11} \exp(-910/T)$	Same	Same
$N_2 + O(^1D) + M \rightarrow N_2O + M$	3.5×10^{-37}	2.8×10^{-36}	Same	Same

Table A-1. (Continued)

Reaction	Rate 1977	Rate 1976	Rate 1974	Rate 1973
$N + NO_2 \rightarrow N_2O + O$	2×10^{-11} exp(-800/T)	1.4×10^{-12}	9×10^{-12}	9×10^{-12}
$NO + O + M \rightarrow NO_2 + M$	1.6×10^{-32} exp(+584/T)	3.96×10^{-33} exp(940/T)	Same	N.I.
$NO + HO_2 \rightarrow NO_2 + OH$	4.28×10^{-11} exp(-500/T)	2.0×10^{-13}	Same	N.I.
$H_2 + O(^1D) \rightarrow OH + H$	9.9×10^{-11}	2.9×10^{-10}	Same	N.I.
$OH + OH \rightarrow H_2O + O$	1.0×10^{-11} exp(-550/T)	Same	Same	N.I.*
$N + O_3 \rightarrow NO + O_2$	5×10^{-12} exp(-650/T)	5.7×10^{-13}	Same	N.I.*
$NO_2 + O_3 \rightarrow NO_3 + O_2$	1.2×10^{-13} exp(-2450/T)	Same	1.23×10^{-13} exp(-2470/T)	N.I.
$HO_2 + hv \rightarrow OH + O$	Q(9)*	Q(9)	N.I.	N.I.
$OH + CH_4 \rightarrow H_2O + CH_3$	2.36×10^{-12} exp(-1710/T)	Same	N.I.	N.I.*
$OH + OH + M \rightarrow H_2O_2 + M$	1.2×10^{-32} exp(900/T)	2.5×10^{-33} exp(2500/T)	N.I.	N.I.
$H_2O_2 + O \rightarrow OH + HO_2$	2.75×10^{-12} exp(-2125/T)	Same	N.I.	N.I.
$O + CH_4 \rightarrow OH + CH_3$	3.5×10^{-11} exp(-4550/T)	Same	N.I.	N.I.
$CO + OH \rightarrow H + CO_2$	1.4×10^{-13}	Same	N.I.	N.I.*
$O(^1D) + M \rightarrow O + M$	2.2×10^{-11} exp(+99/T)	2.2×10^{-11} exp(92/T)	5.95×10^{-11}	3.2×10^{-11} *
$NO_3 + hv \rightarrow NO_2 + O$	10^{-1}	10^{-1}	0.	0.
$NO_3 + hv \rightarrow NO + O_2$	4×10^{-2}	5×10^{-2}	1.	1.
$N + NO_3 \rightarrow 2NO$	N.I.	N.I.	6×10^{-12}	6×10^{-12}
$NO + NO_3 \rightarrow 2NO_2$	8.7×10^{-12}	N.I.	N.I.	N.I.
$NO_2 + O + M \rightarrow NO_3 + M$	1.0×10^{-31}	N.I.	N.I.	N.I.
$NO_2 + NO_3 \rightarrow NO + O_2 + NO_2$	2.0×10^{-13}	N.I.	N.I.	N.I.
$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$	2.92×10^{-12}	N.I.	N.I.	N.I.
$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$	$7 \times 10^{+21}$ exp(-2670/T) + M			
	$6.0 \times 10^{+14}$ exp(-1070/T)	N.I.	N.I.	N.I.
$N_2O_5 + O \rightarrow 2NO_2 + O_2$	$7.0 \times 10^{+21}$ exp(-2670/T) + M			
$N_2O_5 + H_2O \rightarrow 2HNO_3$	1.0×10^{-14}	N.I.	N.I.	N.I.
$N_2O_5 \rightarrow 2NO_2 + O$	1.0×10^{-20}	N.I.	N.I.	N.I.
$Cl + O_3 \rightarrow ClO + O_2$	Q(10)*	N.I.	N.I.	N.I.
$Cl + O_3 \rightarrow ClO + O_2$	2.7×10^{-11} exp(-257/T)	2.97×10^{-11} exp(-243/T)	(No ClX reactions were included in 1973 or 1974 chemistries)	
$Cl + OClO \rightarrow 2ClO$	5.9×10^{-11}	Same	N.I.	N.I.
$Cl + O_2 + M \rightarrow ClO_2 + M$	N.I.	1.7×10^{-13} exp(300/T)	N.I.	N.I.
$Cl + CH_4 \rightarrow HCl + CH_3$	7.3×10^{-12} exp (-1260/T)	5.4×10^{-12} exp(-1133/T)	N.I.	N.I.

Table A-1. (Continued)

Reaction	Rate 1977	Rate 1976	Rate 1974	Rate 1973
$\text{Cl} + \text{ClO}_2 \rightarrow \text{Cl}_2 + \text{O}_2$	N.I.	5.0×10^{-11}		
$\text{Cl} + \text{ClO}_2 \rightarrow 2\text{ClO}$	N.I.	1.4×10^{-12}		
$\text{Cl} + \text{NO} + \text{M} \rightarrow \text{ClNO} + \text{M}$	N.I.	$1.7 \times 10^{-32} \exp(553/T)$		
$\text{Cl} + \text{ClNO} \rightarrow \text{Cl}_2 + \text{NO}$	N.I.	3.0×10^{-11}		
$\text{Cl} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}$	$6.9 \times 10^{-34} \exp(+2115/T)$	Same		
$\text{Cl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{NO}_2$	3×10^{-12}	Same		
$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$	$7.7 \times 10^{-11} \exp(-130/T)$	5.3×10^{-11}		
$\text{NO} + \text{ClO} \rightarrow \text{NO}_2 + \text{Cl}$	2.2×10^{-11}	$2.6 \times 10^{-11} \exp(-50/T)$		
$\text{ClO} + \text{O}_3 \rightarrow \text{ClO}_2 + \text{O}_2$	$1.0 \times 10^{-12} \exp(-4000/T)$	$1.0 \times 10^{-12} \exp(-2763/T)$		
$\text{ClO} + \text{O}_3 \rightarrow \text{OCIO} + \text{O}_2$	$1.0 \times 10^{-12} \exp(-4000/T)$	$1.0 \times 10^{-12} \exp(-2763/T)$		
$\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}$	$5.1 \times 10^{-33} \exp(+1030/T)$	Same		
$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{OCIO}$	$2.1 \times 10^{-12} \exp(-2200/T)$	$2.0 \times 10^{-12} \exp(-2300/T)$		
$\text{ClO} + \text{ClO} \rightarrow 2\text{Cl} + \text{O}_2$	$1.5 \times 10^{-12} \exp(-1230/T)$	$2.0 \times 10^{-13} \exp(-1260/T)$		
$\text{HCl} + \text{O}(^1\text{D}) \rightarrow \text{Cl} + \text{OH}$	1.4×10^{-10}	2×10^{-10}		
$\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$	$3.0 \times 10^{-12} \exp(-425/T)$	$2 \times 10^{-12} \exp(-310/T)$		
$\text{O} + \text{HCl} \rightarrow \text{OH} + \text{Cl}$	$1.14 \times 10^{-11} \exp(-3370/T)$	$1.75 \times 10^{-12} \exp(-2273/T)$		
$\text{O} + \text{OCIO} \rightarrow \text{ClO} + \text{O}_2$	$2 \times 10^{-11} \exp(-1100/T)$	5.0×10^{-13}		
$\text{NO} + \text{OCIO} \rightarrow \text{NO}_2 + \text{ClO}$	3.4×10^{-13}	Same		
$\text{N} + \text{OCIO} \rightarrow \text{NO} + \text{ClO}$	6.0×10^{-13}	Same		
$\text{H} + \text{OCIO} \rightarrow \text{OH} + \text{ClO}$	5.7×10^{-11}	Same		
$\text{Cl} + \text{OH} \rightarrow \text{HCl} + \text{O}$	$1.0 \times 10^{-11} \exp(-2970/T)$	$2.0 \times 10^{-12} \exp(-1878/T)$		
$\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2$	3×10^{-11}	Same		
$\text{Cl} + \text{HNO}_3 \rightarrow \text{HCl} + \text{NO}_3$	$1.0 \times 10^{-11} \exp(-2170/T)$	$4.0 \times 10^{-12} \exp(-1500/T)$		
$\text{ClONO}_2 + \text{O} \rightarrow \text{ClO} + \text{NO}_3$	$4.5 \times 10^{-12} \exp(-840/T)$	Same		
$\text{ClO}_2 + \text{HO}_2 \rightarrow \text{HCl} + 2\text{O}_2$	N.I.	3.0×10^{-12}		
$\text{CH}_3\text{Cl} + \text{OH} \rightarrow \text{Cl} + \text{H}_2\text{O} + \text{HO}_2$	$2.2 \times 10^{-12} \exp(-1142/T)$	Same		
$\text{CH}_3\text{Cl} \rightarrow 2\text{HO}_2 + \text{CO} + \text{Cl}$	QCJ(1)*	QCJ(1)		
$\text{HCl} + h\nu \rightarrow \text{H} + \text{Cl}$	QCJ(2)*	QCJ(2)		
$\text{ClONO}_2 \rightarrow \text{ClO} + \text{NO}_2$	QCJ(3)*	QCJ(3)		
$\text{ClO} + h\nu \rightarrow \text{Cl} + \text{O}$	QCJ(4)*	QCJ(4)		
$\text{ClO} + h\nu \rightarrow \text{Cl} + \text{O}(^1\text{D})$	QCJ(5)*	QCJ(5)		
$\text{ClONO}_2 + h\nu \rightarrow \text{Cl} + \text{NO}_2$	QCJ(7)*	QCJ(7)		

Table A-1. (Continued)

Reaction	Rate 1977	Rate 1976	Rate 1974	Rate 1973
$\text{OCIO} + h\nu \rightarrow \text{ClO} + \text{O}(^1\text{D})$	QC(8)	QC(8)		
$\text{OCIO} + h\nu \rightarrow \text{ClO} + \text{O}$	QC(9)*	QC(9)		
$\text{CF}_2\text{Cl}_2 + h\nu \rightarrow 2\text{Cl}$	QC(10)*	QC(10)		
$\text{CFCl}_3 + h\nu \rightarrow 2.5\text{Cl}$	QC(11)*	QC(11)		
$\text{CCl}_4 + h\nu \rightarrow 2\text{Cl}$	QC(12)*	QC(12)		
$\text{CFCl}_3 + \text{O}(^1\text{D}) \rightarrow 2\text{Cl}$	2.3×10^{-10}	3.0×10^{-10}		
$\text{CF}_2\text{Cl}_2 + \text{O}(^1\text{D}) \rightarrow 2\text{Cl}$	2.0×10^{-10}	2.5×10^{-10}		
$\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$	4.7×10^{-11} exp(-2340/T)	5.7×10^{-11} exp(-2400/T)		
$\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{HCl} + \text{HO}_2$	1.6×10^{-12} exp(-384/T)	1.0×10^{-11} exp(-810/T)		

APPENDIX B

BIBLIOGRAPHY OF PUBLICATIONS PRODUCED IN LLL'S WORK ON THE HIGH ALTITUDE POLLUTION PROGRAM

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Effect of Receiver Orientation on Erythema Dose

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EFFECT OF RECEIVER ORIENTATION ON ERYTHEMA DOSE*†

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Abstract—The analysis of solar erythema dose under changing ozone amount, previously confined to the study of horizontal surfaces, is extended to include the effects of receiver orientation. A semi-empirical model is used to calculate erythema (sunburn) dose for non-horizontal plane areas under cloudless conditions as a function of latitude, season, and ozone amount. According to the model, in middle and high latitudes, surfaces with inclination angles (α) up to 45° receive at least 80% of the daily erythema dose received by a horizontal surface. Much larger reductions in daily erythema dose occur for $\alpha > 45^\circ$, which can result in a significant reduction in the latitudinal gradient of erythema dose. The amplification factor for erythema dose ($\Delta\text{dose}/\Delta\text{O}_3$) varies significantly with latitude, but it is only weakly dependent upon receiver orientation. Additional calculations indicate that the amplification factor may be significantly larger for skin cancer than for erythema.

INTRODUCTION

In recent years, considerable effort has been expended in an attempt to gain a more complete understanding of the physics and chemistry of the stratosphere. Among the more significant findings is the conclusion that man-made pollutants may represent potential threats to the amount of ozone present in the stratosphere (National Research Council, 1976a). Because reductions in total ozone would permit greater amounts of ultra-violet (UV) radiation to reach the surface of the earth (Cutchis, 1974; Halpern *et al.*, 1974), a number of studies have been performed with the goal of assessing biological sensitivity to ozone-induced changes in UV radiation (National Research Council, 1973). One branch of these studies has been concerned with the impact of increased UV radiation on human beings, the principal effects being increased occurrence of skin cancer (Urbach, 1969; Giese, 1968) and increased vitamin D production (Leach *et al.*, 1976). One approach has been to correlate skin cancer incidence data directly with ozone layer thickness. The possible influence of such factors as duration of

sunlight, clothing and exposure habits, and optical path length have been considered (McDonald, 1971; van der Leun and Daniels, 1975). Another approach has been to explicitly consider the dose of UV radiation received as a function of ozone amount and other climatic variables (Green and Mo, 1975). The radiation dose is then related to cancer incidence after weighting by a wavelength dependent function accounting for variation in radiation efficacy. This second approach, though less direct, is appealing because the mechanism of cancer production is more fully represented, and it allows for experimentation with combinations of independent variables outside the rather narrow range of reliable observation.

As the first step in this approach, Green and co-workers developed a semi-empirical model for calculating UV radiation at the surface of the earth in the spectral region 280–340 nm (Green *et al.*, 1974a, b; Mo and Green, 1974). They have calculated erythema (sunburn) dose as a function of total ozone, solar zenith angle, latitude, season, and cloud amount. Their model was also used in the Climatic Impact Assessment Program's analysis of ozone depletion (Green *et al.*, 1975).

One feature of this model, and UV dosimetry in general (Berger *et al.*, 1975), is that the receiver is assumed to be horizontal. The geometry of humans, however, is such that the majority of exposed skin would normally be in a non-horizontal position. In fact, the horizontal projection of an upright person amounts to only a few percent of total surface area (Fanger, 1970).

The report of the National Research Council (1976a) summarizes the specific sites of origin of primary melanoma skin cancer. The data show the predominant localization of sites of origin to areas of the skin that are constantly exposed, such as the

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trunk and legs of males. These are, in general, non-horizontal surfaces which suggests that receiver orientation should be considered in the study of UV dose.

The effect of receiver orientation on incident solar radiation is routinely included in studies of building heating load (e.g. Kasuda, 1973) and human comfort (Morgan, 1972; Burt, 1976). Orientation has also been investigated directly in connection with south-facing plane areas (Dave *et al.*, 1975) and human beings (Terjung and Louie, 1970) using the entire solar spectrum. The purpose of this work is to determine the significance of receiver orientation (inclination angle and azimuth angle) on the solar flux dose received in the wavelength region responsible for sunburn and skin cancer. The effects on erythema dose are considered for different latitudes and seasons, and variations in total ozone and in the erythema weighting curve are also included.

MODEL DESCRIPTION

The procedure employed here involves using the Green model (Green *et al.*, 1974a) to obtain total local UV radiation ($Q_t + q_d$) as a function of wavelength (λ) and solar zenith (θ). Valid for clear sky conditions, it is essentially a Beer-Bouguer formulation for both direct beam (Q_b) and diffuse (q_d) radiation. It is assumed that the latter is isotropically distributed. These fluxes are determined using the relationships

$$Q_b(\theta, \lambda) = H(\lambda) V^2 \exp(-A_b(\theta, \lambda) \cos \theta) \quad (1)$$

and

$$q_d(\theta, \lambda) = H(\lambda) V^2 \exp(-D_b(\theta, \lambda)) \quad (2)$$

where $H(\lambda)$ is the extra-terrestrial solar irradiance at the mean earth-sun distance (taken from Howard *et al.*, 1960). The symbol V , which does not appear in the Green model, is the ratio of mean earth-sun distance to that distance on a particular day. It thus allows for eccentricity in the earth's orbit, which causes variations in the extra-terrestrial flux of $\pm 3.5\%$.

The terms A_b and D_b are optical thickness functions accounting for the presence of ozone, air, and particulate matter, and they are given by Green *et al.* (1974a). For the spectral region considered here, the total ozone optical depth is of special interest.

To calculate the direct beam radiation incident on an inclined surface (Q_p), it is necessary to replace θ in Eq. 1 with the angle between the position of the sun and a line normal to the surface (i).

$$Q_p(\theta, \lambda) = H(\lambda) V^2 \exp(-A_b(\theta, \lambda) \cos i) \quad (3)$$

where

$$\cos i = \cos \alpha \cos \theta + \sin \alpha \sin \theta \cos(a - \alpha') \quad (4)$$

Here α' is the solar azimuth (relative to north), α is the azimuth of the receiver, and α is the angle of the receiver's inclination (relative to horizontal). For a horizontal receiver, $\alpha = 0$. Equations required to find θ and α' as a function of latitude, season, and time of day may be found in Dave *et al.* (1975), Sellers (1965) or the Smithsonian Meteorological Tables (List, 1958). The last reference also contains tabulated values of V .

Diffuse radiation incident on an inclined surface has two components: that arriving from the sky as scattered radiation (q_s) and that reflected from the earth's surface (q_r).

Under the assumption of isotropic reflection and the earlier assumption of isotropic atmospheric scattering, these quantities are given by (Dave *et al.*, 1975):

$$q_s(\theta, \lambda) = \frac{1}{2} q_d(\theta, \lambda) (1 + \cos \alpha) \quad (5)$$

$$q_r(\theta, \lambda) = r/2 [Q_b(\theta, \lambda) + q_d(\theta, \lambda)] (1 - \cos \alpha) \quad (6)$$

The ground reflectivity r is small for surfaces other than snow and ice at UV wavelengths (Kondratyev, 1973). A value of 0.1 was chosen here for r .

The sum $Q_p + q_s + q_r$ represents the total radiation incident per unit area on a plane inclined at an angle and with azimuth α . Because radiation is not equally efficient at all wavelengths in producing a biologic response, it is not possible to integrate incident radiation directly over wavelength and obtain a meaningful measure of skin tissue insult. It is necessary to know the relative response of skin to UV radiation as a function of wavelength. In the case of sunburn, the so-called action spectrum (or erythema efficiency) has been studied using UV lamps (e.g. Coblenz and Stair, 1934; Mangus, 1964; Cripps and Ramsey, 1970) and can be represented by (Green *et al.*, 1974b):

$$\epsilon(\lambda) = \left[4 \exp\left(\frac{\lambda - 297}{3.21}\right) \right] \left[1 + \exp\left(\frac{\lambda - 297}{3.21}\right) \right]^{-2} \quad (7)$$

The action spectrum for skin cancer in humans is not known: it is usually assumed to be the same as for erythema or similar to the DNA action spectrum (Setlow, 1974).

PROCEDURE AND RESULTS

Equations 4-7 may be used to calculate the instantaneous erythema dose for any time of day, date, latitude, ozone amount and receiver position. In analyzing the effects of receiver orientation, we have numerically integrated over wavelength and time to produce daily erythema doses for Northern Hemisphere latitudes assuming the receiver is stationary. Integrations were performed for the 15th day of each month using a time step of approximately 20 min. The total ozone was specified as a function of latitude based on data from the Nimbus III satellite reported by Lovill (1972). The values of total ozone used in the calculation are shown in Table 1. Ozone reductions of 10 and 20% were also considered in the calculations.

The azimuth of the receiver was specified in two ways. First, to obtain a measure of the upper bound on erythema dose at middle latitudes in the Northern Hemisphere, the receiver was held fixed in a south-facing position. Second, to estimate the average dose for a population where there is random orientation (i.e. no preferred orientation), calculations were made while averaging over azimuth angle (a rotated receiver). Doses were computed at 20° intervals in the azimuth angle, and the average of these was used for integration. The inclination angle was held fixed at values of 0°, 45°, and 90°. Introducing time dependence for this term would require modeling specific body sites and activities; we have chosen to present more general calculations.

Figure 1 shows the daily total erythema dose for a south-facing surface as a function of latitude in the Northern Hemisphere for different ozone amounts and receiver inclinations for the 15th day of June

Effect of receiver orientation on dose

Table 1. Values of total ozone in atm. cm.

Months	EQ	10	20	30	Latitude ($^{\circ}$ N)				
					40	50	60	70	80
June	0.256	0.259	0.274	0.295	0.326	0.362	0.391	0.400	0.410
September	0.249	0.246	0.262	0.295	0.316	0.344	0.364	0.372	0.378
December	0.256	0.256	0.273	0.303	0.334	0.366	0.393	0.399	0.402

September and December. The relationship between dose magnitude and inclination is such that inclined surfaces generally receive a less daily integrated dose than a horizontal surface at the same latitude. Exceptions to this occur in some low sun situations (large θ) where the dose on the inclined, south-facing surface slightly exceeds that of the horizontal surface (e.g. $\alpha = 45^{\circ}$, 50–60 $^{\circ}$ N in September and $\alpha = 45^{\circ}$ 20–30 $^{\circ}$ N in December). This result is in contrast to the study of Dave *et al.* (1975) using the full solar spectrum where the total radiation on south-facing surfaces was shown to grow larger than that received by a horizontal surface at high latitudes. At the wavelengths contributing to erythema, the radiation is predominantly diffuse. Consequently, the angle of incidence does not exert as strong an influence as it would when the radiation is predominantly in the direct beam, as was the case in the study by Dave *et al.* (1975).

Figure 1 also indicates that the daily erythema dose does not change uniformly with inclination angle. For example, changing α from 0 to 45 $^{\circ}$ results in less change in the daily erythema dose than results from changing α from 45 $^{\circ}$ to 90 $^{\circ}$.

Variations in α affect the latitudinal gradient of erythema dose. Increasing α decreases the latitudinal gradient in erythema dose poleward of the peak dose. There is a small reduction in the gradient for $\alpha = 45^{\circ}$ as compared to $\alpha = 0^{\circ}$, but the gradient is reduced by approximately half for $\alpha = 90^{\circ}$.

For a horizontal surface, the latitude of the peak daily erythema dose corresponds closely to the solar declination angle. As α increases there is a poleward shift in the latitude of the peak dose. In June, for

example, as α is changed from 0 to 90 $^{\circ}$, the latitude of peak dose moves from 20 $^{\circ}$ N to approximately 40 $^{\circ}$ N. A shift of similar magnitude occurs in September. This shift is the result of several factors.

The inclination angle affects the amount of direct solar flux received by the inclined surface. At latitudes equatorward of the latitude of solar declination, increasing α results in a decrease in the direct solar flux. At higher latitudes there may be either an increase or a decrease depending on the value of α .

Figure 1. Daily total erythema dose for a south-facing surface as a function of latitude, inclination angle α , and ozone amount: (a) June 15, (b) September 15, and (c) December 15.

As already mentioned, the contribution to erythema dose due to diffuse radiation has two components: that arriving from the sky (Eq. 5) and that reflected from the earth's surface (Eq. 6). An inclined surface receives less diffuse radiation from the sky with increasing angle of inclination because less sky is visible. For example, a vertical surface receives half the flux of that received by a horizontal surface assuming isotropic diffuse radiation. On the other hand, as α increases, there is an increase in the diffuse flux component from the earth's surface. This flux

component is generally small, however, because of the low surface albedo assumed.

The net result of the various factors just discussed is that there is a change in the partitioning of the direct and diffuse flux contributions to erythema dose as α is varied. This is illustrated for a south-facing surface in Fig. 2 which shows the fraction of the total erythema dose due to the diffuse flux (sky plus ground reflection). In low sun situations (e.g. at high latitude), increasing α causes a decrease in the diffuse fraction of the total erythema dose, whereas the opposite is true in the case of a high sun (small θ).

Figure 3 shows the daily erythema dose for a rotated, inclined surface as a function of latitude for the same values of total ozone as used in Fig. 1. The dose received by the rotated surface never exceeds that for a horizontal surface, whereas it is possible at times for a south-facing, inclined surface to receive a slightly greater dose than the horizontal surface.

There is not a poleward shift in the latitude of the peak erythema dose with increasing α as was the case for the south-facing surface. Under the assumption of isotropic diffuse radiation, the contribution to erythema doses due to the total diffuse flux is the same for both the south-facing and rotated surfaces for a given α and latitude. Consequently, differences between Figs. 1 and 3 are due to differences in the direct flux component. The direct flux component is generally larger for the rotated surface than for the south-facing surface at latitudes near the equator, and the converse is true at high latitudes. In middle latitudes (30–50°N), the daily erythema dose is smaller for the rotated surface than for the south-facing surface.

Figure 4 shows the daily erythema dose averaged over a year for a south-facing surface assuming cloudless conditions. In middle latitudes, the daily average erythema dose on a surface with $\alpha = 45^\circ$ ranges from 90 to 96% of the dose on a horizontal surface. The dose is significantly less for inclination angles greater than 45° .

Figure 5 shows the daily erythema dose averaged over a year for a rotated surface. In this case the daily average erythema dose in middle latitudes on a surface with $\alpha = 45^\circ$ is approximately 83% of the dose on a horizontal surface. At higher latitudes the dose in the rotated surface is significantly less than that on the south-facing surface.

A semilog scale is used in Figs. 4 and 5 in order to demonstrate the effect of inclination angle on the doubling distance for erythema dose. In middle latitudes the computed erythema dose on a horizontal surface doubles over 16° of latitude moving toward the equator. The angle of inclination has very little effect on the doubling distance as evidenced by the similar slopes of the curves in Figs. 4 and 5.

The computed doubling distance is consistent with measurements of annual average erythema dose (Urbach and Davies, 1975), but it differs from the doubling distance for the incidence of skin cancer.

Figure 2. The fraction of the total daily erythema dose for a south-facing surface which is due to diffuse radiation (sky plus ground reflection): (a) June 15, (b) September 15, and (c) December 15.

Data on the incidences of skin cancer in middle latitudes show a doubling over 8 to 12° of latitude (National Research Council, 1976b), indicating that there are other factors contributing to the incidence

Figure 3. Daily total erythema dose, same as Fig. 1 except for a rotated surface.

Figure 4. Daily erythema dose averaged over a year for a south-facing surface.

rate. Consequently, predicting the effect of a reduction in total ozone on the skin cancer incidence rate is more complex than just assessing the change in erythema dose and scaling proportionately.

The effect of a reduction in total ozone of 10% on the annual-average daily erythema dose for a rotated surface is shown in Fig. 6. The results were almost identical for the south-facing surface. The amplification factor on erythema dose ($\Delta\text{dose}/\Delta\text{O}_3$) varies from 1.3 to 1.4 at low latitudes, from 1.6 to 2.0 at middle latitudes, and is approximately 3 at high latitudes. It is a property of atmospheric transmission that a 10% reduction in the ozone column causes the greatest percent change in transmission for the largest optical depth. Because the ozone column and solar zenith angle both increase with latitude, the amplification factor is largest at high latitudes. While the percent increase in daily erythema dose at high latitudes

Figure 5. Daily erythema dose averaged over a year for a rotated surface.

Figure 6. The percent change in daily erythema dose for a rotated surface averaged over a year due to a 10% reduction in ozone.

is much greater, the total amount of radiation is very small compared to lower latitudes. Since the majority of the world's population lives south of 55°N, amplification factors in the range 1.3 to 2.0 are most realistic.

Reducing the ozone column increases both the direct and diffuse flux components but by different factors. Since the relative contribution of the direct and diffuse flux components to erythema dose depends upon α , the amplification factor also depends upon α . This dependence is lessened at high latitudes where the flux is almost entirely diffuse.

As mentioned earlier, the action spectrum for skin cancer is an unknown function. However, van der Leun and Daniels (1975) argue that the peak in the action spectrum should occur near 270 nm. This is shifted considerably in wavelength from the location of the peak in the erythema action spectrum described by Eq. 7, which occurs at 297 nm. In order to test the sensitivity of dose to action spectrum position, the above calculations were repeated substituting

Figure 7. The percent change in daily erythema dose for a rotated surface averaged over a year with the peak in the action spectrum shifted to 270 nm.

Figure 8. The distance moved south equivalent to a 10% ozone reduction computed for a rotated surface. The shaded area indicates the range of values as the inclination angle is varied from 0 to 90°.

270 nm in Eq. 7. Aside from the expected decrease in dose magnitude, very little changed from the results obtained above. An important exception concerns the percent change in the annual-average daily erythema dose produced by a 10% reduction in ozone, which is shown in Fig. 7. Dose amplification factors are significantly higher at middle and low latitudes compared to the results in Fig. 6. The amplification factor ranges from 1.8 to 2.0 at low latitudes and from 1.9 to 2.3 at middle latitudes. The reason for the larger amplification factors is related to the ozone absorption cross section, which in the region near 300 nm is a rapidly decreasing function of wavelength. Shifting the action spectrum to shorter wavelengths, where the UV fluxes are more sensitive to variations in ozone amount, leads to larger amplification factors.

Figure 8 shows the distance moved south which is equivalent to a 10% reduction in ozone based on the annual average data for a rotated surface shown in Fig. 5. The shaded area indicates the range of values as α is varied from 0 to 90°, the largest values corresponding to $\alpha = 90^\circ$. In middle latitudes the increase in daily average erythema dose due to a 10% ozone reduction is roughly equivalent to moving south a distance of 350–450 km with no ozone perturbation. The equivalent distance is much greater at latitudes equatorward of 30°N. There is no equivalent distance for latitudes less than 15°N since the erythema dose at these latitudes with a 10% ozone reduction is greater than the unperturbed erythema dose at the equator.

CONCLUSION

According to the simplified model used here, erythema doses have a significant dependence upon receiver orientation. Although it is possible at times for an inclined surface to receive a larger erythema dose than a horizontal surface, in general the highest doses are received by horizontal surfaces. In middle

and high latitudes, inclined surfaces (south-facing or rotated) with inclination angles up to 45° receive at least 80% of the daily erythema dose received by a horizontal surface. Much larger reductions in daily erythema dose occur for $\alpha > 45^\circ$, which can result in a significant reduction in the latitudinal gradient of erythema dose. In the case of a south-facing surface, the inclination angle affects the latitude of the peak erythema dose. Varying the inclination angle, however, does not have a significant effect on the doubling distance for average daily erythema dose.

Finally, if the skin cancer action spectrum peaks near 270 nm as argued by van der Leun and Daniels (1975), skin cancer rates may be more sensitive than erythema to variations in total ozone.

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***Effects of Stratospheric Perturbations
on the Solar Radiation Budget***

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EFFECTS OF STRATOSPHERIC PERTURBATIONS ON THE SOLAR RADIATION BUDGET

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ABSTRACT

The changes in solar absorption and in local heating rates due to perturbations to O_3 and NO_2 concentrations caused by stratospheric injection of NO_x and CFM pollutants are assessed. The changes in species concentration profiles are derived from theoretical calculations using a transport-kinetics model. Because of significant changes in our understanding of stratospheric chemistry during the past year, the assessment of the effect of stratospheric perturbations on the solar radiation budget differs from previous assessments. Previously, a reduction in O_3 due to an NO_x injection caused a net decrease in the gaseous solar absorption; now the same perturbation leads to a net increase. The implication of these changes on the surface temperature is also discussed.

INTRODUCTION

During the past several years, many threats to the stratospheric O_3 layer have been proposed, including engine emissions from supersonic aircraft (SST's), the atmospheric release of chlorofluoromethanes (CFM's), and nitrogen oxides (NO_x) produced by atmospheric nuclear explosions. SST engine emissions, in addition to affecting the concentrations of O_3 and NO_2 , also affect the stratospheric burden of water vapor and sulfate aerosols. Changes in stratospheric composition can lead to climatic effects by perturbing the global solar and longwave radiation budgets. This paper will focus on changes in O_3 and NO_2 concentrations and their effect on the solar radiation budget. In order to put these changes in perspective, the potential climatic effects of changes in water vapor abundance and aerosol loading in the stratosphere are also considered.

Over the years there have been many changes to the numerical models used to compute the effects of stratospheric perturbations on O_3 . New species (mostly chlorine containing) and reactions have been added. Poorly known reaction rates have been remeasured using more accurate methods, and the O_3 photodissociation rate calculation has been improved. Temperature coupling and feedback on reaction rates has been added, and diurnal averaging has been accounted for more accurately. These changes have significantly modified the O_3 impact assessments. It is important, therefore, to reanalyze the impact of the potential changes in stratospheric composition on the global radiation budget.

In a previous assessment of the effects of changes in O_3 and NO_2 concentrations on solar absorption and stratospheric heating rates, Luther [3] used species concentration profiles derived from a then-current transport-kinetics model. In updating the assessment, it is desirable to present the results in a more general way so that the radiative effects can be inferred for any transport-kinetics model results. This would also enable the radiative effects to be updated simply whenever there is a significant change in the

stratospheric model assessments. We have attempted to do this for calculations of total solar absorption by O_3 and NO_2 .

COMPARISON OF CHANGES IN SOLAR ABSORPTION BY O_3 AND NO_2

In the case of a stratosphere perturbed by an NO_x injection, Luther [3] showed that the increase in solar absorption by NO_2 at steady state was a significant fraction (35 to 50%) of the decrease in solar absorption by O_3 . Since that time, the sensitivity of the transport-kinetics models to an NO_x injection has decreased. Consequently, the change in solar absorption by NO_2 is now expected to be a much larger fraction of the change in solar absorption by O_3 .

Solar absorption by O_3 is shown in Fig. 1 as a function of O_3 column density. The absorption rate given is the instantaneous value for a solar zenith angle of 60° . The radiative transfer model used to compute the solar absorption rate includes Rayleigh scattering and assumes a cloudless, plane-parallel atmosphere above an isotropically scattering ground [3]. The effect of large changes in O_3 column density can be found by interpolating from Fig. 1. The change in solar absorption due to a small change in O_3 column density can be estimated by the first term of a Taylor series:

$$\Delta \text{Abs}(O_3) = \frac{d\text{Abs}(O_3)}{dO_3} \Delta O_3 \quad (1)$$

Since model results are often presented in terms of the percent change in O_3 , Eq. (1) can be rewritten as

$$\Delta \text{Abs}(O_3) = \frac{d\text{Abs}(O_3)}{dO_3/O_3} \Delta O_3/O_3 \quad (2)$$

or

$$\Delta \text{Abs}(O_3) = \text{Abs}(O_3) \frac{d \ln \text{Abs}(O_3)}{d \ln O_3} \Delta O_3/O_3 \quad (3)$$

FIGURE 1. Solar absorption by ozone for a solar zenith angle of 60° . A_s is the surface albedo.

FIGURE 2. Values of $d \ln(O_3 \text{ abs.})/d \ln (\text{total } O_3)$ for a solar zenith angle of 60° .

Values of $d \ln[Abs(O_3)]/d \ln O_3$ are presented in Fig. 2 (also for a solar zenith angle of 60°). Similar equations can be written for the change in solar absorption by NO_2 . Values of $Abs(NO_2)$ and $d \ln[Abs(NO_2)]/d \ln NO_2$ are presented in Figs. 3 and 4, respectively.

FIGURE 3. Solar absorption by NO_2 for a solar zenith angle of 60° .

FIGURE 4. Values of $d \ln(NO_2 \text{ abs.})/d \ln$ (total NO_2) for a solar zenith angle of 60° .

Ambient and perturbed species concentration profiles were computed using the Lawrence Livermore Laboratory one-dimensional transport-kinetics model (same version used by Luther et al. [5]). Two cases were considered: NO_x injections (as NO_2) at 17 or 20 km at the rate of $1000 \text{ molecules cm}^{-3} \text{ s}^{-1}$ uniformly distributed over a 1-km-thick layer. This corresponds to a hemispheric injection rate of $6.2 \times 10^8 \text{ kg/yr}$. Changes in the O_3 and NO_2 column densities and solar absorption rates for a solar zenith angle of 60° and a surface albedo of 0.25 are summarized in Table 1. The unperturbed column densities are $9.730 \times 10^{18} \text{ molecules/cm}^2$ (0.362 atm.cm) for O_3 and $3.506 \times 10^{15} \text{ molecules/cm}^2$ for NO_2 .

TABLE 1. Increases in total atmospheric solar absorption by O_3 and NO_2 due to NO_x injections at the rate of $6.2 \times 10^8 \text{ kg/yr}$.

Quantity	NO_x Injection Altitude	
	17 km	20 km
ΔO_3	1.06%	0.39%
ΔNO_2	6.87%	15.60%
$\Delta Abs(O_3)$	0.16 W/m^2	0.06 W/m^2
$\Delta Abs(NO_2)$	0.06 W/m^2	0.13 W/m^2

In both cases the injection of NO_x resulted in a small increase in total O_3 . Although the changes in the O_3 column density are small, the change in the local O_3 concentration (Fig. 5) may be several percent. The change in column density reflects the net difference between regions of O_3 increase (below 22 km) and O_3 decrease (above 22 km). Consequently, although the change in the net heating may be small, the redistribution in altitude of where this heating occurs may be significant. The change in the local concentration of NO_2 is shown in Fig. 6.

FIGURE 5. Change in local ozone concentration due to NO_x injections (as NO_2) of 6.2×10^8 kg/yr.

FIGURE 6. Change in local NO_2 concentration due to NO_x injections (as NO_2) of 6.2×10^8 kg/yr.

CHANGES TO THE SOLAR RADIATION BUDGET AND HEATING RATES

In addition to the two NO_x injection cases already described, we also considered the steady-state O_3 reduction due to CFM's at the 1975 release rate, which is assumed to be 290 kilotonnes/yr for CFCl_3 and 425 kilotonnes/yr for CF_2Cl_2 . The change in O_3 column density computed at steady state was -14.4%. For a solar zenith angle of 60° and a surface albedo of 0.25, there is a reduction in solar absorption by O_3 of 2.45 W/m^2 . The change in the local O_3 concentration is shown in Fig. 7. There is a reduction in O_3 concentration at all altitudes with the largest percent reduction occurring at 40 km.

In addition to affecting the gaseous absorption of solar radiation in the stratosphere, changes in stratospheric composition also affect solar absorption in the troposphere by changing the atmospheric transmissivity. A decrease in O_3 column density, for example, allows more solar radiation to reach the troposphere, thereby increasing both the amount of solar absorption and the amount of radiation scattered back to space. Changes to the solar radiation budget are presented in Table 2 for the three perturbation cases. The net solar flux at the top of the atmosphere is defined as the incoming flux minus the outgoing flux. The values for the change in solar absorption in the troposphere include the change in gaseous absorption and the change in absorption by the earth's surface. The changes in the instantaneous solar absorption rates for the NO_x injection cases are small compared with the unperturbed values. The CFM perturbation case, on the other hand, represents a significant perturbation to the solar radiation budget. There is a significant reduction in the solar absorption in the stratosphere and an increase in the troposphere.

TABLE 2. The Perturbed Solar Radiation Budget
(solar zenith angle = 60° , surface albedo = 0.25).

Quantity	Perturbation Case			Unperturbed Value
	NO_x , 17 km	NO_x , 20 km	CFM	
Δ Net solar flux at top of atmosphere	0.1 W/m^2	0.0 W/m^2	-1.0 W/m^2	470 W/m^2
Δ Stratospheric solar absorption	0.13	0.08	-2.35	34.1
Δ Troposphere/surface solar absorption	-0.1	-0.1	1.3	436

FIGURE 7. Change in ozone concentration at steady state due to CFM's at the 1975 release rate.

FIGURE 8. Change in the instantaneous solar heating rates for a solar zenith angle of 60° and $A_s = 0.25$ due to an NO_x injection at 17 km.

The changes in the O_3 and NO_2 solar heating rates are presented in Fig. 8 for the 17-km NO_x injection and in Fig. 9 for the 20-km NO_x injection. O_3 and NO_2 both contribute to an increase in the heating rate in the lower stratosphere. Consequently, the change in solar heating tends to increase the temperature in the lower stratosphere and decrease the temperature in the upper stratosphere.

The change in the solar heating rate due to a CFM perturbation is shown in Fig. 10. The reduction in the solar heating rate in the lower stratosphere is approximately the same magnitude as the increase in heating rate computed for the NO_x injection cases. The change in the solar heating rate is -0.07 K/day at 24 km, -0.02 K/day at 20 km, and -0.01

FIGURE 9. Change in the instantaneous solar heating rates for a solar zenith angle of 60° and $A_s = 0.25$ due to an NO_x injection.

FIGURE 10. Change in the solar heating rate of ozone at steady state for a solar zenith angle of 60° and $A_s = 0.25$ due to CFM's at the 1975 release rate.

K/day at 18 km. In this case there is cooling at all altitudes with the largest effect in the upper stratosphere.

POTENTIAL CLIMATIC IMPACT

The climatic impact of changes in stratospheric composition depends upon both the solar and longwave effects of the perturbation. Changes in temperature, in addition to affecting the transfer of longwave radiation, also affect atmospheric stability and transport. Here we will consider only the global impact of the solar and longwave effects and neglect any potential feedback on transport.

A previous assessment of the effect of changes in O_3 and NO_2 on surface temperature by Ramanathan et al. [8] showed a cooling at the surface associated with a reduction in O_3 due to an NO_x injection. Only reductions in O_3 were considered, and it was assumed that the changes in O_3 and NO_2 were uniform (percentage wise) between 12 and 40 km. Our present results differ from these modeling assumptions in that the changes in O_3 and NO_2 concentrations are not uniform with altitude, and there is a net increase in O_3 column density rather than a decrease. Nevertheless, the work of Ramanathan et al. [8] is useful because it demonstrates the importance of the longwave effect of the perturbation. The reduction in total O_3 tended to warm the troposphere by increasing the transmissivity of the stratosphere for solar radiation. The reduction in stratospheric temperature due to reduced O_3 , however, had a greater effect on the longwave radiation emitted downward from the stratosphere. The net result was a slight reduction in surface temperature.

A similar calculation using our current modeling results would predict an increase in temperature in the lower stratosphere [4]. It is possible that the longwave effect would also dominate in this case. It is clear, however, that the longwave effect would tend to warm the troposphere, whereas the solar effect tends to cool. Based on the results of Ramanathan et al., an increase in NO_2 of 30%, which is larger than the estimated increase, would cause an increase in surface temperature of approximately 0.01 K. The change in surface temperature due to a 1% increase in total O_3 is also likely to be small.

To put these numbers in perspective, consider the potential climatic effect of the water vapor which is injected into the stratosphere along with the NO_x . Assuming an emission index of 1250 g/kg fuel for water vapor and 18 g/kg fuel for NO_x , the associated water vapor injection rate would be 4.3×10^{10} kg/yr. According to model calculations in which the stratospheric water vapor profile is computed [9], this would lead to an increase in the stratospheric water vapor mixing ratio of 0.17 ppmv for a 17-km injection and an increase of 0.50 ppmv for a 20-km injection. Changes in stratospheric water vapor mixing ratio of these magnitudes is estimated to cause an increase in the surface temperature of 0.02 K and 0.06 K, respectively [2].

In addition to NO_x and water vapor, SST engines also emit SO_2 , which is converted to sulfate aerosols. Assuming an emission index of 1.0 g/kg fuel, the SO_2 injection rate would be 3.4×10^7 kg/yr when the NO_x injection rate is 6.2×10^8 kg/yr. This emission rate causes an increase in the stratospheric optical depth ($\Delta\tau$) due to a larger aerosol loading at steady state of approximately 1.1×10^{-3} for a 17-km injection altitude and 2.3×10^{-3} for a 20-km injection altitude [2, p. 43]. The sensitivity of the surface temperature to changes in stratospheric optical depth due to aerosols produced by SST's has been estimated by Pollack et al. [6] to be: $\Delta T_s = -10 \text{ K } \Delta\tau$. The change in surface temperature due to aerosols is thus estimated to be -0.01 K for a 17-km injection altitude and -0.02 K for a 20-km injection altitude.

The climatic effect of the CFM perturbation can be estimated roughly by considering the balance in the net solar and longwave fluxes at the top of the atmosphere. On a global mean basis, any change in the net incoming solar radiation must be compensated for by a similar change in the outgoing longwave radiation.

The decrease in net solar flux at the top of the atmosphere shown in Table 2 is caused by an increase in the upward solar flux scattered to space. Dividing by two to account for day-night averaging, there is an increase of 0.5 W/m^2 in the global mean solar flux

scattered to space. To maintain equilibrium, there must also be a reduction in the long-wave flux to space of 0.5 W/m^2 . Using Budyko's [1] empirical formulation relating the change in outgoing longwave flux to the change in surface temperature ($dF/dT = 1.425 \text{ W m}^{-2} \text{ K}^{-1}$), the required decrease in surface temperature is estimated to be -0.35 K . This should be viewed as a very crude estimate because details of the vertical distribution of O_3 are not included in the assessment. According to the work of Ramanathan et al. [8], a reduction in total O_3 of 14.4% would cause a change in surface temperature of -0.13 K assuming that the O_3 reduction is distributed uniformly between 12 and 40 km.

There is the additional effect of the longwave properties of CF_2Cl_2 and CFCl_3 . At steady state the tropospheric concentrations of the CFM's are computed to be larger than present day levels by 0.6 ppbv for CFCl_3 and 1.52 ppbv for CF_2Cl_2 . The greenhouse effect of CFM's has been studied by Ramanathan [7]. According to the relationship between tropospheric mixing ratio and global surface temperature developed by Ramanathan [7], these changes in concentration would result in an increase in surface temperature of approximately 0.4 K. This implies approximate cancellation of effects on global mean surface temperature for a CFM perturbation. Detailed study is needed to more accurately assess the net climatic effect.

CONCLUSIONS

Changes in O_3 and NO_2 concentrations due to an NO_x injection lead to increases in the total solar absorption of both species. These increases are small, however, when compared to the total energy absorbed by the stratosphere, and the climatic effect is estimated to be negligibly small. Using the criterion that changes in surface temperature less than 0.1 K would not have major consequences [6], none of the SST engine emissions (NO_x , H_2O , and SO_2) are estimated to have a major climatic effect. The largest individual effect on surface temperature is that of water vapor, which is estimated to cause a temperature increase of 0.06 K for a 20-km injection at $4.3 \times 10^{10} \text{ kg/yr}$. The combined effect of all engine emissions on climate is likely to be an increase in global mean temperature of less than 0.1 K.

In the case of a CFM perturbation, there is a significant impact on the solar radiation budget leading to a decrease in the solar heating of the stratosphere and an increase in solar heating of the troposphere and earth's surface. There is also an increase in the solar flux scattered back to space. There is considerable uncertainty about the change in surface temperature at steady state caused by the reduction in O_3 due to CFM's released at the 1975 rate. Our estimates change from -0.13 K to -0.35 K . The greenhouse effect of CFCl_3 and CF_2Cl_2 , on the other hand, tends to warm the surface, possibly by as much as 0.4 K. The net effect on surface temperature is uncertain, but it may be in excess of $+0.1 \text{ K}$, which would be considered significant. The potential climatic effect of a CFM perturbation needs further study to reduce the large uncertainty associated with these results.

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Effect of Changes in Stratospheric Water Vapor on Ozone Reduction Estimates

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Previous studies of the effect of water vapor on the destruction of ozone in the stratosphere perturbed by NO_x or CIX pollutants did not include temperature feedback effects (i.e., they assumed a fixed temperature profile). These studies indicated that if an increase in stratospheric water vapor concentration were induced (perhaps as a result of an increase in the temperature of the tropical tropopause caused by a change in stratospheric ozone), there would be a significant further reduction in total ozone. Our results from using a one-dimensional transport kinetics model with a fixed temperature profile confirm these earlier findings. However, when the temperature profile is allowed to change as the species concentrations change, the sensitivity of total ozone to changes in water vapor abundance is greatly reduced. In the case of an NO_x injection at 20 km there is even a reversal of sign such that an increase in stratospheric water vapor leads to an ozone increase relative to the case with no change in water vapor.

INTRODUCTION

The potential threat to the earth's ozone layer of supersonic transport (SST) engine effluents and chlorofluoromethanes (CFM's) has received a great deal of attention. Early estimates of the potential ozone reduction considered NO_x or CFM pollutants alone. However, recent assessments have also considered the possibility of a simultaneous change in stratospheric water vapor abundance [Liu *et al.*, 1976; Duewer *et al.*, 1977]. Both of these studies showed that increased water vapor caused enhanced ozone reduction for the then accepted rate coefficients.

The H_2O emission index (1.3 kg/kg fuel) is much larger than the NO_x emission index (0.018 kg/kg fuel) for SST's [Grobecker *et al.*, 1974]. An annual fuel consumption rate of 10^{11} kg/yr for a fleet of SST's at a cruise altitude of 20 km would increase the stratospheric water vapor burden by approximately 15% [Grobecker *et al.*, 1974, p. 52]. Changes in atmospheric composition due to stratospheric perturbations might affect stratospheric water vapor abundance indirectly by changing the temperature of the tropical tropopause. Since the saturation vapor pressure of H_2O doubles for a 4 K rise in tropopause temperature and the concentration of water vapor in the stratosphere is thought to be limited by the temperature of the tropical tropopause [Ellsaesser, 1974; Liu *et al.*, 1976], changes in the tropical tropopause temperature could have a larger effect than the direct injection of water vapor into the stratosphere.

The most thorough study to date of the effect of changes in water vapor abundance on the estimated ozone reduction by NO_x and CFM pollutants is that of Liu *et al.* [1976]. They used a one-dimensional transport kinetics model for their calculations. When they imposed an increase in the water vapor mixing ratio of 1 ppmv at their lower boundary (10 km) in addition to an NO_x injection, they obtained an additional reduction in total ozone of 0.3–1.0% (from their Figure 12). When the increase in the water vapor mixing ratio of 1 ppmv was imposed at their lower boundary in addition to a CFM perturbation, there was an additional reduction in total ozone of 0.4–1.4% (from their Figure 5). These changes in water vapor at the lower boundary were intended to simulate the effect of changes in the temperature of the tropical tropopause that might be induced by NO_x or CFM perturbations to the stratosphere. The ranges cited reflect variation of the reaction

rate for $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ between 2×10^{-10} and 2×10^{-11} cm^3/s . The largest sensitivity to changes in water vapor abundance was associated with the slow rate for this reaction. Although the change in stratospheric water vapor abundance was postulated to be due to a change in tropopause temperature, the temperature profile was fixed, and the effect of changes in temperature on chemical reaction rates was not included in their calculations. We have expanded upon the work of Liu *et al.* [1976] by including temperature changes in our calculations. Temperature feedback on chemical reaction rates will be shown to have a significant effect on model sensitivity to changes in stratospheric water vapor abundance.

MODEL DESCRIPTION

In order to include the effect of changes in temperature we used a one-dimensional transport kinetics model coupled with a stratospheric radiative transfer model. The transport kinetics model has been described previously [Chang, 1975; Wuebbles and Chang, 1975; Luther *et al.*, 1977]. The model atmosphere extends from the ground to 55 km and is divided into 44 layers. A total of 83 chemical (and photochemical) reactions are included in the model; 44 reactions describe O_x , NO_x , and HO_x chemistry, and 39 reactions describe CIX chemistry. These reactions are used to describe dynamically the stratospheric vertical distributions of 20 minor atmospheric species ($\text{O}(^1\text{P})$, O_3 , NO , NO_2 , N_2O , HNO_3 , OH , HO_2 , H_2O_2 , Cl , CH_3 , ClO , CH_2Cl , OCIO , ClONO_2 , ClNO_2 , HCl , CCl_4 , CF_2Cl_2 , and CFCl_3). Three species (H , N , and $\text{O}(^1\text{D})$) are assumed to be in instantaneous equilibrium, and the vertical profiles of N_2 , O_2 , H_2 , CO , and H_2O are specified. The boundary conditions, which are species dependent, are assumed to be fixed or time-varying source-dependent concentrations at the earth's surface, and flux conditions are assumed at 55 km, the upper boundary. The chemical reaction rates are listed in Table 1.

Two diffusion coefficient profiles were used in the calculations to describe vertical transport. The first profile (K_{11}) was developed by Chang and his co-workers at Lawrence Livermore Laboratory [Luther, 1976]. This profile is also the same as model E in the report by the National Research Council [1976]. The second profile (K_{22}) is model F in the report by the National Research Council [1976]. This profile was chosen because it has significantly smaller values in the vicinity of the tropopause; thus it represents an extreme variation in the choice of K_z profiles compared with other commonly used profiles. The profile K_{22} is similar to Hunt's [1975] profile,

TABLE 1. Chemical Reactions and Rate Coefficients

Reaction	Rate Coefficient, cm ³ s ⁻¹ , cm ³ s ⁻¹
O + O ₂ → O ₃	1.1 × 10 ⁻¹⁰ exp(510/T)
O + O ₂ → 2O	1.9 × 10 ⁻¹¹ exp(-2300/T)
O + NO → NO ₂ + O ₂	2.3 × 10 ⁻¹¹ exp(-1450/T)
O + NO ₂ → NO + O ₂	9.1 × 10 ⁻¹²
N ₂ O + O(¹D) → N ₂ + O ₂	5.5 × 10 ⁻¹¹
N ₂ O + O(¹D) → 2NO	5.5 × 10 ⁻¹¹
N + O ₂ → NO + O	5.5 × 10 ⁻¹² exp(-3220/T)
N + NO → N ₂ + O	8.2 × 10 ⁻¹² exp(-410/T)
O(¹D) + H ₂ O → 2OH	2.3 × 10 ⁻¹⁰
O(¹D) + CH ₄ → OH + CH ₃ •	1.3 × 10 ⁻¹⁰
O ₃ + OH → HO ₂ + O ₂	1.6 × 10 ⁻¹⁰ exp(-1000/T)
O + OH → O ₂ + H	4.2 × 10 ⁻¹¹
O ₃ + HO ₂ → OH + 2O ₂	1.0 × 10 ⁻¹¹ exp(-1250/T)
O + HO ₂ → OH + O ₂	3.0 × 10 ⁻¹¹
H + O ₂ → HO ₂	2.08 × 10 ⁻¹⁰ exp(290/T)
O ₃ + H → OH + O ₂	1.23 × 10 ⁻¹⁰ exp(-562/T)
HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	1.7 × 10 ⁻¹¹ exp(-500/T)
HO ₂ + OH → H ₂ O + O ₂	2.0 × 10 ⁻¹¹
OH + NO ₂ → HNO ₂	
OH + HNO ₂ → H ₂ O + 0.67NO ₂ + 0.67O + 0.33NO + 0.33O ₂	8.9 × 10 ⁻¹¹
H ₂ O ₂ + OH → H ₂ O + HO ₂	1.0 × 10 ⁻¹¹ exp(-750/T)
N ₂ + O(¹D) → N ₂ O	3.5 × 10 ⁻¹⁰
N + NO ₂ → N ₂ O + O	2.0 × 10 ⁻¹¹ exp(-800/T)
NO + O → NO ₂	1.6 × 10 ⁻¹⁰ exp(584/T)
NO + HO ₂ → NO ₂ + OH	1.7 × 10 ⁻¹¹ exp(-1000/T)
H ₂ + O(¹D) → OH + H	9.9 × 10 ⁻¹¹
OH + OH → H ₂ O + O	1.0 × 10 ⁻¹¹ exp(-550/T)
N + O ₂ → NO + O	5.0 × 10 ⁻¹² exp(-650/T)
NO ₂ + O ₂ → 0.67NO ₂ + 0.67O + 0.33NO + 0.33O ₂	1.2 × 10 ⁻¹¹ exp(-2450/T)
OH + CH ₄ → H ₂ O + CH ₃ •	2.36 × 10 ⁻¹⁰ exp(-1710/T)
OH + OH → H ₂ O ₂	1.2 × 10 ⁻¹⁰ exp(900/T)
H ₂ O ₂ + O → OH + HO ₂	2.75 × 10 ⁻¹⁰ exp(-2125/T)
O + CH ₄ → OH + CH ₃ •	3.5 × 10 ⁻¹⁰ exp(-4550/T)
CO + OH → H + CO ₂	1.4 × 10 ⁻¹⁰
O(¹D) → O	2.0 × 10 ⁻¹⁰ exp(107/T)
Cl + O ₂ → ClO + O	2.7 × 10 ⁻¹¹ exp(-257/T)
Cl + OClO → 2ClO	5.9 × 10 ⁻¹¹
Cl + CH ₄ → HCl + CH ₃ •	7.3 × 10 ⁻¹² exp(-1260/T)
Cl + NO ₂ → ClNO ₂	6.9 × 10 ⁻¹⁰ exp(2115/T)
Cl + ClNO ₂ → 2Cl + NO ₂	3.0 × 10 ⁻¹⁰
ClO + O → Cl + O ₂	7.7 × 10 ⁻¹² exp(-130/T)
NO + ClO → NO ₂ + Cl	2.2 × 10 ⁻¹⁰
ClO + O ₂ → ClO ₂ + O	1.0 × 10 ⁻¹⁰ exp(-4000/T)
ClO + O ₂ → ClO + O ₂	1.0 × 10 ⁻¹⁰ exp(-4000/T)
ClO + NO ₂ → ClONO ₂	5.1 × 10 ⁻¹⁰ exp(1030/T)
ClO + ClO → Cl + ClO	1.5 × 10 ⁻¹⁰ exp(-1238/T)
ClO + ClO → 2Cl + O ₂	4.5 × 10 ⁻¹⁰ exp(-1238/T)
ClO + ClO → Cl + ClO ₂ •	9.0 × 10 ⁻¹⁰ exp(-1238/T)
HCl + O(¹D) → Cl + OH	1.4 × 10 ⁻¹⁰
OH + HCl → H ₂ O + Cl	2.8 × 10 ⁻¹⁰ exp(-400/T)
O + HCl → OH + Cl	1.1 × 10 ⁻¹¹ exp(-3370/T)
O + ClO → ClO + O	5.0 × 10 ⁻¹⁰
NO + ClO → NO ₂ + ClO	3.4 × 10 ⁻¹⁰
N + ClO → NO + ClO	6.0 × 10 ⁻¹⁰
H + ClO → OH + ClO	5.7 × 10 ⁻¹⁰
Cl + OH → HCl + O	2.0 × 10 ⁻¹⁰ exp(-1878/T)
Cl + HO ₂ → HCl + O ₂	3.0 × 10 ⁻¹¹
Cl + HNO ₂ → HCl + 0.67NO ₂ + 0.67O + 0.33NO + 0.33O ₂	6.0 × 10 ⁻¹⁰
CF ₂ Cl + O(¹D) → 2Cl	2.3 × 10 ⁻¹⁰
CF ₂ Cl + O(¹D) → 2Cl	2.0 × 10 ⁻¹⁰
Cl + H ₂ → HCl + H	4.7 × 10 ⁻¹¹ exp(-2340/T)
Cl + H ₂ O → HCl + HO ₂	1.6 × 10 ⁻¹⁰ exp(-384/T)
ClONO ₂ + O → ClO + NO ₂ •	5.0 × 10 ⁻¹⁰ exp(-840/T)
ClONO ₂ + OH → Cl + H ₂ O + NO ₂	2.2 × 10 ⁻¹⁰ exp(-1142/T)

*These species are not actually used in the model. They are assumed to react instantaneously to form other products.

†For the rate coefficient we use an expression developed by W. Tsang (private communication, 1976): $\log_{10}(k) = -A/T + B + C/T + D \log_{10}(T/280)$, where $A = A_1 + A_2T + A_3T^2 + A_4T^3$, $B = B_1 + B_2T + B_3T^2$, $C = \log_{10}(M)$, $A_1 = 31.52273$, $A_2 = -0.258304$, $A_3 = -0.0889287$, $A_4 = 2.520173 \times 10^{-5}$, $B_1 = -327.372$, $B_2 = 44.5586$, and $B_3 = -1.38092$.

which was used by Liu *et al.* [1976], but the stratospheric values have been increased by approximately a factor of 2 to improve agreement between calculated and observed CH₄ and N₂O concentrations above 30 km.

The model has recently been modified to include the effect of multiple scattering, which is incorporated into the photodissociation rate calculation by applying correction factors to the flux used in the pure absorption calculation [Luther and Wuebbles, 1976]. The correction factors were computed for the unperturbed species profiles by using a detailed solar radiation model [Luther and Gelin, 1976]. A separate factor was computed for each of the 44 levels and for each of the 148 wavelength intervals between 133 and 735 nm for a solar zenith angle of 45° and a surface albedo of 0.25. The correction factors (but not the fluxes) are assumed to remain unchanged in time.

A stratospheric radiative transfer model [Luther *et al.*, 1977] is used to compute the temperature profile above 12 km. The temperature profile below 12 km is specified. The model includes solar absorption and long-wave interaction by O₃, H₂O, and CO₂ along with solar absorption by NO₂. The radiative transfer model is the same as Ramanathan's [1974] except that we have added solar absorption by NO₂. There are several differences between this model and Ramanathan's latest model [Ramanathan, 1976] as described in detail in his paper.

We assume that the change in surface temperature is negligible. The change in surface temperature associated with a 10% reduction in ozone due to CFM's at a tropospheric concentration of approximately 2 ppb was computed to be 0.3 K or less by Ramanathan [1975] and by Reck [1976]. Ozone reductions of up to 30% due to NO₂ injections were computed to cause less than a 0.1 K change in surface temperature by Ramanathan *et al.* [1976]. An increase in the stratospheric water vapor mixing ratio of 2 ppmv is estimated to cause an increase in surface temperature of ~0.2 K [Grobecker *et al.*, 1974, p. F125]. Increasing the surface temperature in our model by 0.2 K causes a change in total ozone of ~0.06%. Neglecting changes in surface temperature of this magnitude has no significant effect on the results.

The tropospheric distribution of H₂O is based on the work of Mastenbrook [1974]. The stratospheric mixing ratio of H₂O is assumed to be 4.3 ppmv. Liu *et al.* [1976] computed the stratospheric distribution of H₂O by specifying the mixing ratio at the tropopause and assuming that methane oxidation increases the water content of the upper stratosphere. Their calculations showed that changing the water vapor mixing ratio at the tropopause by some amount ΔH_2O resulted in the same change in the mixing ratio at altitudes up to 50 km. Above 50 km the change in the local H₂O mixing ratio was less than ΔH_2O at the tropopause. In our calculations, when the stratospheric water vapor mixing ratio is changed, the same ΔH_2O is applied at all altitudes above 13 km, the process thus leading to a change in stratospheric water vapor abundance similar to that of Liu *et al.* [1976].

RESULTS

NO₂ Injection

The ambient ozone concentration profiles are shown in Figure 1 for both the K_{11} and the K_{22} diffusion coefficients. Since the K_{22} coefficients have smaller values in the lower stratosphere and at the tropopause, the gradient in ozone concentration is larger in these regions for the K_{11} profile than it is for the K_{22} profile. Both profiles have nearly the same amount of total ozone (0.280 atm cm).

The temperature profiles corresponding to the two ambient ozone profiles are shown in Figure 2. Also included for com-

Fig. 1. Ozone concentration profiles corresponding to the two diffusion coefficient profiles used in the calculations.

parison is the U.S. Standard Atmosphere (1976) temperature profile. Large-scale dynamical processes are neglected in the determination of the temperature profile. These processes have a significant effect on the temperature profile near the tropopause. For our application here the ability of the model to compute the change in temperature is more important than the particular ambient temperature profile. Since changes in atmospheric dynamics brought about by changes in temperature structure and in the radiation balance are not included in the model (or in any other transport kinetics model at the present time), there may be significant errors in the predicted temperature change in the lower stratosphere. Consequently, in discussing the results, we want to emphasize their qualitative nature rather than the quantitative details.

The effect of a change in stratospheric water vapor on total ozone was computed for cases with and without a simultaneous NO_x injection in order to test the sensitivity of the results to the magnitude of the NO_x perturbation. We consider an NO_x injection rate of $1000 \text{ molecules cm}^{-2} \text{ s}^{-1}$ as NO_x over a 1-km-thick layer centered at 20 km, which is a larger injection rate than that used by Liu *et al.* [1976]. Calculations were first performed using the fixed ambient temperature profile in order to verify qualitatively the results obtained by Liu *et al.* [1976]; then the calculations were repeated with temperature feedback included. The results using the K_{21} diffusion coefficients are presented in Figure 3, which shows the change in total ozone at steady state as a function of the change in the stratospheric water vapor mixing ratio.

With no change in H_2O this NO_x injection causes a reduction in total ozone of 2.25% with a fixed temperature profile and 2.03% with temperature feedback. Temperature feedback therefore has approximately a 10% restoring effect on the

Fig. 2. Temperature profiles for the ambient atmosphere corresponding to the eddy profiles K_{21} and K_{22} .

Fig. 3. Change in total ozone versus change in the water vapor mixing ratio above 13 km computed by using the K_{21} profile (a) with no NO_x injection and (b) with an NO_x injection of $1000 \text{ molecules cm}^{-2} \text{ s}^{-1}$ as NO_x over a 1-km-thick layer centered at 20 km.

change in total ozone, which is consistent with our earlier results [Luther *et al.*, 1977].

The results from using a fixed temperature profile are similar to those of Liu *et al.* [1976] for the slow reaction rate of $\text{OH} + \text{HO}_2$. The slope of ΔO_3 versus $\Delta\text{H}_2\text{O}$ is $-0.42\%/ \text{ppmv}$ (at $\Delta\text{H}_2\text{O} = 0$) with the NO_x injection and $-0.64\%/ \text{ppmv}$ with no NO_x injection compared with Liu *et al.*'s value of $-1.0\%/ \text{ppmv}$; thus our model is less sensitive to changes in water vapor abundance. The results also demonstrate that the model sensitivity depends upon the amount of NO_x present. Since the eddy diffusion profile affects the background NO_x , the results can be expected to depend also upon the eddy diffusion profile used in the calculation.

When temperature feedback is included, the results change dramatically. An increase in stratospheric water vapor now causes less reduction in total ozone, the slope being $0.21\%/ \text{ppmv}$ for this NO_x injection. With no NO_x injection the model is virtually insensitive to changes in water vapor.

An analysis of the effect of changes in water vapor with fixed temperature will help one to understand why temperature feedback has such a significant effect. Profiles of the change in ozone concentration due to the NO_x injection at 20 km are shown in Figure 4a for various values of $\Delta\text{H}_2\text{O}$. Destruction of odd oxygen is dominated by HO_2 reactions in the 10- to 20-km and 40- to 50-km regions. In the 10- to 20-km region, odd oxygen destruction is dominated by the reactions

whereas in the 40- to 50-km region the dominant reactions are

Increasing the water vapor mixing ratio increases the ozone destruction rate in these regions because HO_2 increases (Figure 4a). Although relatively large percentage changes occur in the ozone concentration above 40 km, these changes make a relatively small contribution to the change in total ozone because of the small O_3 concentration above 40 km.

Fig. 4. The percent change in ozone concentration as a function of height due to an NO_x injection at 20 km for several values of $\Delta\text{H}_2\text{O}$ (a) with no temperature feedback and (b) with temperature feedback.

The NO_x catalytic cycle dominates odd oxygen destruction in the middle stratosphere. Increased HO_x decreases ozone destruction in the 25- to 35-km region because of two processes. First, more NO_x is converted to HNO_3 by the reaction $\text{NO}_x + \text{OH}$, the NO_x catalytic cycle thus being inhibited. Second, increased HO_x leads to interference with NO_x cycle destruction of odd oxygen through the reactions

Since the rate of destruction of odd oxygen depends upon the amount of HO_x and NO_x in this region, the effect of changing the water vapor mixing ratio will depend to some extent upon the magnitude of the NO_x injection.

Similar results for the calculation including temperature feedback are shown in Figure 4b. Comparing Figures 4a and 4b, we see in the latter less sensitivity to changes in water vapor above 40 km and in the 10- to 20-km region. However, the sensitivity is enhanced in the 25- to 35-km region. In order to demonstrate the effect of changes in water vapor and temperature on ozone more clearly we introduce the quantity $\text{DO}_x(z)$ which is defined by

$$\text{DO}_x(z) = \Delta[\text{O}_3]_z / \text{O}_3(\text{column}) \quad (8)$$

where $\Delta[\text{O}_3]_z$ is the change in local ozone concentration and $\text{O}_3(\text{column})$ is the unperturbed total ozone. The function $\text{DO}_x(z)$ represents the contribution per unit altitude to the change in total ozone. The change in total ozone is therefore given by the integral

$$\Delta\text{O}_3 = \int_0^\infty \text{DO}_x(z) dz \quad (9)$$

In other words, the area under the curve of $\text{DO}_x(z)$ versus z equals ΔO_3 . In order to extract the contribution to DO_x due expressly to changes in the water vapor mixing ratio we introduce the expression $\Delta\text{DO}_x(\text{H}_2\text{O})$, which is defined by

$$\Delta\text{DO}_x(\text{H}_2\text{O}) = \text{DO}_x(\Delta\text{H}_2\text{O}) - \text{DO}_x(\Delta\text{H}_2\text{O} = 0) \quad (10)$$

where $\text{DO}_x(\Delta\text{H}_2\text{O})$ is a function of altitude, although the z dependence is not indicated. This function is plotted for several values of $\Delta\text{H}_2\text{O}$ in Figure 5a for the case with fixed temperature and in Figure 5b for the case with temperature feedback. Those regions in which changes in water vapor either increase or decrease ozone are clearly apparent. With fixed temperature the greatest contribution to the change in total ozone comes from the change in ozone concentration in the 10- to 25-km region, whereas with temperature feedback the greatest contribution comes from changes in the 20- to 30-km region. These differences are related to the sensitivity of various reaction rates to changes in temperature.

The changes in temperature due to the NO_x injection at 20 km along with changes in the water vapor mixing ratio are shown in Figure 6. With no change in water vapor, NO_x injection causes a temperature increase in the vicinity of the tropopause (15 km) and a temperature decrease above 21 km. Increasing the water vapor mixing ratio now decreases the temperature by varying amounts at all altitudes above 13 km. The ozone destruction reactions have positive activation energies; thus they are slowed when the temperature is decreased. In contrast, ozone production is a photolytic process nearly independent of temperature.

Reactions (1) and (2) have relatively high activation energies. Consequently, they are very sensitive to temperature change. As is shown in Figure 5, the ozone destruction due to enhanced water vapor in the 10- to 20-km region is greatly reduced owing to the temperature decrease. The NO_x catalytic reactions, which dominate ozone destruction in the 20- to 40-km region, have moderate activation energies, and the formation of HNO_3 has a negative activation energy. The activation energy for (6) is poorly known but probably small. Therefore the decrease in ozone destruction in this region (which appears as enhanced ozone production in Figure 5) is also significant, but it is not as large as that in the 10- to 20-km region. Reactions (3)-(5) have very low activation energies, so the 40- to 50-km region is least sensitive to changes in temperature.

The increase in stratospheric water vapor is postulated upon the assumption of an increase in the tropopause temperature. The calculation indeed shows (Figure 6) an increase in temper-

Fig. 5. Profiles of $\Delta\text{DO}_x(\text{H}_2\text{O})$ corresponding to various values of $\Delta\text{H}_2\text{O}$ obtained by using the $K_{\text{H}_2\text{O}}$ profile for the case of an NO_x injection at 20 km (a) with fixed temperatures and (b) with temperature feedback. Note that the multiplier 10^{-3} is applied to values along the abscissa.

Fig. 6. Change in temperature for the stratosphere perturbed by an NO_2 injection at 20 km.

ature at the altitude of the tropopause (15 km) for $\Delta\text{H}_2\text{O} = 0$, which occurs because of increased solar absorption by NO_2 and O_3 [Luther *et al.*, 1977]. As $\Delta\text{H}_2\text{O}$ increases, the temperature at this level decreases, a negative feedback process limiting the change in H_2O being formed. The transition from an increase to a decrease in tropopause temperature occurs for a change in the water vapor mixing ratio of less than 1.0 ppmv for this magnitude NO_2 injection. In order to estimate accurately the expected change in the temperature of the tropical tropopause and the change in the stratospheric water vapor mixing ratio we would need a multidimensional model capable of computing changes in dynamics (transport) and temperature. This entails predicting changes in the mean and eddy components of the circulation as well as changes in the energy and moisture budgets. The one-dimensional calculation is useful in that it qualitatively demonstrates that large changes in stratospheric water vapor are unlikely.

In order to test the degree to which these results might be model dependent the calculations were repeated using the K_{22} profile, and the results are shown in Figure 7. The model sensitivity to changes in the water vapor mixing ratio without

Fig. 7. Change in total ozone versus change in the water vapor mixing ratio above 13 km. This is the same as Figure 3 except that the K_{22} profile is used.

Fig. 8. Profiles of $\Delta\text{DO}_2(\text{H}_2\text{O})$ corresponding to various values of $\Delta\text{H}_2\text{O}$ obtained by using the K_{22} profile for the case of an NO_2 injection at 20 km (a) with fixed temperature and (b) with temperature feedback. Note that the multiplier 10^{-2} is applied to the values along the abscissa.

an NO_2 injection (Figure 7) is nearly the same when the K_{22} profile is used as it is when the K_{21} profile is used (Figure 3). The slope of ΔO_3 versus $\Delta\text{H}_2\text{O}$ is $-0.75\%/ \text{ppmv}$ with no temperature feedback compared with $-0.64\%/ \text{ppmv}$ when the K_{21} profile is used. When temperature feedback is included, the slope is nearly zero. However, with the NO_2 injection the model sensitivity changes significantly. First, the ozone destruction with no change in H_2O when a fixed temperature profile is used is considerably larger with the K_{22} profile, 4.66% compared with 2.25%. Second, the slopes of the curves are changed significantly. The amount of ozone reduction due to an increase in H_2O is reduced for the fixed temperature calculation (the slope is $-0.07\%/ \text{ppmv}$ compared with $-0.42\%/ \text{ppmv}$ previously). For the calculation with temperature feedback the reduction in ΔO_3 due to increased H_2O is further enhanced (the slope is $0.63\%/ \text{ppmv}$ compared with $0.21\%/ \text{ppmv}$ previously). Thus the choice of the K profile and the magnitude of the NO_2 injection significantly affect the sensitivity to changes in H_2O .

Profiles of $\Delta\text{DO}_2(\text{H}_2\text{O})$ are shown in Figures 8a and 8b for the calculations with fixed temperature and with temperature feedback, respectively. The results are qualitatively similar to those in Figure 5, but there are some quantitative differences. The ozone production (or destruction, depending upon the sign of $\Delta\text{H}_2\text{O}$) in the 20- to 35-km region approximately

TABLE 2. Updated Reaction Rate Coefficients [Hudson, 1977]

Reaction	New Rate, $\text{cm}^3 \text{s}^{-1}$, $\text{cm}^3 \text{s}^{-1}$
$\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$	$2.1 \times 10^{-10} \exp(-1430/T)$
$\text{O}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{O}_2$	$1.5 \times 10^{-12} \exp(-1000/T)$
$\text{O}_3 + \text{HO}_2 \rightarrow \text{OH} + 2\text{O}_2$	$7.3 \times 10^{-14} \exp(-1225/T)$
$\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$	3.5×10^{-11}
$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	2.5×10^{-14}
$\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	3.0×10^{-11}
$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$	8.0×10^{-12}
$\text{N} + \text{O}_3 \rightarrow \text{NO} + \text{O}_2$	$2.0 \times 10^{-14} \exp(-1070/T)$
$\text{O}(\text{D}) + \text{M} \rightarrow \text{O} + \text{M}$	$2.2 \times 10^{-14} \exp(99/T)^\dagger$
$\text{NO} + \text{ClO} \rightarrow \text{NO}_2 + \text{Cl}$	$1.0 \times 10^{-11} \exp(200/T)$
$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{OClO}$	$2.1 \times 10^{-12} \exp(-2200/T)$
$\text{ClO} + \text{ClO} \rightarrow 2\text{Cl} + \text{O}_2$	$5.0 \times 10^{-13} \exp(-1238/T)^\dagger$
$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{ClO}_2$	$1.0 \times 10^{-12} \exp(-1238/T)$
$\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$	$3.0 \times 10^{-13} \exp(-425/T)$
$\text{O} + \text{OClO} \rightarrow \text{ClO} + \text{O}_2$	$2.0 \times 10^{-11} \exp(-1100/T)$
$\text{Cl} + \text{OH} \rightarrow \text{HCl} + \text{O}$	$1.0 \times 10^{-11} \exp(-2970/T)$
$\text{Cl} + \text{HNO}_2 \rightarrow \text{HCl} + \text{NO}_2$	$1.0 \times 10^{-11} \exp(-2170/T)$
$\text{ClONO}_2 + \text{O} \rightarrow \text{ClO} + \text{NO}_2$	$3.0 \times 10^{-12} \exp(-808/T)$
$\text{ClO} + \text{NO}_2 \rightleftharpoons \text{ClONO}_2$	$3.3 \times 10^{-12} T^{-0.25} \exp(-1000/T)$

[†]Differs from value given by Hudson [1977].

[‡]No recommendation for this rate is given by Hudson [1977].

Fig. 9. Change in total ozone versus change in the water vapor mixing ratio above 13 km. This is the same as Figure 3 except that the chemical rate coefficients in Table 2 are used.

balances the ozone destruction (production) in the 10- to 20-km region for the fixed temperature calculation when the K_{11} profile is used, whereas the lower region is dominant when the K_{11} profile is used. Above 35 km the curves are virtually unchanged. The ozone production (destruction) in the 20- to 35-km region when K_{11} is used shows more enhancement with temperature feedback than when K_{11} is used.

Subsequent to these calculations, there were several new measurements of reaction rate coefficients. The most significant change was a much faster rate coefficient for the reaction $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$ [Howard and Ewenson, 1977]. The model chemistry was updated to include this change as well as the latest recommendations of NASA [Hudson, 1977]. The changes to the model chemistry are listed in Table 2.

The computed change in total ozone due to a change in the water vapor mixing ratio obtained by using the chemical rates listed in Table 2 and the K_{11} profile is shown in Figure 9. Although the model response to a stratospheric NO_2 injection at 20 km (the same as that in Figure 3) has changed from a decrease in total ozone to an increase, the effect on ozone of changing water vapor abundance is nearly unchanged. Compared with Figure 3, the curves are displaced, but the slopes of the curves are changed only slightly.

Fig. 10. Profiles of $\Delta\text{DO}_2(\text{H}_2\text{O})$ corresponding to various values of $\Delta\text{H}_2\text{O}$ obtained by using the chemical rate coefficients in Table 2 for the case of an NO_2 injection at 20 km (a) with fixed temperature and (b) with temperature feedback. Note that the multiplier 10^{-2} is applied to the values along the abscissa.

Fig. 11. Change in total ozone at steady state versus change in the water vapor mixing ratio above 13 km computed by using the K_{11} profile for the case of CFM's released at the 1975 release rate.

Profiles of $\Delta\text{DO}_2(\text{H}_2\text{O})$ are shown in Figures 10a and 10b for the calculations with fixed temperature and with temperature feedback, respectively. The curves are qualitatively similar to those in Figure 5, but quantitatively they are quite different. Although there are similar regions of local ozone increase or decrease, the magnitude of the change in ozone concentration has been significantly affected, particularly in the 25- to 35-km region.

The ozone production in the 20- to 35-km region associated with an increase in H_2O is the net result of competing processes, some which tend to increase ozone and some which tend to destroy ozone. The net result is sensitive to the HO_2 and NO_2 abundances which are affected by the diffusion coefficient profile, key reaction rates such as $\text{OH} + \text{HO}_2$ and $\text{HO}_2 + \text{NO}$, and the magnitude of the NO_2 injection. Because of uncertainties in these quantities there is a significant uncertainty in the quantitative results in the 20- to 35-km region in Figures 5, 8, and 10. These figures, however, illustrate the significant effect which changes in temperature have on the chemistry in the region below 35 km.

CFM Release

The effect of changes in stratospheric water vapor abundance on the ozone reduction due to CIX pollutants was also tested. The perturbation which we considered was a steady state release of CFM's at the 1975 release rate, which is assumed to be 290 kt/yr for CFCl_3 and 425 kt/yr for CF_2Cl_2 .

Fig. 12. Percent change in ozone concentration at steady state as a function of height due to CFM's at the 1975 release rate.

Fig. 13. Change in temperature for the stratosphere perturbed by CFM's at the 1975 release rate.

The long-wave effects of CFCl_3 and CF_2Cl_2 are not included in the radiative transfer model. These effects have been shown to be significant by Ramanathan [1976] for species concentrations of several parts per billion. This introduces considerable uncertainty into the temperature calculation in the 15- to 25-km region for the perturbed stratosphere. The effect of changes in water vapor abundance on total ozone is not altered, since the incremental change in temperature due to $\Delta\text{H}_2\text{O}$ is not changed significantly. It will, however, affect the ozone reduction for the temperature feedback calculation with $\Delta\text{H}_2\text{O} = 0$. Thus the curve of ΔO_3 versus $\Delta\text{H}_2\text{O}$ will be displaced, but the slope will not be significantly affected.

The steady state reduction in total ozone computed by using the K_{11} profile is shown in Figure 11 as a function of $\Delta\text{H}_2\text{O}$. The reduction in total ozone is 6.9% for the fixed temperature calculation with no change in water vapor. The sensitivity to changes in water vapor is enhanced by the CFM injection, unlike our findings for an NO_x injection. The slope of ΔO_3 versus $\Delta\text{H}_2\text{O}$ is $-1.2\%/ \text{ppmv}$ compared to $-0.64\%/ \text{ppmv}$ with only a change in water vapor (Figure 3a). Our results with fixed temperature agree very well with those of Liu *et al.* [1976], who got a value of $-1.4\%/ \text{ppmv}$ with 1 ppb of ClX.

Including temperature feedback reduces the sensitivity to changes in H_2O but not sufficiently to change the sign of the slope of ΔO_3 versus $\Delta\text{H}_2\text{O}$ as was the case with the NO_x injection. The slope with temperature feedback is $-0.6\%/ \text{ppmv}$, which is half that with fixed temperature. The change in slope due to temperature feedback is approximately the same as the difference between the slopes of the curves in Figure 3b.

Figure 12 shows the change in ozone concentration versus height for the fixed temperature and temperature feedback calculations with $\Delta\text{H}_2\text{O} = 0$. The differences between these two calculations are attributed directly to the change in temperature (shown in Figure 13). The temperature decreases above 30 km, the decrease thus slowing the ozone destruction reactions and resulting in less ozone destruction with temperature feedback. Below 30 km the temperature increases, a process which, an activation energy argument again being used, results in less ozone production or more ozone destruction.

With no change in water vapor the temperature change at the tropopause was -0.03 K. The concentration of CFM's at the tropopause was 0.7 ppb for CFCl_3 and 1.7 ppb for CF_2Cl_2 . Radiative transfer calculations which include the long-wave effect of CFM's at this concentration show a warming at the tropopause of about 1 K (S. C. Liu, private communication, 1977). This would enhance slightly the difference between the two curves shown in Figure 12 in the 10- to 20-km region. The negative feedback between changes in water vapor and tem-

perature discussed above for the NO_x perturbation is also apparent in Figure 13; thus it is unlikely that the water vapor mixing ratio will increase more than about 1 ppmv owing to this CFM perturbation.

The profiles of $\Delta\text{DO}_3(\text{H}_2\text{O})$ are presented in Figure 14 for the CFM perturbation. The results differ significantly from those shown in Figure 5 for the NO_x injection. Although there is a region of reduced sensitivity near 30 km, there is no longer a crossover region. Temperature feedback causes a shift in sensitivity similar to that in the NO_x perturbation case. For smaller CFM release rates there is a crossover similar to that shown in Figure 5, which illustrates the dependence upon the magnitude of the CFM perturbation.

The effect of changes in water vapor is somewhat different for the CFM perturbation because of the importance of the reaction

Although increased HO_x in the lower atmosphere tends to increase O_3 owing to conversion of NO_x to HNO_3 and to production of odd oxygen through (6) and (7), it also releases more free chlorine through (11), a process which tends to enhance the ozone reduction. The results depend upon the magnitude of the CFM perturbation because of its effect on the concentration of HCl. Again, we are seeing in Figure 14 the net effect of many competing processes.

CONCLUSIONS

Liu *et al.* [1976] have called attention to the large influence of water vapor in the stratosphere on the catalytic destruction of ozone by NO_x and by ClX. Our fixed temperature calculations, which show the sensitivity of changes in total ozone to changes in water vapor concentration, are in good agreement with their results. The rate coefficients for the reactions responsible for this sensitivity are sensitive to changes in temperature, particularly for the lower stratosphere. Consequently, when changes in temperature are included in the calculation, there is a significant change in the model sensitivity. Inclusion of temperature feedback makes the model nearly insensitive to changes in stratospheric water vapor when this is the only perturbation. When changes in water vapor are coupled with an NO_x perturbation, temperature feedback leads to a reversal in the sensitivity such that an increase in H_2O decreases ΔO_3 . In the case of changes in water vapor coupled with a CFM perturbation, there is a reduction in sensitivity, but there is not a sign reversal. The change in the slope of ΔO_3 versus $\Delta\text{H}_2\text{O}$ due to inclusion of temperature feedback is approximately the same for both the NO_x and the CFM perturbations.

Fig. 14. Profiles of $\Delta\text{DO}_3(\text{H}_2\text{O})$ corresponding to various values of $\Delta\text{H}_2\text{O}$ obtained by using the K_{11} profile for the case of CFM's at the 1975 release rate (a) with fixed temperature and (b) with temperature feedback. Note that the multiplier 10^{-2} is applied to values along the abscissa.

In analyzing the effect of changes in water vapor on the ozone profile the region between 10 and 35 km was shown to be most sensitive. In the 25- to 35-km region an increase in H_2O may either increase ozone or decrease ozone depending upon the concentrations of NO_x and Cl ; the larger the NO_x perturbation, the more H_2O tends to increase ozone, whereas the larger the CFM perturbation, the more H_2O tends to decrease ozone.

The results depend quantitatively upon the reaction rates and the K_1 profile used for the calculation. Because of uncertainties in these quantities the qualitative nature of the results should be emphasized rather than their quantitative nature. The change in O_3 depends upon the net effect of several competing mechanisms, particularly in the 25- to 35-km region. A change in the relative importance of these mechanisms, caused perhaps by changing a key reaction rate, might lead to a significant quantitative difference.

In addition to illustrating the importance of changes in temperature to the model sensitivity to changes in water vapor, which is the main point of the paper, these calculations illustrate an important feedback mechanism. These calculations show that an increase in water vapor concentration tends to cool the atmosphere in the vicinity of the tropopause, the change in H_2O concentration thus being limited. Consequently, changes in stratospheric H_2O of the magnitude postulated by Liu *et al.* [1976] would not be expected. However, the effect of changes in dynamics was not included in the temperature calculation, an omission which introduces significant uncertainty into the calculation of ΔT .

The results presented above should be considered a sensitivity study rather than an assessment of the effect of atmospheric perturbations on total ozone. Ideally, the model used to perform such an assessment should include the feedback between changes in atmospheric composition and transport coupled with changes in the radiation budget in addition to modeling the tropical tropopause cold trap. In this way the change in water vapor concentration would be predicted rather than specified. Doing this, however, would require a multi-dimensional model in which the photochemical kinetics, transport, radiative transfer, moisture budget, cloud cover, and energy budget are all modeled in detail. Such a model would essentially be a multidimensional climate model with detailed photochemistry. Although it is easy to define the desirable features of the ideal model, unfortunately, it does not seem possible to create and operate such a model at this time. Consequently, a hierarchy of models is needed spanning the range from one-dimensional models with detailed photochemistry to three-dimensional models with detailed transport.

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***Effect of Multiple Scattering on Species
Concentrations and Model Sensitivity***

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Effect of Multiple Scattering on Species Concentrations and Model Sensitivity

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Multiple scattering significantly affects atmospheric photodissociation rates, particularly at wavelengths greater than 290 nm. Incorporating the effects of multiple scattering into a one-dimensional transport-kinetics model led to dramatic changes in the concentration profiles of many trace species; thus it is important to include multiple scattering when model results are compared with observational data. The effect on model sensitivity of including multiple scattering ranged from no change in ΔO_3 compared with the pure absorption calculation to a significant increase in ΔO_3 , depending upon the model chemistry. The change in ΔO_3 due to multiple scattering was small in comparison with the change in ΔO_3 resulting from varying chemical reaction rates. Variations in surface albedo had little effect on model sensitivity.

INTRODUCTION

Molecular multiple scattering, the earth's surface reflection, clouds, and aerosols have all been shown to have a significant effect on stratospheric and tropospheric radiative intensities at photodissociative wavelengths. The importance of molecular scattering and surface albedo and their effect on atmospheric photodissociation rates have been discussed by Luther and Gelinis [1976]. Parameterizations of the effect of multiple scattering on photodissociative flux densities have been included in one-dimensional transport-kinetics models by Crutzen *et al.* [1978], Callis *et al.* [1976], Ashby [1976], and Kurzeja [1976]. Crutzen *et al.* [1978] used a two-flux approximation to account for the direct and scattered radiation. Callis *et al.* [1976], using a detailed solar radiation model, computed correction factors which were then applied to the photodissociative rates computed by assuming a purely absorbing atomic and molecular atmosphere. The correction factors vary with altitude for each photodissociative reaction, and they are assumed to be unaffected by changes in atmospheric composition.

This paper assesses in detail the effect of molecular multiple scattering and surface reflection on ambient species concentration profiles and on model sensitivity to perturbations affecting stratospheric ozone. This theoretical assessment is conducted by using a one-dimensional transport-kinetics model which has been carefully studied and documented through numerous sensitivity studies and model intercomparisons [Chang, 1975; Wuebbles and Chang, 1975; Duewer *et al.*, 1977; Luther *et al.*, 1977; Luther and Duewer, 1978].

MODEL DESCRIPTION

The model atmosphere of the transport-kinetics model extends from the ground to 55 km and is divided into 44 layers. A total of 83 chemical (and photochemical) reactions are included in the model; 44 reactions describe O_3 , NO , and HO_2 chemistry, and 39 reactions describe CIX chemistry. These reactions are used to describe the stratospheric vertical distributions of 20 minor atmospheric species ($O(^1P)$, O_3 , NO , NO_2 , N_2O , HNO_3 , OH , HO_2 , H_2O_2 , Cl , CH_4 , ClO , CH_3Cl , $OCIO$, $ClONO_2$, $ClNO_2$, HCl , CCl_4 , CF_3Cl , and $CFCl_3$). Three species (H , N , and $O(^1D)$) are assumed to be in instantaneous equilibrium, while the vertical profiles of N_2 , O_2 , H_2 , CO , and H_2O are specified. The boundary conditions, which are species dependent, are assumed to be fixed or time-varying source-

dependent concentrations at the earth's surface and flux conditions at 55 km, the upper boundary.

The diffusion coefficient profile used in the calculations to describe vertical transport was developed at the Lawrence Livermore Laboratory (LLL) on the basis of an analysis by R. E. Dickinson using the lifetimes of CH_4 and N_2O as given by this model. (This profile is also the same as model E in the National Research Council [1976] report.) The chemical reaction rates used in the model are shown in Table 1. Detailed spectral data used in the calculations are described by Gelinis [1974].

The effect of multiple scattering was incorporated into the photodissociation rate calculation by applying correction factors to the shortwave fluxes used in the pure absorption calculation. The solution of the one-dimensional purely absorbing radiative transfer equation at a particular altitude z_p , solar zenith angle θ_0 , time t , and atmospheric composition (N_A) is given by

$$F_\lambda(z_p, \theta_0, [N_A], t) = F_\lambda(\infty) \exp \{-\tau_\lambda(z_p, \theta_0, [N_A], t)\} \quad (1)$$

where $F_\lambda d\lambda$ is the flux of photons in the wavelength interval $d\lambda$ about λ . $F_\lambda(\infty)$ $d\lambda$ represents the solar flux at the top of the atmosphere. The optical depth τ_λ is given by

$$\tau_\lambda(z_p, \theta_0, [N_A], t) = \int_{z_p}^{\infty} dz \sum_A N_A(z, t) \sigma_T^A[\lambda, T(z)] \sec \theta_d(t) \quad (2)$$

In (2) the summation on A includes all atmospheric absorbers, each having number density $N_A(z, t)$ and a total absorption cross section $\sigma_T^A[\lambda, T(z)]$. Generally, $\sigma_T^A[\lambda, T(z)]$ is a function of the temperature $T(z)$.

The photodissociation rate for transforming species i to species j is denoted by $J_{i \rightarrow j}(z_p, \theta_0, t) N_A(z_p, t)$, where

$$J_{i \rightarrow j}(z_p, \theta_0, t) = \int_{\lambda_{\min}}^{\lambda_{\max}} d\lambda \sigma_D^i[j, \lambda, T(z_p)] F_\lambda(z_p, \theta_0, [N_A], t) \quad (3)$$

The microscopic photodissociation cross-section $\sigma_D^i[j, \lambda, T(z_p)]$ is often written in terms of the quantum yield $Q_\lambda(i \rightarrow j)$ as

$$\sigma_D^i[j, \lambda, T(z_p)] = \sigma_T^i[\lambda, T(z_p)] Q_\lambda(i \rightarrow j) \quad (4)$$

It should be noted that significant uncertainties remain in the data used to calculate the photodissociation coefficients in

TABLE 1. Chemical Reactions and Rate Coefficients

Reaction	Rate Coefficient, $\text{cm}^3 \text{s}^{-1}, \text{cm}^6 \text{s}^{-1}$
$\text{O} + \text{O}_2 \xrightarrow{\Delta} \text{O}_3$	$1.1 \times 10^{-34} \exp(510/T)$
$\text{O} + \text{O}_2 \rightarrow \text{O}_3$	$1.9 \times 10^{-11} \exp(-2300/T)$
$\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$	$2.3 \times 10^{-12} \exp(-1450/T)$
$\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$	9.1×10^{-12}
$\text{N}_2\text{O} + \text{O}(\text{D}) \rightarrow \text{N}_2 + \text{O}_2$	5.5×10^{-11}
$\text{N}_2\text{O} + \text{O}(\text{D}) \rightarrow 2\text{NO}$	5.5×10^{-11}
$\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$	$5.5 \times 10^{-12} \exp(-3220/T)$
$\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$	$8.2 \times 10^{-11} \exp(-410/T)$
$\text{O}(\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$	2.3×10^{-10}
$\text{O}(\text{D}) + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_3^*$	1.3×10^{-10}
$\text{O}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{O}_2$	$1.6 \times 10^{-12} \exp(-1000/T)$
$\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$	4.2×10^{-11}
$\text{O}_3 + \text{HO}_2 \rightarrow \text{OH} + 2\text{O}_2$	$1.0 \times 10^{-12} \exp(-1250/T)$
$\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$	3.0×10^{-11}
$\text{H} + \text{O}_2 \xrightarrow{\Delta} \text{HO}_2$	$2.08 \times 10^{-22} \exp(290/T)$
$\text{O}_3 + \text{H} \rightarrow \text{OH} + \text{O}_2$	$1.23 \times 10^{-10} \exp(-562/T)$
$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$1.7 \times 10^{-11} \exp(-500/T)$
$\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	2.0×10^{-11}
$\text{OH} + \text{NO}_2 \xrightarrow{\Delta} \text{HNO}_3$	$\dagger$
$\text{OH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + 0.67\text{NO}_2$ $+ 0.67\text{O} + 0.33\text{NO} + 0.33\text{O}_2$	8.9×10^{-14}
$\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$	$1.0 \times 10^{-11} \exp(-750/T)$
$\text{N}_2 + \text{O}(\text{D}) \xrightarrow{\Delta} \text{N}_2\text{O}$	3.5×10^{-37}
$\text{N} + \text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{O}$	$2.0 \times 10^{-11} \exp(-800/T)$
$\text{NO} + \text{O} \rightarrow \text{NO}_2$	$1.6 \times 10^{-12} \exp(584/T)$
$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$	$1.7 \times 10^{-11} \exp(-1000/T)$
$\text{H}_2 + \text{O}(\text{D}) \rightarrow \text{OH} + \text{H}$	9.9×10^{-11}
$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$	$1.0 \times 10^{-11} \exp(-550/T)$
$\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$	$5.0 \times 10^{-12} \exp(-650/T)$
$\text{NO}_2 + \text{O}_3 \rightarrow 0.67\text{NO}_2 + 0.67\text{O}$ $+ 0.33\text{NO} + 0.33\text{O}_2$	$1.2 \times 10^{-12} \exp(-2450/T)$
$\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3^*$	$2.36 \times 10^{-12} \exp(-1710/T)$
$\text{OH} + \text{OH} \xrightarrow{\Delta} \text{H}_2\text{O}_2$	$1.2 \times 10^{-20} \exp(900/T)$
$\text{H}_2\text{O}_2 + \text{O} \rightarrow \text{OH} + \text{HO}_2$	$2.75 \times 10^{-12} \exp(-2125/T)$
$\text{O} + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_3^*$	$3.5 \times 10^{-13} \exp(-4550/T)$
$\text{CO} + \text{OH} \rightarrow \text{H} + \text{CO}_2$	1.4×10^{-12}
$\text{O}(\text{D}) \xrightarrow{\Delta} \text{O}$	$2.0 \times 10^{-11} \exp(107/T)$
$\text{Cl} + \text{O}_2 \rightarrow \text{ClO} + \text{O}$	$2.7 \times 10^{-11} \exp(-257/T)$
$\text{Cl} + \text{OCIO} \rightarrow 2\text{ClO}$	5.9×10^{-11}
$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3^*$	$7.3 \times 10^{-12} \exp(-1260/T)$
$\text{Cl} + \text{NO}_2 \xrightarrow{\Delta} \text{ClONO}_2$	$6.9 \times 10^{-26} \exp(2115/T)$
$\text{Cl} + \text{ClONO}_2 \rightarrow 2\text{Cl} + \text{NO}_2$	3.0×10^{-12}
$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$	$7.7 \times 10^{-11} \exp(-130/T)$
$\text{NO} + \text{ClO} \rightarrow \text{NO}_2 + \text{Cl}$	2.2×10^{-11}
$\text{ClO} + \text{O}_2 \rightarrow \text{ClO}_2 + \text{O}$	$1.0 \times 10^{-12} \exp(-4000/T)$
$\text{ClO} + \text{O}_2 \rightarrow \text{OCIO} + \text{O}_2$	$1.0 \times 10^{-12} \exp(-4000/T)$
$\text{ClO} + \text{NO}_2 \xrightarrow{\Delta} \text{ClONO}_2$	$5.1 \times 10^{-20} \exp(1030/T)$
$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{OCIO}$	$1.5 \times 10^{-12} \exp(-1238/T)$
$\text{ClO} + \text{ClO} \rightarrow 2\text{Cl} + \text{O}_2$	$4.5 \times 10^{-12} \exp(-1238/T)$
$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{ClO}_2^*$	$9.0 \times 10^{-12} \exp(-1238/T)$
$\text{HCl} + \text{O}(\text{D}) \rightarrow \text{Cl} + \text{OH}$	1.4×10^{-10}
$\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$	$2.8 \times 10^{-12} \exp(-400/T)$
$\text{O} + \text{HCl} \rightarrow \text{OH} + \text{Cl}$	$1.1 \times 10^{-11} \exp(-3370/T)$
$\text{O} + \text{OCIO} \rightarrow \text{ClO} + \text{O}_2$	5.0×10^{-12}
$\text{NO} + \text{OCIO} \rightarrow \text{NO}_2 + \text{ClO}$	3.4×10^{-12}
$\text{N} + \text{OCIO} \rightarrow \text{NO} + \text{ClO}$	6.0×10^{-12}
$\text{H} + \text{OCIO} \rightarrow \text{OH} + \text{ClO}$	5.7×10^{-11}
$\text{Cl} + \text{OH} \rightarrow \text{HCl} + \text{O}$	$2.0 \times 10^{-12} \exp(-1878/T)$
$\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2$	3.0×10^{-11}
$\text{Cl} + \text{HNO}_3 \rightarrow \text{HCl} + 0.67\text{NO}_2$ $+ 0.67\text{O} + 0.33\text{NO} + 0.33\text{O}_2$	6.0×10^{-14}
$\text{CFCl}_3 + \text{O}(\text{D}) \rightarrow 2\text{Cl}$	2.3×10^{-10}
$\text{CF}_2\text{Cl}_2 + \text{O}(\text{D}) \rightarrow 2\text{Cl}$	2.0×10^{-10}
$\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$	$4.7 \times 10^{-11} \exp(-2340/T)$
$\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{HCl} + \text{HO}_2$	$1.6 \times 10^{-12} \exp(-384/T)$
$\text{ClONO}_2 + \text{O} \rightarrow \text{ClO} + \text{NO}_2^*$	$5.0 \times 10^{-12} \exp(-840/T)$
$\text{CH}_3\text{Cl} + \text{OH} \rightarrow \text{Cl} + \text{H}_2\text{O} + \text{HO}_2$	$2.2 \times 10^{-12} \exp(-1142/T)$

*These species are not actually used in the model. They are assumed to react instantaneously to form other products.

†We use an expression developed by W. Tsang (private communication, 1976): $\log_{10}(k) = -A/T(B+T) - 0.5 \log_{10}(T/280)$, where $A = A_1 + A_2Z + A_3Z^2 - A_4Z^3$, $B = B_1 + B_2Z + B_3Z^2$, $Z = \log_{10}[\text{M}]$, $A_1 = 31.62273$, $A_2 = -0.258304$, $A_3 = -0.0889287$, $A_4 = 2.520173 \times 10^{-2}$, $B_1 = -327.372$, $B_2 = 44.5586$, and $B_3 = -1.38092$.

Fig. 1. Concentration profiles for O_3 species. Fig. 2. Concentration profiles for HO_2 species. Fig. 3. Concentration profiles for NO_2 species.

Fig. 4. Concentration profiles for species containing chlorine.

TABLE 2. Photodissociation Processes Included in the Model

Photodissociation Process	Spectral Type
$O_3 \rightarrow O(^1P) + O(^1D)$	1
$O_3 \rightarrow O(^1P) + O(^1D)$	3
$O_3 \rightarrow O(^1D) + O(^1D)$	2
$NO_2 \rightarrow NO + O(^1D)$	2
$N_2O \rightarrow N_2 + O(^1D)$	1
$NO \rightarrow N + O(^1D)$	1
$HNO_2 \rightarrow OH + NO_2$	2
$H_2O_2 \rightarrow 2OH$	2
$HO_2 \rightarrow OH + O(^1D)$	1
$CH_3Cl \rightarrow CH_3 + Cl$	1
$HCl \rightarrow H + Cl$	1
$ClONO_2 \rightarrow ClO + NO_2$	2
$ClO_2 \rightarrow ClO + O(^1D)$	1
$ClO \rightarrow Cl + O(^1D)$	1
$ClO \rightarrow Cl + O(^1D)$	1
$ClONO_2 \rightarrow Cl + NO_2$	2
$OCIO \rightarrow ClO + O(^1D)$	3
$CF_2Cl_2 \rightarrow 2CF_2$	1
$CFCl_3 \rightarrow 2CF_2 + Cl$	1
$CCl_4 \rightarrow 2CCl_2$	1

the models. For example, major uncertainties remain in the branching of O_3 photolysis near 310 nm to either $O(^1P)$ or $O(^1D)$, in the branching and quantum yield for NO_2 photolysis, and in the methodology for calculating the photolysis of species having banded or line absorption cross-section structures, such as O_3 or NO_2 .

When molecular multiple scattering and surface albedo are included in the radiative transfer calculation, (1) is no longer the solution of the radiative transfer equation. However, the flux in the direct solar beam F_{λ}^d is given by an equation similar to (1):

$$F_{\lambda}^d(z_p, \theta_0, \{N_{\lambda}\}, t) = F_{\lambda}^d(\infty) \exp[-\tau_{\lambda}^d(z_p, \theta_0, \{N_{\lambda}\}, t)] \quad (5)$$

where the optical depth τ_{λ}^d along the slant path is given by

$$\tau_{\lambda}^d(z_p, \theta_0, \{N_{\lambda}\}, t) = \int_{z_p}^{\infty} dz \sum_{\lambda} N_{\lambda}(z, t) \sigma_{\lambda}^d(\lambda, T(z)) \sec \theta_0(z) + \int_{z_p}^{\infty} dz \sum_i N_i(z, t) \sigma_{\lambda}^i(\lambda) \sec \theta_0(z) \quad (6)$$

In (6) the summation on i includes all atmospheric species, and σ_{λ}^i is the Rayleigh scattering cross section for species i . $F_{\lambda}^d(z_p, \theta_0, \{N_{\lambda}\}, t)$ differs from $F_{\lambda}(z_p, \theta_0, \{N_{\lambda}\}, t)$ as defined by (1) in that attenuation due to both absorption and scattering is included in (5), whereas only absorption is included in (1).

The photodissociation coefficient also depends upon the scattered (diffuse) radiation, given by

$$J_{\lambda}(z_p, \theta_0, t) = \int_{\text{all } \lambda} d\lambda \sigma_{\lambda}^d[j, \lambda, T(z_p)] \times \left[F_{\lambda}^d(z_p, \theta_0, \{N_{\lambda}\}, t) + \int_{\omega} I_{\lambda}(z_p, \omega) d\omega \right] \quad (7)$$

where I_{λ} is the specific intensity of the diffuse radiation and ω is the solid angle. Including the effect of molecular multiple scattering and surface albedo in the calculation is simply expressed by changing the value of F_{λ} appearing in (3). For clarity, we define

$$F_{\lambda}^{MS} = F_{\lambda}^d(z_p, \theta_0, \{N_{\lambda}\}, t) + \int_{\omega} I_{\lambda}(z_p, \omega) d\omega \quad (8)$$

TABLE 3. Comparison of Photodissociation Rates Calculated With and Without Multiple Scattering

Altitude, km	J_{λ}^d, s^{-1}	J_{λ}^{MS}, s^{-1}	$J_{\lambda}^{MS}/J_{\lambda}^d$
$O_3 + h\nu \rightarrow O(^1P) + O(^1D)$			
40	2.74×10^{-4}	3.49×10^{-4}	1.27
30	2.40×10^{-4}	3.18×10^{-4}	1.33
20	2.06×10^{-4}	2.95×10^{-4}	1.43
10	2.01×10^{-4}	2.94×10^{-4}	1.46
$O_3 + h\nu \rightarrow O(^1D) + O(^1D)$			
40	9.10×10^{-4}	9.09×10^{-4}	1.00
30	5.30×10^{-4}	5.30×10^{-4}	1.01
20	7.49×10^{-4}	9.66×10^{-4}	1.29
10	5.44×10^{-4}	8.26×10^{-4}	1.52
$O_3 + h\nu \rightarrow O + O$			
40	3.01×10^{-10}	3.01×10^{-10}	1.00
30	1.83×10^{-11}	1.74×10^{-11}	0.95
20	5.73×10^{-12}	4.42×10^{-12}	0.77
10	7.64×10^{-10}	8.91×10^{-10}	1.17
$NO_2 + h\nu \rightarrow NO + O$			
40	4.97×10^{-3}	7.73×10^{-3}	1.56
30	4.85×10^{-3}	7.67×10^{-3}	1.58
20	4.74×10^{-3}	7.74×10^{-3}	1.63
10	4.72×10^{-3}	7.74×10^{-3}	1.64
$HNO_2 + h\nu \rightarrow OH + NO_2$			
40	3.50×10^{-3}	3.51×10^{-3}	1.00
30	4.66×10^{-3}	4.54×10^{-3}	0.97
20	3.25×10^{-3}	4.54×10^{-3}	1.40
10	2.61×10^{-3}	4.16×10^{-3}	1.59
$H_2O_2 + h\nu \rightarrow 2OH$			
40	2.11×10^{-3}	2.14×10^{-3}	1.01
30	3.79×10^{-3}	4.07×10^{-3}	1.07
20	1.30×10^{-3}	1.85×10^{-3}	1.42
10	1.10×10^{-3}	1.75×10^{-3}	1.59
$HO_2 + h\nu \rightarrow OH + O$			
40	6.50×10^{-3}	6.49×10^{-3}	1.00
30	3.35×10^{-3}	3.19×10^{-3}	0.95
20	1.05×10^{-3}	8.08×10^{-4}	0.77
10	1.55×10^{-3}	1.81×10^{-3}	1.17
$ClONO_2 + h\nu \rightarrow ClO + NO_2$			
40	2.21×10^{-4}	2.37×10^{-4}	1.07
30	5.09×10^{-4}	6.83×10^{-4}	1.34
20	3.41×10^{-4}	5.46×10^{-4}	1.60
10	3.28×10^{-4}	5.40×10^{-4}	1.65
$ClONO_2 + h\nu \rightarrow Cl + NO_2$			
40	6.03×10^{-4}	7.42×10^{-4}	1.23
30	3.41×10^{-4}	4.89×10^{-4}	1.43
20	2.73×10^{-4}	4.46×10^{-4}	1.63
10	2.64×10^{-4}	4.42×10^{-4}	1.67
$OCIO + h\nu \rightarrow ClO + O(^1D)$			
40	2.27×10^{-4}	3.02×10^{-4}	1.33
30	1.53×10^{-4}	2.29×10^{-4}	1.50
20	1.40×10^{-4}	2.23×10^{-4}	1.59
10	1.39×10^{-4}	2.23×10^{-4}	1.60
$ClO + h\nu \rightarrow Cl + O$			
40	1.61×10^{-3}	1.62×10^{-3}	1.01
30	1.77×10^{-3}	1.78×10^{-3}	1.01
20	2.37×10^{-3}	2.86×10^{-3}	1.21
10	1.57×10^{-3}	2.29×10^{-3}	1.46
$CF_2Cl_2 + h\nu \rightarrow 2CF_2$			
40	5.12×10^{-11}	5.14×10^{-11}	1.00
30	6.17×10^{-11}	5.83×10^{-11}	0.94
20	1.92×10^{-10}	1.45×10^{-10}	0.76
10	1.09×10^{-10}	1.28×10^{-10}	1.17

TABLE 3. (continued)

Altitude, km	J_{PA}, s^{-1}	J_{MS}, s^{-1}	J_{MS}/J_{PA}
<i>CFC1₂ + hν → 2.5Cl</i>			
40	4.39×10^{-8}	4.40×10^{-8}	1.00
30	5.20×10^{-7}	4.94×10^{-7}	0.95
20	1.79×10^{-9}	1.36×10^{-9}	0.76
10	1.53×10^{-10}	1.78×10^{-10}	1.16

The values correspond to a solar zenith angle of 45° and half sun to account for day-night averaging.

where the superscript MS indicates multiple scattering. Henceforth F_A^{PA} (pure absorption) will refer to the flux defined by (1). Aside from substituting F_A^{MS} for F_A^{PA} in (3), all other aspects of the photodissociation rate calculation are the same as those for the purely absorbing molecular atmosphere.

The effect of multiple scattering was incorporated into the photodissociation rate calculation by applying correction factors to the flux F_A used in the pure absorption calculation. These correction factors, which are given by the ratio F_A^{MS}/F_A^{PA} , were computed for the unperturbed species profiles by using the same detailed solar radiation model as *Luther and Gelinas* [1976]. A separate factor was computed for each of the 44 levels and for each of the 148 wavelength intervals between 133 and 735 nm. Different sets of correction factors were computed for each assumed value of surface albedo A_s by using a solar zenith angle of 45°.

Correction factors for a solar zenith angle of 45° are qualitatively similar to, although somewhat larger than, those computed by *Luther and Gelinas* [1976] for $\theta = 60^\circ$. The correction factors are nearly constant with height above 20 km, but they may vary significantly with height in the region below 20 km, which is where most scattering events occur.

RESULTS

Including multiple scattering in the photodissociation rate calculation affects the photodissociation coefficients, the ambient species concentration profiles, and the model sensitivity to perturbations by NO_x and CIX pollutants. Each of these effects will be discussed separately.

Photodissociation Coefficients

The photodissociation processes included in the model are listed in Table 2 along with their spectral type as defined by

Fig. 5. Change in concentration of O_3 species due to multiple scattering with $A_s = 0.25$.

Fig. 6. Change in concentration of HO_2 species due to multiple scattering with $A_s = 0.25$.

Luther and Gelinas [1976]. The spectral type is related to the wavelength regime in which photodissociation predominantly occurs. For spectral type 1, photodissociation predominantly occurs at wavelengths less than 290 nm. This is a region of strong absorption, and virtually no radiation is transmitted to altitudes below 10 km. For spectral type 3, photodissociation predominantly occurs at wavelengths greater than 330 nm. In this region the atmospheric transmissivity is high. Consequently, surface albedo has a significant effect on the scattered radiation. Spectral type 2 refers to the transition region between 290 and 330 nm.

Table 3 compares photodissociation coefficients for pure absorption and for multiple scattering computed for the same ambient model atmosphere. These coefficients were computed for a solar zenith angle of 45° and a surface albedo of 0.25. For reactions of spectral type 1, multiple scattering has the most significant effect on the photodissociation coefficients below 25 km. The coefficients are changed only slightly above 25 km. Reactions of spectral types 2 and 3 show enhancement at all altitudes due to multiple scattering. At altitudes above 10 km the photodissociation rates are increased by factors of 1.27–1.46 for O_3 , 1.56–1.64 for NO_2 , 1.23–1.67 for $CINO_2$, 1.07–1.65 for $CIONO_2$, and 1.33–1.60 for $OCIO$. There is less than a 7% change in the photodissociation rates above 30 km for O_3 , HNO_3 , H_2O_2 , HO_2 , ClO , CF_2Cl_2 , and $CFCl_3$. At lower altitudes there is significant enhancement for several of these

Fig. 7. Change in concentration of NO_2 species due to multiple scattering with $A_s = 0.25$.

Fig. 8. Change in concentration of species containing chlorine due to multiple scattering with $A_s = 0.25$.

species due to multiple scattering. For example, at 10 km the photodissociation rate increased by a factor of 1.59 for HNO_3 , 1.59 for H_2O_2 , and 1.46 for ClO .

Species Concentration Profiles

The concentration profiles for selected O_3 , HO_2 , and ClX species are shown in Figures 1-4 for the ambient atmosphere prior to inclusion of multiple scattering. These figures define the reference conditions for assessing the fractional change in concentration caused by multiple scattering.

The changes in concentration of chemical species due to multiple scattering relative to the pure absorption calculation for a surface albedo of 0.25 are shown in Figures 5-8. Figure 5 shows the effect of multiple scattering on O_3 species concentrations. The large percentage increase in $\text{O}(^1\text{D})$ near 10 km occurs where the ambient concentration is very small; nevertheless, it has a significant effect on atmospheric chemistry. The increases in $\text{O}(^1\text{P})$ and $\text{O}(^1\text{D})$ in the 20- to 30-km region are due to increased photolysis of O_3 . Because of differences in ambient concentrations a small percentage decrease in O_3 causes large percentage increases in the other species. The increase in $\text{O}(^1\text{P})$ near 40 km is due primarily to increased photolysis of NO_2 . Ozone at this height is increased largely as a result of the reduction in the efficiency of the NO_2 catalytic destruction cycle caused by the increased rate of NO_2 photolysis. The ratio of column-integrated total O_3 computed with multiple scattering to that with pure absorption is 0.90.

TABLE 4. Change in Total Ozone Due to an NO_2 Injection of 1000 molecules $\text{cm}^{-2} \text{ s}^{-1}$ as NO_2 Over a 1-km-Thick Layer Centered at 20 km

Case	ΔO_3 , %	$R(\text{MS}/\text{PA})$
$\text{OH} + \text{HO}_2$ rate coefficient of $2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$		
Pure absorption	-2.34	...
Multiple scattering, $A_s = 0.25$	-2.36	1.01
Multiple scattering, $A_s = 0.75$	-2.40	1.03
$\text{OH} + \text{HO}_2$ rate coefficient of $5.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$		
Pure absorption	-3.44	...
Multiple scattering, $A_s = 0.25$	-3.50	1.02
Rate changes given in Table 5		
Pure absorption	-0.07	...
Multiple scattering, $A_s = 0.25$	+0.39	...

$R(\text{MS}/\text{PA})$ is the ratio $\Delta\text{O}_3(\text{multiple scattering})/\Delta\text{O}_3(\text{pure absorption})$.

*Ratio is not meaningful for such small quantities

Figure 6 shows the effect of multiple scattering on HO_2 species. Increased OH below 30 km results from increased rates for the reaction $\text{HNO}_3 \rightleftharpoons \text{OH} + \text{NO}_2$ and $\text{H}_2\text{O}_2 \rightleftharpoons 2\text{OH}$. Since the concentration of H_2O_2 below 35 km is much larger than the concentrations of the other hydrogen oxide species, a small percentage decrease in H_2O_2 can cause a much larger percentage change in OH and HO_2 , as evidenced near 10 km. The increase in $\text{O}(^1\text{D})$ leads to an increase in the production rate of HO_2 by $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$, yet there is actually a decrease in HO_2 in the region around 10 km. This occurs because conversion of H_2O_2 to 2OH by photolysis substantially increases the HO_2 destruction rate through the reactions $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ and $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$.

Figure 7 shows the effect of multiple scattering on NO_2 species. Because the NO_2 photolysis rate is increased, the concentration of NO and the ratio NO/NO_2 are both increased at all altitudes. There is very little HNO_3 above 30 km, so NO_2 decreases in this region because of increased photolysis. Below 30 km, NO_2 increases because of increased photolysis of HNO_3 , which is the most plentiful NO_x species in this region.

Multiple scattering has a large effect on NO_2 photolysis but negligible effect on HNO_3 above 30 km (see Table 3). The reduction in HNO_3 above 30 km therefore is due to a decrease in the HNO_3 production rate brought about primarily by the decrease in NO_2 . The percentage decrease in NO_2 is greater than the increase in OH ; consequently, there is a net decrease in the rate of the reaction $\text{OH} + \text{NO}_2 \rightleftharpoons \text{HNO}_3$. The ratio of total column abundances computed with multiple scattering to that with pure absorption is 0.94 for NO_2 and 1.36 for NO .

The effect of multiple scattering on species containing chlorine is shown in Figure 8. The concentration of ClONO_2 is reduced 35-45% between 20 and 30 km, which is the region of its maximum concentration. Photolysis of ClONO_2 affects several other chlorine-containing species through a complex chain of reactions. Certain key reactions are

TABLE 5. Updated Reaction Rate Coefficients [Hudson, 1977]

Reaction	New Rate, $\text{cm}^3 \text{ s}^{-1}$, $\text{cm}^3 \text{ s}^{-1}$
$\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$	$2.1 \times 10^{-12} \exp(-1450/T)$
$\text{O}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{O}_2$	$1.5 \times 10^{-12} \exp(-1000/T)$
$\text{O}_3 + \text{HO}_2 \rightarrow \text{OH} + 2\text{O}_2$	$7.3 \times 10^{-11} \exp(-1225/T)$
$\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$	3.5×10^{-11}
$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	2.5×10^{-12}
$\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	3.0×10^{-11}
$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$	8.0×10^{-12}
$\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$	$2.0 \times 10^{-11} \exp(-1070/T)$
$\text{O}(^1\text{D}) + \text{M} \rightarrow \text{O} + \text{M}$	$2.2 \times 10^{-11} \exp(99/T)^*$
$\text{NO} + \text{ClO} \rightarrow \text{NO}_2 + \text{Cl}$	$1.0 \times 10^{-11} \exp(200/T)$
$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{ClO}_2$	$2.1 \times 10^{-12} \exp(-2200/T)$
$\text{ClO} + \text{ClO} \rightarrow 2\text{Cl} + \text{O}_2$	$5.0 \times 10^{-12} \exp(-1238/T)$
$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{ClO}_2$	$1.0 \times 10^{-12} \exp(-1238/T)$
$\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$	$3.0 \times 10^{-12} \exp(-425/T)$
$\text{O} + \text{ClO} \rightarrow \text{ClO} + \text{O}_2$	$2.0 \times 10^{-11} \exp(-1100/T)$
$\text{Cl} + \text{OH} \rightarrow \text{HCl} + \text{O}$	$1.0 \times 10^{-11} \exp(-2970/T)$
$\text{Cl} + \text{HNO}_2 \rightarrow \text{HCl} + \text{NO}_2$	$1.0 \times 10^{-11} \exp(-2170/T)$
$\text{ClONO}_2 + \text{O} \rightarrow \text{ClO} + \text{NO}_2$	$3.0 \times 10^{-12} \exp(-808/T)$
	$3.3 \times 10^{-12} T^{-1.25}$
$\text{ClO} + \text{NO}_2 \rightleftharpoons \text{ClONO}_2$	$1 + 8.7 \times 10^{-17} T^{-0.4} \text{ M}^{0.1}$

*Differs from the value given by Hudson [1977].

†No recommendation for this rate is given by Hudson [1977].

TABLE 6. Change in Total Ozone Due to CFM's at the 1975 Release Rate

Case	$\Delta O_3, \%$	$R(\text{MS/PA})$
OH + HO ₂ rate coefficient of $2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$		
Pure absorption	-6.31	...
Multiple scattering, $A_s = 0.25$	-7.31	1.16
Multiple scattering, $A_s = 0.75$	-7.41	1.17
OH + HO ₂ rate coefficient of $5.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$		
Pure absorption	-3.86	...
Multiple scattering, $A_s = 0.25$	-4.70	1.22
Rate changes given in Table 5		
Pure absorption	-11.95	...
Multiple scattering, $A_s = 0.25$	-14.42	1.21

$R(\text{MS/PA})$ is the ratio $\Delta O_3(\text{multiple scattering})/\Delta O_3(\text{pure absorption})$.

The peak concentration of ClONO₂ occurs near 25 km, so photolysis of ClONO₂ acts as a strong source of ClO in this region. The large increase in NO between 20 and 30 km tends to shift ClO to Cl, leading to a net decrease in ClO in this region and an increase in Cl. This leads to an increase in HCl production through reaction of Cl with CH₄. The decrease in ClONO₂ above 40 km occurs because of the effect of decreased NO_x on the ClONO₂ production rate ($\text{ClO} + \text{NO}_2 \rightleftharpoons \text{ClONO}_2$).

Model Sensitivity

In addition to affecting the concentration of many species in the model, multiple scattering affects the model sensitivity to perturbations. This was tested for an NO_x perturbation and a chlorofluoromethane (CFM) perturbation. The NO_x perturbation was an injection of NO_x at a rate of 1000 molecules $\text{cm}^{-2} \text{ s}^{-1}$ as NO_x over a 1-km-thick layer centered at 20 km. The change in total ozone at steady state is shown in Table 4 for both the pure absorption and the multiple scattering calculations. The ratio of the percent change in ozone with multiple scattering to the percent change with pure absorption, $R(\text{MS/PA})$, is also presented in Table 4. Including multiple scattering has very little effect on the model sensitivity to an NO_x injection at 20 km ($R = 1.01$) in spite of significant differences in the ambient species profiles. Increasing the surface albedo from 0.25 to 0.75 also has a very small effect on the model sensitivity ($R = 1.03$). Consequently, the choice of A_s used in the photodissociation rate calculations is not a critical factor in NO_x perturbation studies which include multiple scattering, where one is primarily interested in the change in total ozone. It should be noted, however, that the choice of A_s significantly affects the photodissociation rates and the ambient species profiles (see Luther and Wuebbles [1976] for details).

The effect of variations in model chemistry on the above results was tested initially by varying the reaction rate for $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$. A recent measurement by Burrows *et al.* [1977] gives a value of 5.1×10^{-11} for the rate coefficient of $\text{OH} + \text{HO}_2$. Chang and Kaufman [1977] report an upper limit of 5×10^{-11} for the rate coefficient, whereas their experimental results are best fitted by using a value of 2×10^{-11} [Chang and Kaufman, 1977]. The calculations described above were repeated by using a value of 5.1×10^{-11} , and the results are presented in Table 4. Changing this rate coefficient significantly increased the ozone reduction due to this NO_x perturbation, but there was no significant change in $R(\text{MS/PA})$.

Subsequent to these calculations, there were several new

measurements of reaction rate coefficients. The most significant change was a much faster rate coefficient for the reaction $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$ [Howard and Evenson, 1977]. The model chemistry was updated to include this change as well as the latest recommendations of the National Aeronautics and Space Administration [Hudson, 1977]. The changes to the model chemistry are listed in Table 5. When these rate coefficients were incorporated into the model, there was a significant reduction in the magnitude of the change in total ozone (see Table 4). Including multiple scattering in this case caused the slight reduction in total ozone to change to a small increase. The change in ΔO_3 due to the inclusion of multiple scattering was small, however, in comparison with the change in ΔO_3 resulting from the changes in model chemistry.

For the CFM perturbation we consider the steady state ozone reduction due to CFM's at the 1975 release rate, which is assumed to be 290 kt/yr for CFCl₃ and 425 kt/yr for CF₂Cl₂. Results for both the pure absorption and the multiple scattering calculations are presented in Table 6. For the CFM perturbation, including multiple scattering increased the ozone reduction by a factor of 1.16 for a surface albedo of 0.25. As in the case of the NO_x perturbation, changing the surface albedo had little effect on the change in total ozone; e.g., the ozone reduction increased by a factor of 1.17 relative to the pure absorption calculation using a surface albedo of 0.75. When the rate coefficient for $\text{OH} + \text{HO}_2$ was increased to 5.1×10^{-11} , the ozone reduction with multiple scattering increased by a factor of 1.22 (Table 6) relative to the pure absorption calculation.

Using the rate coefficients listed in Table 5 nearly doubled the predicted ozone reduction due to CFM's. In this case, including multiple scattering still caused a significant increase in ΔO_3 (i.e., $R = 1.21$).

In addition to affecting model sensitivity, including multiple scattering changes the altitude distribution of the ozone reduction. In order to describe more clearly the change in the vertical distribution of ΔO_3 , we introduce the quantity $DO_3(z)$ which is defined by

$$DO_3(z) = \Delta[O_3]_z / O_3(\text{column}) \quad (9)$$

where $\Delta[O_3]_z$ is the change in local ozone concentration and $O_3(\text{column})$ is the unperturbed total ozone. The function $DO_3(z)$ represents the contribution per unit altitude to the change in total ozone. The change in total ozone is given by the integral

$$\Delta O_3 = \int_{-z_{\text{max}}}^{z_{\text{max}}} DO_3(z) dz \quad (10)$$

Fig. 9. Profiles of $DO_3(z)$ for pure absorption and multiple scattering calculations. (a) CFM release perturbation and (b) NO_x injection at 20 km.

Thus the integrated area under the curve of $DO_3(z)$ versus z equals ΔO_3 . Profiles of $DO_3(z)$ for both the CFM and the NO_2 perturbations are shown in Figure 9 for the pure absorption and multiple scattering calculations. In the case of a CFM perturbation, multiple scattering enhanced the ozone reduction at all altitudes above 24 km. Below 24 km there is less ozone destruction with multiple scattering, but the difference only partially compensates for the opposite effect at higher altitudes. The net effect is enhanced ozone reduction with multiple scattering.

In the case of an NO_2 perturbation there are alternating regions of enhanced and reduced ozone destruction. The altitude of the peak ozone reduction is lowered, and the magnitude of the peak is increased, but the net change in total ozone is very small ($R = 1.01$).

DISCUSSION

Calculated reductions in total ozone due to stratospheric injections of NO_2 or CIX are the net effect of a number of interlinked photochemical and transport processes. As such there is some hazard in attempting to simplify the system and discuss individual processes. However, in an attempt to explain the sensitivity of the system to multiple scattering, we have plotted the rates for five reactions in Figure 10 for the unperturbed model atmosphere using the rate data in Table I both with and without multiple scattering. The reactions plotted are those considered to be rate limiting for various

catalytic ozone destruction mechanisms. As is seen in Figure 10a, the rate of the reaction $HO_2 + O \rightarrow HO + O_2$ is virtually unaffected above 40 km, where this reaction is most important. The reaction $HO_2 + O_2 \rightarrow 2O_3 + OH$ is similarly unaffected by multiple scattering in the 10- to 25-km region, where it is dominant.

In Figure 10b we have plotted the key rate-limiting reactions for the major catalytic cycles for NO_2 and CIX. Significant increases in both rates due to multiple scattering are found below 30 km largely because $O(^1P)$ is increased and because NO_2 and CIX are shifted from 'reservoir' species (HNO_2 , $ClONO_2$) to more reactive species in this region. Above 30 km the rate of $ClO + O \rightarrow Cl + O_2$ is still increased, but the rate of $NO_2 + O \rightarrow NO + O_2$ has decreased owing to multiple scattering (because of increased NO_2 photolysis). Therefore the net effect of multiple scattering and surface albedo on model sensitivity depends upon the relative magnitudes of the decrease in NO_2 (and the fraction of added NO_2 that exists as NO_2) and the increase in $O(^1P)$. Table 4 shows that the net effect may range from no change in ΔO_3 to an increase in ΔO_3 depending upon the model chemistry. A similar type of cancellation of effects is observed for the CIX system.

The increased ozone reduction with multiple scattering (Table 6) is not due to increased CIO brought about by enhanced photolysis of $ClONO_2$, as might be expected. From Figure 8 we see that the chlorine released from $ClONO_2$ through photolysis does not result in increased CIO but rather ends up as HCl (through $Cl + CH_4$).

CONCLUSIONS

Multiple scattering significantly affects atmospheric photo-dissociation rates, particularly at wavelengths greater than 290 nm. The magnitude of the effect varies with spectral type, and there is a strong altitude dependence. Incorporating the effects of multiple scattering into a transport-kinetics model leads to dramatic changes in the ambient concentration profiles and total abundances of many trace species. These effects are described for important O_2 , HO_2 , NO_2 , and CIX species. It is important therefore that multiple scattering be included when model-derived concentration profiles are compared with observational data.

For the cases studied the effect on model sensitivity of including multiple scattering ranged from no change in ΔO_3 compared with the pure absorption calculation to a significant increase in ΔO_3 depending upon the model chemistry. The change in ΔO_3 due to multiple scattering, however, was small in comparison with the change in ΔO_3 resulting from varying chemical reaction rates. In the case of a CFM perturbation the ozone reduction was enhanced while multiple scattering was included. Variations in surface albedo had little effect on the computed change in total ozone. Changes in model sensitivity are the net effect of changes in many competing mechanisms; thus the magnitude of the change in sensitivity due to multiple scattering varies as the chemical rate data are varied.

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the FAA on the High Altitude Pollution Program—1978***

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PREFACE

Since July 1, 1975, Lawrence Livermore Laboratory (LLL) has been participating in the High Altitude Pollution Program sponsored by the U.S. Department of Transportation's Federal Aviation Administration. This report describes the major accomplishments and significant findings during the fiscal year ending September 30, 1978, for work performed at LLL under Reimbursable Agreement DOT-FA76WA1-653. Two major research areas are covered by this agreement: (1) numerical modeling of the atmospheric response to stratospheric perturbations, and (2) the processing, archiving, and analysis of satellite ozone data. Progress on the second research area has recently been published in a report by Lovill *et al.* (1978). Only work performed in the first area will be reported here. The successful accomplishment of the many subtasks within the numerical modeling area has required contributions and cooperation from many participants. The work reported here is the result of the collective effort of all those listed below.

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1. INTRODUCTION

The High Altitude Pollution Program (HAPP) was initiated by the Federal Aviation Administration to ensure that aircraft engine emissions in the stratosphere will not result in unacceptable effects on the biosphere. Lawrence Livermore Laboratory (LLL) has participated in HAPP since July 1975. The primary research emphasis at LLL is on numerical modeling of the atmospheric response to stratospheric perturbations. A fundamental tool in the LLL effort has been the one-dimensional transport-kinetics model. We are also in the process of developing a two-dimensional transport-kinetics model.

Support for model development is shared between HAPP and another project at LLL involving assessment of the chemical and climatic effects of atmospheric nuclear explosions. The latter project is funded by the Division of Military Application (DMA) of the Department of Energy. Although the same numerical models are used for both studies, the applications of the models are quite different. For example, the study of the climatic effect of nuclear explosions is primarily concerned with the time-dependent response of the atmosphere to pulse injections of NO_x , whereas the HAPP study is concerned with steady-state injections of NO_x and other species.

In August 1976, LLL's participation in HAPP was extended to include a feasibility study to determine whether good quality total ozone values could be derived from infrared measurements by a multi-channel filter radiometer (MFR) sensor carried aboard a series of satellites operated by the U.S. Air Force. Infrared radiance data became available in March 1977 from the first of a new series of satellites, which are a part of the Defense Meteorological Satellite Program Block 5D series. The MFR sensor aboard these satellites is unique in that it is the first cross-track scanning sensor capable of providing ozone measurements, thus increasing the amount of ozone data collected. The instrument has a higher resolution than previous instruments, and it provides global coverage day and night. Since mid-1977, this series of satellites has provided the only available global ozone data. The second satellite began transmitting MFR measurements in July 1977, and the third in the series began transmitting MFR measurements in September 1978. The fourth (and last) satellite in the series is yet to be launched. The

designed lifetime of each satellite is two years. The ozone data derived from these satellite measurements are potentially useful to the scientific community for assessing changes in the ozone layer that may be due to natural or man-made causes.

The feasibility study was completed in June 1978, with the successful processing of 20 days of data taken during 1977. The quality of the data was demonstrated by comparison with corresponding ozone data obtained at selected stations in the world surface network of Dobson observatories. A description of the methodology used and a presentation of the results of the feasibility study are contained in a report by Lovill *et al.* (1978). The project is now undergoing a transition into the operational phase during which all of the MFR data from the satellites will be processed and made available for distribution to the scientific community.

In this annual report we describe LLL's major accomplishments and findings since October 1, 1977. Earlier HAPP work is described in our previous annual reports (Luther *et al.*, 1976, 1977). In the present report we discuss the results in only the atmospheric modeling area; the work on satellite ozone-data processing and analysis has recently been reported separately.

A modeling effort is important to HAPP for two primary reasons. First, modeling constitutes a means of relating engine emissions and other man-made perturbations to changes in atmospheric composition. Because of the complex physical processes and feedback mechanisms involved, it is essentially impossible to assess the effects of emissions without incorporating these processes into a model and allowing them to interact. Second, modeling contributes to the interpretation and analysis of experimental results and helps determine the relative priorities for carrying out this work.

Due to the ever-increasing complexity of the system of governing physical and chemical processes, theoretical models of atmospheric trace species distributions have become essential tools both diagnostically and prognostically. Such models are based on a set of conservation equations describing the effect on individual trace species of atmospheric transport, chemical and photochemical kinetics, and various natural and anthropogenic sources.

Since the detailed modeling of atmospheric chemistry is a relatively young science and since overall information is limited, although rapidly increasing, most models have been diagnostic in their scope. The most comprehensive validation of all classes of models remains diagnostic. Within limits, the distributions and variabilities of most of the trace species have been modeled reasonably well.*

When the question of anthropogenic influence of the ozone layer was raised, there was a demand for the models in prognostic applications. The prognostic capability of the models for making predictions over decades or centuries has never been demonstrated and in all likelihood will never be demonstrated without a well-developed long-term atmospheric monitoring program of comparable duration. Limited prognostic validations, such as the model predictions of the effects of Polar Cap Absorption (PCA) events on polar stratospheric ozone and the current stratospheric chlorofluoromethane distributions, are reassuring but not conclusive. In particular, the study of PCA events requires reexamination because of the strong coupling of NO_x , ClO_x , and HO_x cycles in the current chemistry, which was not accounted for in the original study. In a sensitivity study with one-dimensional models, Duewer *et al.* (1977) demonstrated that under limited circumstances diagnostically similar one-dimensional models of the stratosphere can indeed yield very different predictions on the effect of NO_x effluents from SST's on ozone. Consequently, it is necessary to recognize the distinction between prognostic and diagnostic applications of the same model and affirm their individual limitations and uncertainties.

Diagnostically and prognostically, box models can provide only limited information. In fact, due to its simple structure, in certain applications it is highly sensitive to uncertainties in input variables. For example, analysis of atmospheric lifetime of long-lived halocarbons with box models is highly sensitive to uncertainties in the ratio of measured global abundance to the total amount released. For F-11 and F-12, an uncertainty of 5-10% in this ratio would lead to an uncertainty of 25-50% in the deduced atmospheric lifetime (Chang and Penner, 1978). Understanding this type of uncertainty is of particular importance for the box model because of its application in lifetime analysis. Similar uncertainties are in the more complex models but their applications are normally beyond such simple analysis. At present

there exist several useful techniques for the analysis of box model sensitivity and uncertainty. Therefore one would expect such an analysis prior to the interpretation of modeling results. Box models, with or without associated sensitivity analysis, can best serve to establish the relative importance of physical processes and suggest those problems that are most worthy of detailed examination with more complex models.

The structure of one-dimensional models has been analyzed in detail in the report by the National Research Council (1976b) and in the NASA report (Hudson, 1977). The vertical transport parameterization is based on globally averaged values of vertical distributions of tracers such as N_2O and CH_4 . Consequently, for other predominantly upward moving tracers the one-dimensional model should be considered to be a globally averaged model. This is probably also true for the net downward moving tracers in the altitude range of the tropopause. But in the stratosphere the detailed representation of the photochemical interactions is such that only local variables such as temperature and solar flux intensity (both in space and time) can be used. This is a necessary condition that significantly complicates the interpretation of model results. The local chemical lifetime of all stratospheric chemical trace species depends on the local concentrations of ozone and the closely coupled atomic oxygens $\text{O}(^1\text{P})$ and $\text{O}(^1\text{D})$. These concentrations are directly proportional to the local solar flux. As a result, the self-consistently derived odd oxygen concentrations in the one-dimensional model are positively correlated with the seasonal solar flux intensity, contrary to observation of the seasonal variation of hemispherical and global ozone distributions. In the absence of detailed information on the spatial and temporal variations of all the trace species, either from measurements or more complex models, it is not possible to derive the proper averaging (weighting) factors for the nonlinear photochemical and chemical interaction processes in the one-dimensional model. Therefore, all one-dimensional models are limited to representing local stratospheric conditions, in particular that latitudinal region and season where the model-derived ozone profile closely represents the local measurements. Typically, one-dimensional models best represent the photochemistry of about 30°N latitude at about the fall equinox. That this is not completely satisfactory is quite obvious since this is also the region where there is considerable stratospheric and tropospheric exchange, hence we expect local concentrations of trace species in the altitude range of 10-30 km to be strongly affected by fluctuations in atmospheric

*The most notable exceptions may be the high ClO measurements of Anderson (1978).

transport processes. Consequently, because of this mix of partially local and global representations, both the diagnostic and prognostic application of the one-dimensional model must be applied and analyzed with great care with regard to the intrinsic compatibility of the model and its intended use, case by case.

The results of a model calculation can be evaluated by comparison with suitably obtained atmospheric measurements. Several basic types of information have proven to be useful: height and latitudinal distributions of individual species and groups of species, partitioning of related species, and local diurnal and seasonal variations of individual species. These comparisons when available constitute a necessary test mostly for the diagnostic and at times prognostic adequacy of the model. Interpretation of the results from such tests are not always

simple. Many of the comparisons must be accepted with degrees of qualification. It is the overall reasonableness of the models and their predictions that provide a high level of confidence in their basic correctness. Of course, this is often a matter of judgment.

The measured atmospheric trace species concentrations, which constitute the data base for comparison with model results, have shown a significant level of local variability. This atmospheric variability has caused such comparisons between measurement data and modeling results to be influenced by judgment and at times provided a ready excuse for inconclusiveness. As data base and theoretical models continue to improve, a more precise formulation of atmospheric variability and its influence on data interpretation must be developed and applied.

2. MODEL SIMULATION OF OBSERVED STRATOSPHERIC VARIATIONS

2.1 The Natural Stratosphere

A fundamental tool in the LLL effort has been the one-dimensional transport-kinetics model (Chang and Wuebbles, 1977; Luther *et al.*, 1977). This model, which includes as complete a set of the important chemical and photochemical reactions as is feasible, is designed for time-dependent perturbation and sensitivity studies. The model includes 30 chemical species and 97 chemical and photochemical reactions. The chemical rate coefficients currently used in the model are listed in Table A-1 (Appendix A). Stratospheric water vapor concentrations are now computed at altitudes above 12 km in our standard model, although a fixed concentration profile may be specified as a user option.

Species concentrations are computed at 44 levels in the atmosphere, extending from the ground to an altitude of 55 km. The model uses an accurate numerical method for solving stiff systems of differential equations. Vertical transport is parameterized using a one-dimensional diffusion formulation that describes hemispheric-average net vertical transport by an altitude-dependent diffusion coefficient. The Chang (1976) diffusion coefficient profile was used for all of the calculations presented in this annual report. The model can include temperature coupling between changes in composition and reaction rate coefficients, but this feature is not used in

the standard model. The standard model includes a totally self-consistent diurnal averaging procedure for nonlinear chemical reaction terms (Luther *et al.*, 1977). Unless otherwise stated, the standard model was used for the calculations presented in the following sections. Changes made to the model during the past year are described in Appendix A. In this section we describe the natural stratosphere as computed by the model. The sensitivity of the model to various stratospheric perturbations is described in Sec. 3.1.

The ambient stratospheric species concentrations that are presented here correspond to a simulation of present-day conditions. The historical release of CFM's is included assuming constant production since 1975. Since the chlorine budget of the stratosphere is continuously increasing, this time-dependent calculation not only provides a current stratosphere for diagnostic purposes, but it also provides a test for the model in predicting the accumulation of CFM's in the troposphere and their vertical distribution in the stratosphere. In this calculation it is assumed that presently observed tropospheric concentrations of CCl_4 and CH_2Cl are the sources for background chlorine. The species CH_3CCl_3 is not used because of difficulties with data precision and accuracy and the apparent conflict with measured HO concentrations in the lower troposphere (see the discussion on CH_3CCl_3). With or without CH_3CCl_3 as a source of present stratospheric chlorine, the

analysis of the following sections is the same with certain exceptions as noted.

The computed stratospheric distributions of minor trace species corresponding to January 1978 are shown in Figs. 1 through 6. These are all diurnally (24-hr) averaged quantities. The relevant noontime and nighttime values are discussed in individual sections. The performance of stratospheric models in predicting the vertical distribution of known trace species that are believed to be important to ozone chemistry are discussed in the following sections.

FIG. 1. Species concentration profiles for O_3 and $O(^3P)$ computed for January 1978.

Trace Species With Long Stratospheric Chemical Lifetimes

The trace species N_2O , CF_2Cl_2 , $CFCl_3$, CCl_4 , CH_3CCl_3 , CH_4 , CH_3Cl , and H_2O all have stratospheric chemical lifetimes of at least a year. Consequently, their stratospheric abundance is totally determined by fluxes from the troposphere (strictly speaking this is not true for H_2O as will be explained). In fact, these species are the sources for all the minor trace species in the stratosphere that are known to be essential in ozone chemistry.

N_2O :

The basic input variable for modeling N_2O is its observed tropospheric mixing ratio. Models can either use this number directly or convert it to a source flux derived from the measured mixing ratio and an assumed atmospheric lifetime. As a result, agreement with observations in the troposphere is expected (320 ppbv vs $325 \pm 10 \text{ ppbv}$). In the stratosphere, the N_2O local chemical lifetime increases from 6 months at 35 km to thousands of years near the tropopause. In fact, one may state that the variability of its vertical concentration profile in the stratosphere is strictly due to atmospheric transport processes. One-dimensional, and even two-dimensional models, can at best provide a global

FIG. 2. Concentration profile for species containing nitrogen computed for January 1978.

FIG. 3. Concentration profiles for species containing chlorine as computed for January 1978.

FIG. 4. Concentration profile for species containing hydrogen computed for January 1978.

FIG. 5. Trace species mixing ratios computed for January 1978.

qualitative picture but no exact quantitative agreement locally. As is well known, one-dimensional models can indeed simulate the average vertical distribution of N_2O . It should be emphasized that both N_2O and CH_4 have been used as tracers for deriving the effective net vertical diffusion coefficient in one-dimensional models. Therefore, such agreement between data and model results is a necessary condition. It confirms that the model is functioning as expected, i.e., the more complex full model does not change the expected chemical cycles of N_2O and CH_4 , hence no reevaluation of the effective diffusion coefficient is necessary.

FIG. 6. Theoretical and measured concentrations of OH.

CH₄:

Methane behaves much the same as N₂O in the atmosphere, except that it has a comparatively short lifetime in the troposphere. The model used 1.31 ppmv based on earlier data, which is 20% less than current data (1.65 ± 0.1 ppmv). This leads to similar underestimates throughout the stratosphere. It also leads to lesser HO_x from CH₄, which would have a small effect on the effectiveness of added chlorine on ozone. Since the local chemical lifetime of CH₄ increases from 6 months at 40 km to more than 10 years at the tropopause, its stratospheric variability is also controlled by transport processes. In particular the qualitative latitudinal similarity in the vertical profiles of N₂O and CH₄ from 5°S and 40°N confirms this view.

CCl₄ and CH₃Cl:

The model used approximately the measured concentrations as input parameters. The tropospheric concentration of CCl₄ is 112 ppbv, which is at least 10% lower than the currently available averages but certainly within the limits of data uncertainty. The CCl₄ is not destroyed in the troposphere but begins to photodissociate quickly in the stratosphere. Its local chemical lifetime is of the order of 6 months at about 24 km. Therefore, in addition to the instrumentation difficulties associated with grab sampling, there should be a high level of transport variability which makes stratospheric measurement of CCl₄ and its data interpretation a rather difficult task. The CH₃Cl measurement data have shown such fluctuations that it is difficult to assess the adequacy of model results. Nevertheless, with an input of 746 pptv at the surface (which is approximately in the middle of the range for Rasmussen's data in 1977), the model estimates 580 pptv at the tropopause, which seems to be consistent with the 550 pptv reported by Cronn *et al.* (1977). The estimated local chemical lifetime is approximately 1 year up to 26 km. This again makes transport variability an important factor in the interpretation of CH₃Cl data.

CF₂Cl₂ and CFCl₃:

The total abundance and vertical distributions of F-11 and F-12 serve as true tests of the ability of simple one-dimensional models to represent the average net vertical transport of trace species. Together with CH₃CCl₃ the release rates of these man-made chemicals are well documented. Since the model uses the time-dependent release rate in computing its atmospheric distribution, a comparison of both the

model-derived tropospheric and stratospheric budgets with measurement data would be a stringent test of the adequacy of the model. Global averages of F-11 and F-12 in the troposphere are not easily obtainable. If the observed northern-hemispheric averages in January 1977 are used to estimate the global average in January 1978, then the model is at most 10% lower in the tropospheric burdens of F-11 and F-12. About 5-8% of this is attributable to the accuracy of the source function approximation used in the model. This then provides a partial (but important) confirmation that the transport approximations based primarily on N₂O and CH₄ indeed have a more general validity and applicability. Similar to other trace species with long local chemical lifetimes, both F-11 and F-12 are sensitive to variations in local transport processes (at altitudes up to 30 km for CFCl₃ and up to 40 km for CF₂Cl₂). This is again consistent with observation. In general the model-predicted stratospheric vertical profiles of CF₂Cl₂ and CFCl₃ are both slightly on the high side of the data averages (taking the model tropopause to be at 12 km). The model seems to show slightly more destruction in the lower stratosphere (5-10 km above tropopause) for CFCl₃ than the data suggest. On the other hand, this could be due to weaker net upward transport in the model. Fortunately, in the regions of maximum destruction of CFCl₃ and CF₂Cl₂ (20-30 km and 25-35 km, respectively), the model-predicted profiles are in reasonable agreement with available data.

CH₃CCl₃:

At this time there is considerable uncertainty in the interpretation of data and the modeling of atmospheric concentrations of CH₃CCl₃. A simple box model analysis based on measurement data would yield a CH₃CCl₃ atmospheric lifetime of 5-12 years, which in turn would imply an average tropospheric HO concentration of less than 10^6 molecules/cm³. However, most coupled stratospheric-tropospheric models have more HO than this estimate, which then leads to a much lower CH₃CCl₃ concentration in the atmosphere if the well-known release rates are used (Neely and Plonka, 1978). Furthermore, there is no generally accepted set of HO measurements in the troposphere. Although CH₃CCl₃ is estimated to be a major source of stratospheric chlorine and could provide another direct test on the adequacy of models at this time, it is not constructive to include it in the one-dimensional model in the

same manner as the other sources of stratospheric chlorine. The model used for these calculations did not include this source, which could contribute from 0.2 to 0.3 ppbv of chlorine. This omission is of no practical consequence to the present study.

H₂O:

Methane is the principal source of stratospheric water. At the tropopause H₂O is maintained both by a downward flux from the stratosphere and an upward flux from the troposphere. At this altitude the tropospheric-stratospheric exchange process serves to maintain H₂O at the saturation level. This fixed boundary condition helps maintain the H₂O concentration in the rest of the stratosphere. With such control it is not surprising to see one-dimensional models generate reasonable H₂O vertical profiles, starting with 3 ppmv at the tropopause and slowly increasing to 5 ppmv at 50 km. This is well within the uncertainty of the data. Again, since stratospheric water vapor has only weak chemical sources and sinks, its variability is mostly due to transport fluctuations.

Table 1 summarizes the sources of chlorine in the model and compares them with estimates from tropospheric data. As was already pointed out, the model underestimates the total budget by not including the uncertain contribution of methyl chloroform. With a total ClO_x mixing ratio of 2 ppbv in the troposphere, the ClO_x mixing ratio is reduced to 1.7 ppbv at 40 km due to the natural time delay in upward transport and the photochemical destruction of the source molecules at lower altitudes. In comparison, the total NO_x mixing ratio at 40 km is 15.9 ppbv, and the total HO_x mixing ratio at 40 km is 3.2 ppbv.

Table 1. Sources of stratospheric chlorine.

Species	Estimate from tropospheric data, ppbv	LLL model, ppbv
CH ₃ Cl	0.47-0.77	0.75
CH ₃ CCl ₃	0.12-0.27	0.00
CF ₂ Cl ₂	0.48	0.42
CFCI ₃	0.42	0.38
CCl ₄	0.49	0.45
Total	1.98-2.43	2.00

Trace Species with Intermediate Stratospheric Chemical Lifetimes

Trace species such as HNO₃ and HCl have stratospheric chemical lifetimes of about a week. Similarly, the trace species families O₃ (O(¹D) + O(³P) + O₃) and NO_x (N + NO + NO₂ + NO₃ + HNO₃ + 2N₂O₅) also have net stratospheric chemical lifetimes of about a week. The chlorine family ClO_x (Cl + ClO + HCl) has a somewhat shorter stratospheric chemical lifetime on the order of 1/2 to 1 day. This is due to the strength of the coupling reaction ClO + NO₂ + M → ClONO₂ + M, since none of the above (usual) families includes ClONO₂. If we consider the broader family ClO_x (ClO_x + ClONO₂), then it becomes a pure tracer with no chemical loss, except possibly through the yet-to-be completely quantified reactions involving HOCl. In other words, if simultaneous measurements are made of all the members of the ClO_x family, then all variability in the data must be due to physical processes other than photochemistry. On the other hand, if only ClO_x family members are measured simultaneously (i.e., without ClONO₂), then the variations due to chemical reactions involving ClONO₂ must be considered.

Together with HO_x (H + HO + H₂ + 2H₂O₂), the O₃, NO_x, and ClO_x families include almost all the trace species that are of major interest in stratospheric chemistry. Their short net stratospheric chemical lifetimes signify the dominance of chemistry in their life cycles and their primary stratospheric origin. The O₃, HNO₃ and HCl downward fluxes from the stratosphere represent almost all the transport loss of the trace species in their respective families, and the transport time scales are all of the order of a year or more. Because of these similarities and relations, it is appropriate to discuss these families here and leave the partitioning within individual families to the next sections.

O₃:

For the most part, the stratospheric O₃ species are in the form of O₃. The O(³P) begins to contribute more than a few percent only at altitudes above approximately 45 km. A comparison of model-derived O₃ distribution with atmospheric data actually represents an evaluation of the whole O₃ family in the stratosphere. The model-derived vertical profile of O₃ (Fig. 1) compares well with the average profile obtained by Watanabe and Tohmatsu (1976) at 30°N. Below 25 km the O₃ concentrations are less than the midlatitude profile of Krueger and Minzner (1976). This is an expected result since the midlatitude profile included contributions from high-latitude ozone distributions that are the result of meridional transport. Within the one-

dimensional model framework, this translates to a lower average vertical diffusion coefficient in the range of 15-20 km.

NO_y:

The principal source of odd nitrogen in the stratosphere is N₂O through the reaction with O(¹D). There is also a small amount produced from cosmic ray bombardment. Since most of the production is below 35 km with a small net loss from the N + NO reaction above 45 km, total NO_y is fairly uniformly distributed between 30-45 km with a mixing ratio of 19 ppb at 40 km. The corresponding NO_x mixing ratio of 10.4 ppbv at 25 km compares well with observations, whereas at 35 km the NO_x mixing ratio from the model (15.4 ppbv) is at the high end of the stratospheric data range.

Throughout the stratosphere, the local chemical lifetimes of NO_x are of the order of several days. Consequently, all (except a set of exactly simultaneous) measurements of NO, NO₂, and HNO₃ could be subject to unknown influences due to chemical and transport processes. The HNO₃ concentrations computed by the model are on the high side of the data range, but this is quite typical of all one-dimensional models. The HNO₃ mixing ratio peaks at about 23-28 km and is consistent with all the available data. The HNO₃ has a local chemical lifetime of 10-20 days throughout the altitudes where HNO₃ is most abundant and can vary significantly over a few days, as was found by Murcray *et al.* (1978). Qualitatively, the increase toward the pole in column HNO₃ is consistent with the present photochemical theory, but two-dimensional models have not provided sufficiently detailed quantitative analysis yet.

ClO_y:

Since the total stratospheric chlorine in the model can only be removed as HCl through downward transport across the tropopause, its stratospheric mixing ratio is approximately the same as that of the source species. If we reject the three high values of ClO vertical profiles by Anderson (1978), then the total ClO_y mixing ratio at 20 km is approximately 0.5-1.0 ppbv, and at 35 km it is 1.6-2.3 ppbv. The LLL model gives 0.75 ppbv at 20 km and 1.65 ppbv at 35 km, which are quite comparable to the experimental values. The high ClO profiles by themselves would indicate a ClO_y mixing ratio of 1.8-9.0 ppbv of chlorine at about 40 km. Together with the estimated 1.0-1.5 ppbv of HCl, this would require a source of 3-10 ppbv of tropospheric chlorine. This is simply not accounted for by

current understanding of the sources and sinks of chlorine in the atmosphere. Although Waters *et al.* (1978) provided some data suggesting disagreement with one of the three high-profile measurements, a more definitive explanation on the source of error either on the photochemical theory or the measurements by Anderson is still required. In the lower stratosphere, HCl is the predominant form of ClO_y. The model gives 0.28 ppbv at 15 km and 0.55 ppbv at 20 km, which can be compared to the measured values of 0.2 ppbv and 0.3-0.7 ppbv at 15 and 20 km, respectively. If these values are used to estimate the downward flux of odd chlorine, then theory and experiment are within a factor of 2.5. This again provides another independent estimate on the uncertainty due to transport. The dip of the HCl vertical profile at 30 km as reported by Lazrus *et al.* (1977) and Williams *et al.* (1976) is not explainable within the context of one-dimensional models. But a preliminary two-dimensional calculation by Pyle (1978) suggests that HCl has local maxima and minima in the vertical direction extending from near the equator to the polar region. If one were to fly a balloon around 32°N, it would quite likely sample through this minimum region and obtain a dip in the vertical profile. This result coupled with the ClO result (see next section) further demonstrates the limitations of a one-dimensional model and at the same time expresses a strong vote of confidence for the potential benefit of two-dimensional models.

Trace Species with Short Stratospheric Chemical Lifetimes

The trace species NO, NO₂, NO₃, N₂O₃, O(¹P), Cl, ClO, ClONO₂, HO, HO₂ and H₂O₂ all have much shorter chemical lifetimes than the previously discussed species. As a result, their individual local concentrations are quite variable, usually on the time scale of hours to seconds. They all vary diurnally (except for H₂O₂), seasonally, and probably even on the time scale of changing albedos due to the presence of aerosols and clouds at lower altitudes. As is expected, it is not possible (and usually impossible) to always obtain local conditions such as solar flux, temperature, and local concentrations of other trace species when doing a particular measurement. Hence, it is rarely possible to quantitatively interpret the available data on these trace species with theoretical models. However, if individual collections of data are used as a group, then the total local variability in the data is often a good guiding criterion for

testing the theory. Furthermore, variability in the shape of individual vertical profiles is also a useful indicator of the domain of physical results.

NO, NO₂, NO₃ and N₂O₅:

Since 1972 there have been a considerable number of NO measurements in the stratosphere. By now its stratospheric variability is well established and any attempt to model a particular set of data has long been deemed as relatively unimportant, except for the diurnal variations of the NO_x species. As was pointed out in our previous work (Luther *et al.*, 1976), successful modeling of the NO_x diurnal variations confirmed locally some of the chemical mechanisms important in the catalytic cycles affecting ozone. Our one-dimensional model yields an NO mixing ratio of 0.1 ppbv at 20 km, gradually increasing to 9.0 ppbv at 50 km. This theoretical profile is approximately in the middle of the available data. Without a simultaneous measurement of NO₂, individual NO data will be of steadily declining usefulness in the future.

Modeling of stratospheric NO₂ distributions suffers the same difficulty as that of NO due to their coupling through the NO_x catalytic cycle. Although a one-dimensional model can approximate the low NO₂ column measurement above 50°N by using the proper seasonal solar flux, temperature, and ozone (Noxon *et al.*, 1978a), a full explanation involves the coupling of three-dimensional transport and photochemistry (Noxon, 1978). Nevertheless, on the average, simple one-dimensional models do produce NO and NO₂ distributions that are consistent with stratospheric data.

Stratospheric NO₃ abundance as estimated by photochemical models falls far short of the observed amount (Noxon *et al.*, 1978b). This could be due to errors in the accepted kinetics rate coefficients as suggested by Noxon *et al.* (1978a). But this involves extrapolation of preliminary data at higher temperatures than are in the stratosphere. Fortunately, this unsettled state of affairs is of minimal importance to this study.

The current estimates on stratospheric N₂O₅ concentrations are all consistent with the model. The upper limit of 0.1 ppbv at 18.3 km by Murcray *et al.* (1978) and the 3 ppbv at 30 km deduced by Evans *et al.* (1978) compare well with the results from diurnal calculations under comparable conditions of 0.06 ppbv and 2.1 ppbv, respectively.

O(³P):

The local concentrations of O(³P) are directly proportional to the local ozone concentrations and solar flux intensity. Any disagreement between theory and experimental data on O(³P) can be directly traced to disagreement in O₃, which is more dependent upon atmospheric motions.

Cl, ClO and ClONO₂:

The only available data on Cl and ClO are from Anderson *et al.* (1977, 1978). As the discussions on ClO_x indicated, the high values of ClO are not reconcilable with current theoretical understanding and must be considered the major weakness in current theory. The low ClO measurements are in good agreement with theoretical models. The only possible exception is the rate of decrease in ClO as one approaches the tropopause. One-dimensional models yield a much more gradual decrease. The two-dimensional calculation by Pyle (1978) shows that near 30°N (where Anderson *et al.* (1977) collected their data) there indeed is a much sharper vertical gradient from 25 to 35 km. This is apparently a direct result of the detailed transport processes in this region. It should be pointed out that these two-dimensional model results, although preliminary, are highly encouraging. Although ClONO₂ was shown to be a critical species in the assessment of CFM impact on stratospheric ozone, up to now only an upper limit on stratospheric abundance has been suggested. The limit of 0.3 ppbv at 20 km is at least a factor of 2 higher than the model indicates. Hence, it is an inconclusive result, although somewhat reassuring.

HO, HO₂ and H₂O₂:

The concentrations of HO, shown in Fig. 4 are all diurnally averaged values. Both HO and HO₂ undergo gradual changes throughout the daylight hours. For both HO and HO₂ the ratio of noon values to the diurnally averaged values could be as much as 5 in the winter hemisphere high latitudes. In the present case (30°N, fall equinox) the ratio is approximately 2.5 in the altitude range of 10-20 km, and then gradually decreases to around 2 at 45 km. Because of this large averaging factor and the gradual diurnal changes, only diurnal models should be used to compare with experimental data. Between 30-40 km, the model-estimated HO₂ profile at comparable times of the day and fall conditions falls on the low side of the data by Anderson *et al.* (1978), the computed average concentration being $4.6 \times 10^7 \text{ cm}^{-3}$ as compared to an

average measured value of $8 \times 10^7 \text{ cm}^{-3}$. At 30 km the local value near sunset is about a factor of 2 less than the data by Mihelcic *et al.* (1977).

The HO diurnal profiles compare very well with the available data between 30-40 km. At the corresponding time the theoretical profiles both (solar zenith angles of 41° and 80°) fall in the middle of the data range (Fig. 6). This is probably fortuitous since there is no corroborating data on CH_4 , H_2O , and ozone which are essential in determining the local concentrations of HO. Unfortunately, in the critical region of 10-30 km there are no data on HO and HO_2 .

The only estimated upper limit value for H_2O_2 at 20 km is well above the model concentrations to be of real use. Due to the central role played by HO₂ in determining the effect of changes in NO_x concentrations on ozone, measurements of HO, HO_2 , and H_2O_2 in the lower stratosphere have become more important than ever.

Overall, the data on HO₂ seem to support the adequacy of the theory for the present application, but for other prognostic applications refinement on the HO₂ budget and chemical cycles must be carried out.

2.2 Possible Variations in Stratospheric Ozone Related to the 11-Year Solar Cycle

The suggestion of a relationship between ozone and the solar cycle dates to at least 1910 (Humphreys, 1910), and various researchers have found correlations of sunspot number with total ozone (Willet, 1962; Paetzold *et al.*, 1972; Christie, 1973; Angell and Korshover, 1976). Researchers studying total ozone fluctuations for the period from 1958 to the present have in general found less evidence to support an ozone-solar correlation (Angell and Korshover, 1978a; London and Oltmans, 1977), but the period over which ozone was studied may not have been long enough to properly establish a long-term cycle. Several plausible mechanisms linking the hypothesized ozone variations with the solar cycle have been suggested. Ruderman and Chamberlain (1975) first proposed that solar modulation of the source of nitric oxide produced by galactic cosmic rays might explain the ozone record, since the cosmic ray source of NO is approximately 30% smaller at solar maximum than at solar minimum. A subsequent study by Crutzen (1975) failed to support this mechanism (see also Ruderman *et al.*, 1976). Zerefos and Crutzen (1975) suggested that solar

proton events may also provide a link between ozone variations and the solar cycle, but the study was not conclusive. Since solar proton events are localized and of short duration (Heath *et al.*, 1977), it is not clear how they may affect global ozone concentrations.

Long-term variations in the solar uv flux provide a third mechanism of potentially much greater significance for ozone variability in a global sense. We have only a few sets of measurements that suggest there may be a significant variation in the solar flux between 180 and 340 nm from solar maximum to solar minimum (Heath and Thekaekara, 1977). In view of the possible importance of solar uv variability on ozone, we shall attempt to estimate the effects such a variability would have had on the ozone record to date. We are particularly concerned with the ozone record near 40 km where both the proposed variability and chlorine increases due to past fluorocarbon release should have had their greatest effects. Callis and Nealy (1978) first studied this problem with a steady-state model without chlorine chemistry. Our time-dependent model (Luther *et al.*, 1977; NAS, 1976) includes a full set of chlorine chemistry reactions and calculates temperature self-consistently. As we shall see, our calculated ozone and temperature responses differ significantly from those calculated by Callis and Nealy.

The radiative transfer model for the temperature calculation used is described in Luther *et al.* (1977). The full set of chemical reactions is given in Appendix A (Table A-1). Photolysis rates are computed at each altitude and time step consistent with all minor species distributions and the specified solar conditions. These calculations were made using the version of the model in which the water vapor profile is held constant. Consequently, our total HO₂ at solar maximum and minimum is somewhat over- and under-estimated, respectively. The effects should not seriously alter our main results, since the calculated local variation for HO₂ in our model is at most 20%.

Variability in the Solar Flux and Its Effect on Ozone

Figure 7 shows the ratio of the ultraviolet (uv) flux at solar minimum to the uv flux at solar maximum as a function of wavelength (Heath and Thekaekara, 1977; NASA, 1977). The measurements shown by Δ and $\square$ represent broad-band photometric observations. Those shown by $\bullet$ were obtained using identical double monochromators. The measured variability below 255 nm depends on only three photometric observations taken near 180 nm in 1966, 1969, and 1970. The flux variation

FIG. 7. Ratio of ultraviolet flux at solar minimum to the flux at solar maximum.

measured with these instruments at longer wavelengths overlaps the region measured by the double monochromators. The photometers show about a 15% larger variation than the double monochromators. We believe the double monochromator measurements at these wavelengths are more nearly correct, because they were made with identical instruments. Since there are no monochromator data below 255 nm, we applied a correction of about 15% to the average of the photometric measured flux variation near 180 nm. The curve in Fig. 7 marked "B" thus represents what we consider to be the largest probable variation. The curve marked "A" gives more weight to the measured variation near 255 nm and is also consistent with balloon measurements which indicate that the flux variation between 200 and 220 nm was not larger than 10% from 1972 to 1976 (Simon, 1978). The curve marked "C" represents an intermediate case and is used for most of the calculations shown in the following sections.

The calculated ozone response in our model depends fairly critically on the relative flux variation above and below 255 nm. Photons with wavelengths less than 255 nm can add to the total atmospheric reservoir of odd oxygen according to the reaction, $O_2 + h\nu \rightarrow O + O$. Photons in the entire range of wavelengths considered here are able to shift the balance between atomic oxygen and ozone according to $O_3 + h\nu \rightarrow O + O_2$, but by far the most efficient are those with wavelengths longer than 255 nm. The point is illustrated in Fig. 8. The curves marked A1 and B1 show the calculated ozone increase when the solar flux is only varied below 255 nm by the amounts indicated in curves A and B of Fig. 7, respectively. A larger flux at these wavelengths produces more ozone. The curves marked A2 and B2 show the ozone response to flux variations above 255 nm only. A large flux at these longer wavelengths shifts the balance of odd oxygen in favor of atomic oxygen so that ozone is decreased. The net result for flux variations over the entire wavelength range is to increase

FIG. 8. Percent change in O_3 from solar minimum to solar maximum $[(\text{max}-\text{min})/\text{min} \times 100]$. The letters A and B refer to the flux change curves given in Fig. 1. For cases A1 and B1 the solar flux was only varied below 255 nm. For cases A2 and B2 the solar flux was only varied above 255 nm.

ozone over most altitudes, as shown by the curves marked B and A, and the total ozone response is approximately the sum of the variations calculated separately. This demonstrates the need for a precise determination of the relative flux variations in these wavelength bands. Since the net ozone response depends on the superposition of two effects of opposite sign, it is clear that the altitude of the maximum response depends on this relative flux variation.

Effects of Temperature Feedback

The primary source of heating for the upper stratosphere is the absorption of solar photons in the Hartley (200-300 nm) and Huggins (>300 nm) bands of ozone. We use the method of Lindzen and Will (1973) to calculate the heating rate from these bands. Figure 3 shows the calculated change in temperature and ozone when the solar flux is perturbed from minimum conditions by the amount shown by curve B in Fig. 7. Our calculations show a temperature increase of no more than about 13 degrees near 45 km. The Lindzen and Will parameterization ignores flux perturbations below 237.5 nm, but since these wavelengths contribute no more than about 10% of the ambient heating rate at 45 km our calculated temperature change should be correct to within 10%. The left panel of Fig. 3 shows the effects of including temperature feedback on calculated O_3 concentrations. With temperature feedback the peak response of ozone is reduced due to the temperature dependence of the reactions $O + O_3 \rightarrow O_2 + O_2$ and $O + O_2 + M \rightarrow O_3 + M$, and the altitude above which ozone decreases is lowered from 50 km to 41 km.

Our calculated temperature increase at solar maximum is significantly smaller than that calculated by Callis and Nealy (1978). This remains true

even for assumed flux perturbations as large as their case 1. We believe their primary thermal response is due to heating by wavelengths below 210 nm, since an examination of their calculated temperature response for case 3 (symbol Δ of their paper) shows a significant increase in temperature (20K near 45 km) even though the solar flux is not perturbed above 210 nm and their calculated ozone concentration at that altitude is decreased (compare Figs. 2 and 5 of their paper). A detailed calculation of the ambient heating rate from O_3 absorption at 45 km shows that the heating by wavelengths below 210 nm is only 0.07% of that for the entire interval from 175 to 350 nm, so that flux perturbations in this region should not greatly affect stratospheric temperature. Figure 9 shows that temperature feedback is important for calculating the change in ozone above about 25 km, but the calculated temperature change is not nearly so sensitive to flux variations as that calculated by Callis and Nealy.

Comparison With the Ozone and Temperature Records

The calculations described thus far were performed using a steady-state version of our model. Here we use our time-dependent model to examine the atmospheric response to a time-varying solar flux. We used the release rates for $CFCl_3$ and CF_2Cl_2 of McCarthy *et al.* (1977) and the solar flux variation C in Fig. 7 to calculate a time history for ozone over the past 47 years. The flux variation followed a sinusoidal 11-year cycle with maximum and minimum corresponding to the years 1936, 1947, 1958, 1969 and 1942, 1953, 1964, 1975, respectively. The calculation included all of the feedback mechanisms discussed above and simulates average conditions for 30° latitude. Seasonal variations in the solar flux were not included, since all one-dimensional models fail to accurately simulate the seasonal behavior of ozone due to their lack of horizontal transport. We compare our results to the analysis by Angell and Korshover (1978a,b,c) in which seasonal effects are partly removed by plotting seasonal deviations from seasonal means.

The calculated percentage deviation of total ozone from the mean is shown in Fig. 10 for the period 1957 to 1978 along with the total ozone record for 11 stations in North America and 14 stations in Europe (Angell and Korshover, 1978a). The record from North America and Europe was chosen for comparison because these areas have the largest number of stations (other than the Soviet Union) and are considered to be the most accurate and reliable. The error bars for the observations are two standard deviations of the mean. It should be pointed out that,

as shown in Fig. 9, the largest changes in O_3 concentration occur above 25 km where the chemical time constant for odd oxygen is only of the order of weeks to months. Consequently, the results in Fig. 10 show very little time delay.

Clearly, our calculated ozone variation for this period is at least not inconsistent with this record. The observed ozone increase during the late 1960's appears to be reasonably consistent with our assumed change in solar flux. We calculate an increase in total O_3 from the solar minimum in 1964 to the solar maximum in 1969 of 5.1%. For a similar variation in the solar flux before the introduction of CFM's we obtain an increase of 5.5%. This may be compared to the observed 5% increase in total O_3 for the Northern Hemisphere from the early 60's to 1970 and 2% increase for total O_3 for the Southern Hemisphere from 1960 to 1968. We calculate a decrease from 1970 to 1972 of 2.5% which agrees well with the observed 1-2% decrease in the Northern Hemisphere. The decrease in observed ozone appears to have leveled off after 1972, but we calculate a further

FIG. 9. Percent change in O_3 [(max-min)/min $\times 100$] and temperature change from minimum to maximum.

FIG. 10. Comparison of calculated total ozone deviations to the analysis of data by Angell and Korshover (1978a).

decrease through 1975. Our calculated decrease is primarily due to the solar flux variation, since the 1975 minimum is only 1.3% smaller than that calculated without the influence of increasing chlorofluoromethanes.

Clearly there are local disagreements between theory and observation throughout the period shown. Evidently some processes that control ozone on shorter time scales (3-4 years) are not accounted for by the model, and the solar uv connection and the effects of increasing chlorofluoromethanes will only be revealed by looking at the general long-term picture. Thus, the apparent discrepancy between theory and observation after 1972 does not necessarily invalidate the background ozone cycle caused by solar uv flux variations and chlorine changes.

The calculated ozone deviation for the levels 32-46 km is compared to Umkehr measurements (Angell and Korshover, 1978a) in Fig. 11. Again, the two regions with the largest number of stations were chosen for comparison. Umkehr measurements are much more difficult to make than measurements for total ozone. The observations should accordingly be viewed with caution (see Dutsch and Ling, 1973). At these levels, Angell and Korshover estimate there was an 8% increase in north temperate latitudes between 1962 and 1973, and a slight decrease after 1974. (The observed decrease may be fictitious due to the presence of aerosols in the stratosphere after the eruption of Fuego in 1974.) We calculate a 5.8% increase for this layer from the solar minimum in 1964 to the maximum in 1969, and an 8.2% decrease from 1969 to 1975. This may be compared to an

increase of 6.8% from solar minimum to maximum and a decrease of 6.4% from maximum to minimum for the pre-CFM atmosphere. As shown in Fig. 11, our calculated decrease begins earlier and is larger than the observed decrease. This difference between the model and observation may be indicative of the presence of other physical processes controlling the local ozone concentrations that are not included in this model (see London *et al.*, 1977).

As Fig. 12 shows, our calculated decrease after 1969 is consistent with the ozonesonde data for lower altitudes. The Umkehr data for 32-46 km is shown again along with our calculations and the ozonesonde record for the layers 24-32 km and 16-24 km (Angell and Korshover, 1978c). Our calculations agree fairly well with the record for Europe for these lower layers. Angell and Korshover estimate a 4% decrease in each of the two lower layers as an average for the north temperate latitudes as a whole. We calculate a decrease from the solar maximum in 1969 to the minimum in 1975 of 7.8% for the 24-32 km layer and 4.8% for the 16-24 km layer.

For the layers shown in Fig. 12, we calculate decreases of 6.4%, 6.9%, and 4.6%, respectively, for the same solar flux variations from the maximum in 1969 to the minimum in 1975 without the influence of increasing chlorofluoromethanes. For this period changes in ozone due to the release of CFM's are apparently small compared to changes resulting from our assumed solar flux variation. Therefore any effort to detect a trend in ozone due to the CFM releases must take into account the effects of solar uv variability.

FIG. 11. Comparison of calculated layer-mean ozone variations to the analysis of Umkehr data by Angell and Korshover (1978a).

FIG. 12. Comparison of calculated layer-mean ozone variations to the analysis of ozone data by Angell and Korshover (1978c).

Figure 13 compares our calculated temperature variations for the layers 26-35 km, 36-45 km, and 46-55 km to rocketsonde temperature data (Angell and Korshover, 1978b). The temperature maxima and minima appear to be nearly in phase with the solar cycle variation except for the highest layer before 1968 (although the equatorial stations show a decrease through the entire time interval, see Angell and Korshover, 1978b). We calculate a decrease in temperature from 1969 to 1975 of 8.5 K, 6.5 K, and 3.1 K for layers 46-55 km, 36-45 km, and 26-35 km, respectively, in reasonable agreement with Angell and Korshover's estimate of about a 5 K decrease for the middle and upper stratosphere after 1970.

FIG. 13. Comparison of calculated layer-mean temperature changes to the analysis of rocketsonde data by Angell and Korshover (1978b).

Summary and Conclusions

The ozone response to a variety of solar conditions was examined and shown to depend on the relative ratio of uv variability above and below about 255 nm. The temperature increase due to increased heating by ozone absorption significantly affects the total ozone variation above 30 km. Ozone changes associated with solar flux variations are primarily due to changes in the photolysis rates for O_2 and O_3 , and only secondarily due to changes in other minor species. We used what we consider to be the most reasonable variation in the solar uv flux consistent with available data to calculate a time history for ozone and temperature. We conclude that

the ozone record as published by Angell and Korshover (1978a,c) is apparently consistent with solar flux variations of the magnitude used, although more data are required to fully establish this relationship. Some of the less satisfactory results above 32 km require further analysis and more quantitatively reliable data. We calculate an ozone decrease of 3.6% for the 32-46 km layer from solar average conditions in 1966 to average conditions in 1977 due to the release of ClO_x from fluorocarbons. In our view this decrease would be difficult if not impossible to detect from the given ozone record if solar flux variations of the magnitude considered here were present during this period because the local ozone variations caused by solar flux variations could be as large as 13%. Insofar as the present calculations should be considered tentative, a long time series of measurements of the uv flux as a function of wavelength is needed to further establish the validity of these effects.

2.3 Effects of a Solar Eclipse on Stratospheric Chemistry

Solar eclipses are known to affect measurable quantities in the upper atmosphere. Various studies have discussed the response of ionospheric electron and positive ion densities to an eclipse (Landmark *et al.*, 1970; Marriott *et al.*, 1972; Anastasiades, 1970).

Other studies have discussed the possibility of changes in stratospheric and mesospheric ozone during an eclipse. Stranz (1961), using a Dobson ozonometer, measured approximately a 4% increase in total ozone shortly after the maximum phase of an eclipse in which only about 80% of totality was reached. Hunt (1965) attempted to explain this total ozone increase by using Chapman reactions in a theoretical study of the effect on ozone resulting from an eclipse. Hunt found that, at most, an increase of only 0.6% is to be expected, and that ozone should be affected only above 45 km.

In later observations, Randhawa (1968) and Ballard *et al.* (1969), both using rocket-borne ozonsondes, found measurable increases in ozone density above 50 km for the November 1966 eclipse near 22°S. Randhawa, for example, measured a factor of 2.6 increase in ozone at 57 km relative to the day before. However, Randhawa (1973) found no significant ozone change between 50 and 55 km for the July 1972 eclipse at 65°N. Grasnack *et al.* (1974) found no change in total ozone using a Dobson ozonometer for the March 1970 eclipse. They concluded that previous measurements had not corrected for solar limb darkening. However, Oshervich *et al.* (1974),

for the July 1972 eclipse, claim to have accounted for limb darkening and yet find approximately a 5% increase in the total ozone column.

Clearly, inconsistencies exist in the observations and in their utilization for validating ozone-related atmospheric chemistry as presently understood. In addition to ozone observations, measurements of other minor constituents during a solar eclipse could provide validation of the short lifetime chemistry used in atmospheric models. Consequently, experiments for upcoming solar eclipses, when properly supported by theoretical analysis, could contribute significantly to present understanding of atmospheric chemistry. In fact, proper measurements of trace species concentrations during an eclipse could provide a direct demonstration that currently proposed NO_x , HO_x , and ClO_x catalytic cycles are indeed concurrently functioning in the stratosphere in the manner suggested by laboratory chemistry. While detailed measurements of diurnal variations could provide similar knowledge, the difference in time scale between the diurnal cycle and a solar eclipse event suggests that the latter event may provide a clearer picture for understanding, as will be discussed.

The purpose of this study is to examine theoretically the expected effect of a solar eclipse on stratospheric minor constituents. Primary emphasis is given to calculations in advance of the total eclipse that will occur over North America on February 26, 1979 (Fiala and Lukac, 1977). Variations similar to those computed for this particular case should be expected for other total eclipses.

Methodology

The LLL one-dimensional model of tropospheric and stratospheric transport-kinetic processes from 0-55 km was used in these calculations. The full set of chemical reactions is given in Appendix A (Table A-1).

Fifty degrees north is the latitude at which totality will be the longest (3 minutes) for the February 1979 eclipse. In attempting to simulate typical expected atmospheric conditions for the February 26, 1979, solar eclipse, we modified the model by setting the temperature (Louis, 1974), tropospheric water vapor (Oort and Rasmussen, 1971), and the ozone distribution (Wilcox and Belmont, 1977) at 50°N winter conditions. Latitude and the solar declination angle in the model, necessary to calculate the solar zenith angle for photodissociation, were set to 50° and -8.8°, respectively.

While ozone in the model was held fixed for most calculations in order to simulate February 50°N conditions, the model was also run with calculated ozone to examine the expected response of

ozone to an eclipse. Our analysis has shown that fixing the ozone distribution does not significantly affect the temporal variations calculated for other species during the eclipse.

Assuming fixed total odd nitrogen and odd chlorine as calculated for midlatitudes, the model was run diurnally to equilibrium. The calculated daytime total column for NO_2 at 50°N of 1.9×10^{15} molecules/cm² is consistent with the observations of Noxon (1978).

Solar flux variations during the eclipse were based on Hunt (1965). The eclipse was assumed to start at 9:30 a.m. and end at 12:00 noon, corresponding to the February 1979 eclipse for 50°N in southern Canada. Totality was assumed to occur for 3 minutes beginning at 10:43:30 a.m. Based on measurements of sky brightness during an eclipse (Velasquez, 1971 and Dandekar and Turtle, 1971), the solar flux at totality, was reduced to 10^{-4} of the unobscured flux.

Results and Discussion

Those species having chemical lifetimes less than a few hours should be expected to vary significantly from normal diurnal behavior during a solar eclipse. In this study, we will emphasize the variations expected for those species most important to the chemistry of stratospheric ozone. Local concentrations of the species could be quite variable, and therefore we should focus on relative effects in the calculations rather than their absolute magnitudes.

The model calculated response of ozone during an eclipse essentially agrees with Hunt (1965). A significant increase in O_3 is to be expected in the upper stratosphere and in the mesosphere due to the conversion of $\text{O}(^1\text{P})$ to ozone through the reaction $\text{O}(^1\text{P}) + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$ accompanied by decreased photolysis of O_2 and O_3 . The maximum increase in O_3 , found at the end of totality, was computed to be 14 and 45% at 50 and 55 km, respectively. Larger percent changes should be expected in the mesosphere. Since most of the atmospheric ozone is at lower altitudes in the stratosphere, an insignificant change in the total ozone column is to be expected.

Figure 14 shows the variations expected during the eclipse in the concentration of nitric oxide, NO , and nitrogen dioxide, NO_2 , at altitudes of 20, 30, and 40 km. The solid line indicates normal diurnal behavior from 8 a.m. to 2 p.m., while the dotted line shows the change in concentration expected during the eclipse. The decreased solar flux results in the NO_2 photolysis rate decreasing during the eclipse. Also, the rapid conversion of $\text{O}(^1\text{P})$ to O_3 decreases the importance of $\text{NO}_2 + \text{O}(^1\text{P}) \rightarrow \text{NO} + \text{O}_2$. The NO is then rapidly converted to NO_2 during the eclipse primarily by the reactions $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ and $\text{NO} + \text{ClO} \rightarrow \text{NO}_2 + \text{Cl}$. By the end of totality, over a

FIG. 14. Calculated responses of NO and NO₂ to a solar eclipse. The solid line indicates normal diurnal behavior; the dotted lines shows the expected solar eclipse effect.

factor of 10 decrease is calculated for NO at 20 and 30 km, with a factor of 6.5 decrease at 40 km. The maximum NO₂ concentration also occurs at the end of totality with values ranging from a factor of 1.4 higher than normal at 20 km to 6.4 at 40 km.

Except in the upper stratosphere (i.e., 40 km), the NO₂ increase is not directly proportional to the NO decrease. This is due to the relatively slow, yet significant, formation rates for ClONO₂ and N₂O₅ from NO₂. The peak increase in the ClONO₂ concentration occurs approximately 15 minutes after

totality due to the slow formation rate (ClO + NO₂). ClONO₂ is increased by 20% at 20 km and 42% at 30 km. N₂O₅ concentration increases by 11% at 20 km and 20% at 30 km. The slow reconversion of ClONO₂ and N₂O₅ to NO₂ causes the NO₂ to fall below the normal diurnal concentration at the end of the eclipse. The NO to NO₂ conversion is not affected in the upper stratosphere where neither ClONO₂ nor N₂O₅ is important as a temporary sink for NO₂.

The expected variations for Cl and ClO are shown in Fig. 15. Rapid conversion of Cl to ClO

FIG. 15. Calculated response of Cl and ClO to a solar eclipse.

during the eclipse occurs primarily through $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$. The net effect on the ClO concentration is a decrease, however, due to more rapid formation of ClONO_2 resulting from increased NO_2 and reduced ClONO_2 photolysis. The minimum in ClO occurs approximately 25 minutes after totality. This time lag is caused by the slow formation rate of ClONO_2 . As the solar flux increases after totality, the ClO concentration increases due to increased photolysis of ClONO_2 . Little change in ClO is expected at 40 km where ClONO_2 formation is not important.

Both OH and HO_2 should decrease in concentration during an eclipse, as shown in Fig. 16. OH concentrations were reduced relative to the normal diurnal concentrations by a factor 2.7, 17.0, and 5.9 at 20, 30, and 40 km, respectively, with a minimum occurring at the end of totality. Smaller decreases are calculated for HO_2 , with the minimum in HO_2 occurring approximately 15 minutes after totality. With the decreased importance of $\text{O}(^1\text{P})$ and NO during the eclipse, a balance between OH and HO_2 is maintained by the rapidly occurring reaction $\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$ and the slightly slower reaction $\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$. Odd hydrogen (OH and HO_2) loss occurs at a slower rate through conversion to water ($\text{OH} + \text{HO}_2$), H_2O_2 ($\text{HO}_2 + \text{HO}_2$) and HNO_3 ($\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3$). Insignificant changes in the concentrations of H_2O_2 and HNO_3 were calculated. At 40 km, a slight increase in HO_2 is expected at totality due to the large rapid conversion of OH to HO_2 followed by the slower HO_2 loss mechanisms.

Summary and Conclusions

The results from this study suggest that significant and detectable variations are expected for some of the important stratospheric minor constituents during a solar eclipse. Such observations, particularly simultaneous observations of trace species, would demonstrate clearly the simultaneous functioning of the various important photochemical catalytic cycles in the stratosphere.

In principle, a similar type of information can be obtained by observations during a normal diurnal cycle, especially during sunrise and sunset. However, observations during a solar eclipse offer several advantages over that of the diurnal cycle. First, as was discussed, the relatively short time duration for the event followed a more clear identification of some of the major reactions in the important catalytic cycles. The same short time duration (2-3 hr) also minimizes the influence of atmospheric transport process in altering the local trace species concentrations. A longer observation period would subject the local chemistry to the influence of significant and usually unquantifiable mixing processes. Thus it is difficult to assess the relative role of chemistry and dynamics in determining the observation data. Also, because of the longer time scale, more interference through conversion to such temporary sinks as ClONO_2 , N_2O_5 and HNO_3 should be expected. This increased interference makes it even more difficult to sort out the effects of the

FIG. 16. Calculated response of OH and HO_2 to a solar eclipse.

catalytic cycle reactions. Finally, at sunrise and sunset there is considerable uncertainty on the proper treatment for the direct and scattered solar flux as a function of altitude when the sun is near the horizon. This then leads to uncertainty in the representation of photodissociation processes in the theoretical calculations. At least for the coming eclipse this will not be a limitation on the model, i.e., the eclipse takes place near local noontime. We would like to reemphasize the point that the theoretical predictions should be viewed mostly in a qualitative sense. The rates of decrease and increase in individual trace species concentrations and the relative changes in magnitudes at totality are the interesting parameters for comparison in the measurements. If an experimental program can be

established, and sufficient local conditions are known, new calculations can be carried out to truly test our understanding of stratospheric chemistry.

Although we have focused mainly on the local changes at individual altitudes, clearly total column changes are also observable. Since the variations for individual species at all altitudes all follow the same general individual trends, the total column for them also varies in the same manner. For example, the ClO column shows the same approximately 25-min delay in reaching minimum as is shown in Fig. 15, and the NO_2 column shows a factor 2 increase at totality. For those interested experimentalists, a more detailed report including various changes in total column and individual vertical profiles is available.

3. ASSESSMENT STUDIES

3.1 Change in Ozone because of SST Emissions, Chlorofluoromethanes, and Nitrous Oxide

The one-dimensional transport-kinetics model has been used to assess the potential chemical effects of several man-made perturbations to the stratosphere. Whenever significant changes occur to the model chemistry or the treatment of other physical processes, the assessment studies are repeated in order to assess the effect of the changes on the model sensitivity. The results presented here were obtained using the latest version of the model.

SST Emissions

The perturbation we use as a test case is an NO_x injection at a rate of 1000 molecules $\text{cm}^{-3}\text{s}^{-1}$ over a 1-km-thick layer centered at either 17 or 20 km altitude. This is equivalent to an annual injection rate of 6.2×10^5 kg/yr of NO_x into the Northern Hemisphere. Using the NO_x emission indexes from the CIAP Report of Findings (Grobeck *et al.*, 1974), this injection rate is approximately equivalent to a fleet of 1200 Concorde-type SST's with a cruise altitude of 17 km or approximately 600 advanced SST's with a cruise altitude of 20 km.

With current technology the NO_x emission index is 18 g/kg of fuel. In the future it may be possible to reduce the NO_x emission index to 6 g/kg fuel. In addition to NO_x , water vapor is also emitted as a product of combustion but with an emission index of 1250 g/kg fuel. Future reductions in the NO_x emission index would not change the water vapor

emission index. Consequently, for an NO_x injection rate of 1,000 molecules $\text{cm}^{-3}\text{s}^{-1}$, the H_2O injection rate would be 177,000 molecules $\text{cm}^{-3}\text{s}^{-1}$, for current technology and 531,000 molecules for future technology. The latter case is equivalent to increasing the SST fleet size by a factor of three since the total NO_x injection remains unchanged.

The computed change in total ozone is given in Table 2 for various NO_x and H_2O injections into an ambient atmosphere that includes current levels of chlorofluoromethanes. The ambient concentration of ClO_x is 1.19 ppbv.

Injecting only NO_x results in an increase in total ozone of slightly more than 2% for both 17- and 20-km injections. These increases in total ozone are larger than those computed a year ago (Luther *et al.*, 1977). Injecting only water vapor into the stratosphere results in a net reduction of total ozone. In the

Table 2. Change in total ozone due to emissions of NO_x and H_2O at injection altitudes of 17 and 20 km.

Species	Injection rate molecules $\text{cm}^{-3}\text{s}^{-1}$	Change in total ozone, %	
		17-km injection	20-km injection
NO_x	1,000	1.90	2.25
H_2O	0		
NO_x	1,000	1.72	1.82
H_2O	177,000		
NO_x	1,000	1.38	0.90
H_2O	531,000		

calculations in which both NO_x and H_2O are injected, the effect of the water vapor is small compared with that of NO_x . The change in the local ozone concentration is shown in Fig. 17 for the 17-km injection altitude.

FIG. 17. The ΔO_3 vs NO_x injection with/without H_2O injection.

Chlorofluoromethanes

The perturbation we considered was the historical release of CFM's up to 1975 followed by a constant release rate at 1975 levels until steady state. The steady-state release rates are assumed to be 308 kt/yr for CFCl_3 and 380 kt/yr for CF_2Cl_2 . The computed change in total ozone at steady state is -15.9%, which is slightly greater than the ozone reduction we computed a year ago (Luther *et al.*, 1977, p. 20). The model calculations indicate a present-day reduction in total ozone of 2.2% relative to 1950. The change in local ozone concentration versus altitude at steady state is shown in Fig. 18.

Nitrous Oxide

Denitrification resulting from the use of nitrogen-base fertilizers has been proposed as a source of increased N_2O concentrations in the atmosphere (Crutzen, 1974). Increased world-wide use of nitrogen-base fertilizers may result in a doubling of N_2O concentration in the next 50-100 years, but the rate of increase of N_2O is highly uncertain. We have computed the change in total ozone for a range of increases of the N_2O concentration in the troposphere, and the results are shown in Fig. 19. A small

FIG. 18. The ΔO_3 vs z for CFM release at steady state.

FIG. 19. Change in total ozone due to an increase in N_2O concentration at the earth's surface.

increase ($<0.5\%$) in total ozone is computed for increases in N_2O up to a doubling of the present tropospheric concentration (320 ppbv). Further increases in N_2O result in a decrease in total ozone ($\Delta\text{O}_3 = -2.0\%$ for $3 \times \text{N}_2\text{O}$ and $\Delta\text{O}_3 = -5.4\%$ for $4 \times \text{N}_2\text{O}$).

3.2 Potential Effects of Space-Shuttle Emissions

In 1976, we studied the potential effect of HCl in the exhaust of the space shuttle on the stratosphere.

Assuming 60 space-shuttle flights per year, we calculated a 0.25% reduction in total ozone at steady state using the LLL one-dimensional transport-kinetics model. Subsequent to these calculations, numerous changes occurred in the measured values of chemical reaction rates important to stratospheric chemistry. Probably the most important of these changes was the measurement of the rate of $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$ by Howard and Evenson (1977). This reaction was found to have a rate approximately 20 times faster than previously estimated, with a measured room temperature value of $8 \times 10^{-12} \text{ cm}^3/\text{sec}$. In addition there were a number of smaller but nonetheless significant changes to other reaction rates (due to new measurements or estimates), particularly to reactions involving chlorine species. Details of these changes can be found in Chang *et al.* (1977). Because of these changes to model chemistry, it is useful to reexamine the potential stratospheric effects from future utilization of the space shuttle.

Besides emissions of approximately 60,000 kg of HCl per flight into the stratosphere (based on NASA estimates), there are also other exhaust products to be considered. There are expected to be approximately 260,000 kg of H_2O , 130,000 kg of CO, and 4,200 kg of NO emitted per flight in the exhaust. Aluminum oxides emitted in the exhaust may also be important to particulate formation, but the impact of this effect will not be assessed here. Water vapor and carbon monoxide are important minor constituents in the stratosphere with mixing ratios by volume of approximately 4-5 ppm for H_2O and 30 ppb for CO. This is to be compared with approximately 1.6 ppb of total odd chlorine, ClO_x (Cl , ClO , ClONO_2 , and HCl), calculated for the present atmosphere in the model. Assuming 60 flights per year for the shuttle, emissions of HCl lead to approximately a 5% increase in ClO_x . Nitrogen oxide emissions are approximately 15 times smaller than the HCl emission, while the natural NO_x (NO , NO_2 and HNO_3) concentrations are approximately 8-10 times larger than the ClO_x concentration. Therefore, the NO emissions from space shuttles should be insignificant relative to the natural concentrations. The emissions of H_2O and CO from space shuttles are much larger than that of HCl, but their ambient concentrations are also much larger such that space shuttles should not be a significant perturbation to water vapor and carbon monoxide.

Model Results

The effect of chlorine emissions from space shuttles has been tested with the LLL one-dimensional transport-kinetics model. The chemistry in the model is essentially that recommended by the recent evaluation in the NASA report on Chloro-

fluoromethanes and the Stratosphere (Hudson, 1977). The hemispherically averaged HCl source function used in the calculation is shown in Fig. 20. This source function is based on data provided by NASA assuming 60 space shuttle flights per year. There are also emissions below 10 km, but these are in the troposphere where it is assumed that the HCl is rapidly removed from the atmosphere by heterogeneous or rainout processes.

FIG. 20. Hemispherically averaged HCl emission rate in the stratosphere for an assumed 60 space-shuttle flights per year.

The calculated concentrations of atmospheric species derived for current levels of chlorofluoromethanes (CFCl_3 and CF_2Cl_2) were used as the initial conditions for this study. The model was then run to steady state (approximately 20 years of model time) using the assumed space shuttle HCl emission rate in Fig. 20. At steady state, total ozone was reduced 0.27% resulting from an increase in atmospheric ClO_x of 0.08 ppbv (a 5% increase in stratospheric odd chlorine). The calculated change in local ozone concentration is shown in Fig. 21. The maximum ozone reduction of approximately 1% occurs near 40 km. This is probably too small to have a significant impact on stratospheric circulation or climate.

The calculated change in total ozone is very similar to that computed previously in 1976. Based on calculations of the effect of chlorofluoromethanes on the stratosphere, a doubling in the computed effect of ozone would have been expected from the change in the rate for $\text{HO}_2 + \text{NO}$ (Hudson, 1977). However, other changes to model chemistry since the previous calculations have compensated for

FIG. 21. Percent changes in local ozone at steady state resulting from space shuttle calculations.

this. In particular, reductions in the rates for the reactions $\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$ and $\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$ have occurred. The rate for $\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$ has increased slightly, and the N atom sink (Duewer *et al.*, 1977) for nitrogen oxides has been reduced in importance due to rate changes. In addition, the previous calculations had a smaller background ClO_2 concentration because present levels of CFCl_3 and CF_2Cl_2 were not included. The additional ambient chlorine should reduce slightly the computed effects of an HCl injection.

3.3 Potential Effects of Solar Power Satellite Launch Vehicles

The feasibility of using giant solar power satellites to transmit energy to the earth is being studied by the Department of Energy. The system currently proposed would involve as many as 100 solar power satellites in geosynchronous orbit. Each satellite would provide 5 GW of electrical power which would be beamed to receiving stations at the ground by microwave transmission. Partial assembly of the satellites would be done at low-earth orbit before moving them to a geosynchronous orbit. A

Heavy Lift Launch Vehicle (HLLV) would be used to get raw materials into low-earth orbit. The two-staged (orbiter and booster) winged launch vehicle would carry a payload of about 400,000 kg. The booster would be capable of flying back to the launch site using air-breathing engines. The orbiter would glide back to the launch site upon returning from orbit. CH_4 and O_2 would be used as fuel for the booster and H_2 and O_2 would be used for the orbiter. The primary exhaust products of the HLLV are H_2O and CO_2 . Some NO_x would be produced in the trailing shock wave.

Using preliminary estimates of the injection rates of NO_x and H_2O , we have examined the potential effect on the stratosphere of HLLV rocket-engine emissions. The one-dimensional transport-kinetics model was used for these calculations. Using data from Boeing for its proposed launch vehicle and assuming 391 flights per year, we used a source rate for H_2O in the model of 1.9×10^6 metric tons/km per year between the altitudes of 16 and 50 km and 6.8×10^3 metric tons/km per year above 50 km. All material is assumed to be deposited into the Northern Hemisphere in the calculation. The source rate for CO_2 should be comparable to that for water vapor, but this is expected to have a negligible effect on the amount of CO_2 in the stratosphere because of the high concentration of carbon dioxide relative to that for water vapor. The results indicate a maximum increase in water vapor of 1%, whereas there is a factor of 10^2 more ambient CO_2 than H_2O in the stratosphere.

The NO_x injection rates, shown in Fig. 22, are based upon data from NASA Langley. Estimates are for solid fuel motors of the type used with the space shuttle and have been scaled up by the number of rocket engines to be used in the HLLV (16) and by the projected number of flights per year (391). The NO_x injection rates were input into the model as nitric oxide. Again, the injections are assumed to be in the Northern Hemisphere.

The ambient atmosphere assumed in these calculations is that containing natural sources of odd chlorine but no chlorofluoromethanes. The added chlorine from chlorofluoromethanes should have little impact on these results. The unperturbed concentrations of H_2O and NO_x are given in Table 3. The model was run to equilibrium with the source rates described above.

A change in total ozone of -0.03% was calculated. Local percent changes in H_2O , HO_2 , and O_3 are given in Table 4. The maximum calculated change in local ozone was -0.25% near the top of the stratosphere, corresponding to an increase in water vapor of 1.03%. The decrease in ozone is due to the added HO_2 resulting from $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$.

FIG. 22. The NO_x injection rate vs altitude, as caused by 391 HLLV flights per year.

Perhaps a more important effect on the atmosphere may come from the launch vehicle injections of water vapor into the mesosphere, since this might affect ion recombination rates. Because our model has a maximum altitude of 55 km and does not treat ion chemistry in detail, we were unable to examine this effect.

Table 3. Unperturbed species profiles.

Altitude, km	Water vapor mixing ratio, ppmv	NO_x mixing ratio, ppmv
16	2.28	1.37×10^{-3}
18	2.35	2.59×10^{-3}
20	2.45	4.57×10^{-3}
22	2.58	7.40×10^{-3}
24	2.71	9.80×10^{-3}
26	2.80	1.13×10^{-2}
28	2.88	1.24×10^{-2}
30	2.95	1.34×10^{-2}
32	3.01	1.44×10^{-2}
35	3.10	1.57×10^{-2}
40	3.23	1.77×10^{-2}
45	3.31	1.82×10^{-2}
50	3.35	1.72×10^{-2}
55	3.36	1.64×10^{-2}

Table 4. Changes in species concentrations.

Altitude, km	Local percent changes ^a			
	H_2O	HO_x^b	NO_x^c	O_3
20	0.20	0.06	0.04	0
25	0.50	0.46	0.09	-0.01
30	0.63	0.53	0.07	-0.01
35	0.74	0.49	0	-0.10
40	0.84	0.49	0	-0.17
45	0.95	0.48	0	-0.23
50	1.02	0.44	0	-0.25
55	1.03	0.41	0	-0.25

^aMany of these percent changes are based on the last significant figure in computer printout from the model.

^b $\text{HO}_x = \text{OH} + \text{HO}_2 + 2 \times \text{H}_2\text{O}_2$.

^c $\text{NO}_x = \text{NO} + \text{NO}_2 + \text{HNO}_3$.

3.4 Effects of a Massive Pulse Injection of NO_x into the Stratosphere

In the early nineteen-seventies, the important role of NO_x in regulating stratospheric ozone was recognized (Crutzen, 1970; Johnston, 1971) and potential anthropogenic sources of NO_x comparable to the natural sources were identified. These anthropogenic sources of NO_x have included emissions from supersonic transports (Grobecker *et al.*, 1974; Johnston, 1971; National Research Council, 1975a), N_2O produced as a result of denitrification from fertilized soils (Crutzen, 1974), and NO_x from past nuclear tests (Foley and Ruderman, 1973) or from a future nuclear war (Hampson, 1974).

Largely as a result of the incorporation of recent measurements of chemical reaction rates that had previously been poorly known (Burrows *et al.*, 1977; DeMore *et al.*, 1977; Howard and Evenson, 1978; Molina *et al.*, 1977), model-predicted ozone reductions from NO_x sources designed to simulate a stratospheric aviation effluent (Broderick, 1977; Popoff *et al.*, 1978; Wuebbles *et al.*, 1977), N_2O increases (Logan *et al.*, 1978) or nuclear tests (Chang *et al.*, 1978) have been greatly reduced, and ozone increases are calculated for some scenarios. However, it has been estimated that the NO_x input to the stratosphere after a nuclear exchange might be nearly two orders of magnitude greater than that produced by the other hypothesized NO_x sources (MacCracken and Chang, 1975; National Research Council 1975a, b). Because the processes that have led to major

changes in model sensitivity to other types of NO_x injection might be overwhelmed by such perturbations, we have reinvestigated model response to very large NO_x pulse injections comparable to those that might be produced in a nuclear exchange.

We have used our one-dimensional transport-kinetics model to examine its response to large pulse NO_x injections. The reaction rates are the same as those given in Table A-1 (Appendix A) with the exception of the reactions listed in Table 5.

The perturbations we considered consisted of pulse injections of NO_x into the layers 9.5-16.5 km (approximately the stabilization altitude range expected for a 0.25-Mt device), 12.5-21.5 km (the approximate stabilization altitude range expected for a 1-Mt device), and 17.5-28.5 km (the approximate stabilization altitude range expected for a 4-Mt device). It was assumed that 6.7×10^{31} molecules of NO were produced per megaton of yield (COMESA, 1975) and that the NO produced is distributed uniformly over the Northern Hemisphere. NO_x injections corresponding to total nuclear yields of 100, 1000, 5000, and 10000 megatons were considered for each of the three injection altitudes. These injection scenarios were designed to explore the effects of a range of device yields and total nuclear yield over a range that might be plausible and were not intended as realistic scenarios.

Results and Discussion

Two computed changes in total ozone are shown in Fig. 23 as functions of time. Very large ozone reductions are computed for a total yield of 10⁴ Mt for 1- and 4-Mt devices. These ozone reductions differ little from those we obtained in 1975 for these device yields and total yield (MacCracken and Chang, 1975). In contrast, the ozone reductions computed for smaller total yield or smaller device yield are currently much smaller than computed previously.

Figure 24 shows the computed ozone profiles at 0.05, 0.5, and 1 year after the injection for a 10⁴ Mt total yield and different device yields. The corresponding changes in local ozone concentration are shown in Fig. 25. For 4-Mt devices, ozone is greatly depleted at early times in the region of the initial injection, and substantial changes occur in the troposphere as a result of the increase in tropospheric photodissociation rates even before much injected NO_x is transported into the troposphere. At later times the injected NO_x mixes to higher and lower altitudes, reducing ozone at high altitudes while increasing ozone in the lower stratosphere and troposphere. Similar effects are shown for the results using 1-Mt devices, although tropospheric ozone is affected by NO_x even at 0.05 years. For 0.25-Mt devices much of the perturbation appears in the

Table 5. Reaction rates that differ from 1977 Chemistry.

Reaction	k	
$O + HO_2 \rightarrow OH + O_2$	3.5×10^{-11}	a
$OH + HO_2 \rightarrow H_2O + O_2$	3.0×10^{-11}	a
$NO + HO_2 \rightarrow NO_2 + OH$	8×10^{-12}	a
$N + O_3 \rightarrow NO + O_2$	$2 \times 10^{-11} e^{-1070/T}$	a
$CO + OH \rightarrow CO_2 + H$	$1.4 \times 10^{-13} + 7.3 \times 10^{-33} M$	b
$NO + ClO \rightarrow NO_2 + Cl$	$1 \times 10^{-11} e^{+200/T}$	a
$NO_2 + ClO + M \rightarrow ClNO_3 + M$	$\frac{3.3 \times 10^{-23} T^{-3.34}}{1 + 8.7 \times 10^{-9} T^{-0.6} M^{0.5}}$	a
$ClNO_3 + O \rightarrow ClO + NO_3$	$3 \times 10^{-12} e^{-808/T}$	a
$H_2O_2 + h\nu \rightarrow 2OH$	Molina <i>et al.</i> (1977)	b
$O_3 + h\nu \rightarrow O_2 + O(^1D)$	We now use quantum yields from Demore <i>et al.</i> (1977)	

^aThese changes were made to bring us into consistency with the recommendations of Demore *et al.* (1977).

^bBased on our evaluation of recent measurements.

FIG. 23. Calculated change in total ozone vs time for various total nuclear yields in megatons. Calculations apply to individual device yields of 0.25, 1.0, and 4.0 megatons.

troposphere immediately after the injection, and relatively small changes in ozone occur above the height of injection.

To understand the small change since 1975 in model sensitivity to very large NO_x injections in the middle stratosphere, it is necessary to understand the sources of altered model sensitivity to smaller injections. Two factors have been materially affected by

FIG. 24. Calculated ozone concentration vs altitude after a 10^4 Mt total yield pulse for various device yields.

changes in chemical reaction rates involving HO_2 used in the model.

Use of $3 \times 10^{-11} \text{ cm}^3/\text{sec}$ (DeMore *et al.*, 1977) rather than $2 \times 10^{-10} \text{ cm}^3/\text{sec}$ for the reaction

has substantially increased the computed concentrations of HO_2 radicals in the model stratosphere. As a result, reactions of HO_2 radicals with O and O_3 are more important sinks for ozone in current models than they used to be.

Use of $8 \times 10^{-12} \text{ cm}^3/\text{sec}$ (Howard and Evenson, 1978) rather than $2 \times 10^{-13} \text{ cm}^3/\text{sec}$ for the reaction

FIG. 25. Calculated change in ozone concentration versus altitude after a 10^4 Mt total yield pulse for various device yields.

has caused HO_x and NO_x catalyzed-ozone destruction cycles to interfere with each other to a greater extent, and has increased the efficiency of the NO_x enhanced methane "smog" mechanism for producing ozone. Both HO_x catalyzed-ozone destruction and methane "smog" ozone production are important in the lower stratosphere, and the use of newer data for HO_x reactions has led to a situation in which calculated ozone increases below about 20 km can be comparable to ozone decreases computed in the 20-45 km region. (NO_x induced ozone changes above ~45 km are small for NO_x injections below 30 km.) There is also an interference between NO_x and ClO_x ozone destruction cycles as a result of the reactions

and

It should be noted that ozone production via the "smog" mechanism is ultimately limited by the methane flux, and if ozone destruction via HO_x or ClO_x is suppressed to the point it becomes negligible, further suppression of these processes will not cause further O_3 increases. Thus, the NO_x induced increases in lower stratospheric ozone cannot be increased without limit. Our largest injection scenarios result in 100-fold increases in the stratospheric burden of NO_x , and more than 10-fold increases in the burden of NO_x ($\text{NO} + \text{NO}_2 + \text{HNO}_3 + \text{NO}_3 + 2\text{N}_2\text{O}_5$). If a large NO_x pulse reaches the middle stratosphere, it will cause a very substantial computed ozone reduction which can overwhelm the

relatively modest ozone increases computed in the lower stratosphere and troposphere.

If NO_x is injected at a low enough altitude, most of it is transported into the troposphere partly in the form of HNO_3 and NO_2 where it is assumed to be removed by rainout processes. As a result, very little is transported into the midstratosphere where it would effectively reduce ozone. Thus the computed ozone increases in the lower stratosphere and troposphere are the dominant effects even for very large NO_x injections below approximately 15 km.

Conclusions

From these results we see that in contrast to other perturbation scenarios we continue to compute very large reductions in stratospheric ozone following a massive pulse injection of NO_x akin to that expected if several thousand megatons of nuclear explosives in the megaton range were to be detonated. However, smaller injections or injections from devices of 0.25 Mt or less yield would be expected to have a smaller effect on the total column of stratospheric ozone.

The ozone column recovers more rapidly in these calculations than it did in our earlier calculations (MacCracken and Chang, 1975). To a very large extent this is a reflection of our use of substantially faster transport above 22 km than in the earlier calculations. The growth of lower stratospheric ozone increases is a lesser contributor to the faster recovery.

A major limitation of these calculations is that no attention is paid to interactions of changes in stratospheric chemistry with the atmospheric structure. For perturbations as large as some of those

calculated here, such interactions might be important. Because of this as well as the other limitations of one-dimensional models (Chang *et al.*, 1978), the computed recovery rates should be interpreted cautiously. The computed peak ozone depletions are only weakly dependent on the transport parameters, K_z , for the very large injection scenarios at the higher altitudes. However, both the recovery time and the computed sensitivity to intermediate injections are sensitive to K_z since K_z influences the residence time of injected NO_x and the ambient distributions of NO_x and other species.

3.5 Effects of Stratospheric Perturbations on the Earth's Radiation Budget, and the Climatic Implications

Since the end of the CIAP program in 1975, there have been many changes to the numerical models used to compute the effects of stratospheric perturbations on O_3 . New species (mostly chlorine containing) and new reactions have been added. Poorly known reaction rates have been remeasured using more accurate methods, and the O_3 photodissociation rate calculation has been improved. Temperature coupling and feedback on reaction rates have been added, and diurnal averaging has been accounted for more accurately. These changes have significantly modified the O_3 impact assessments. It is important, therefore, to re-analyze the impact of the potential changes in stratospheric composition on the global radiation budget.

In a previous assessment of the effects of changes in O_3 and NO_2 concentrations on solar absorption and stratospheric heating rates, Luther (1976) used species concentration profiles derived from our then-current transport-kinetics model. In updating the assessment, it is desirable to present the results in a more general way so that the radiative effects can be inferred for any transport-kinetics model results. This would also enable the radiative effects to be upgraded simply whenever there is a significant change in the stratospheric model assessments. We have attempted to do this for calculations of total solar absorption by O_3 and NO_2 .

Comparison of Changes in Solar Absorption by O_3 and NO_2

In the case of a stratosphere perturbed by an NO_x injection, Luther (1976) showed that the increase in solar absorption by NO_2 at steady state was a significant fraction (35 to 50%) of the decrease in solar absorption by O_3 . Since that time, the sen-

sitivity of O_3 to an NO_x injection has decreased in the transport-kinetics models. Consequently, the change in solar absorption by NO_2 is now expected to be a much larger fraction of the change in solar absorption by O_3 .

Solar absorption by O_3 is shown in Fig. 26 as a function of O_3 column density. The absorption rate given is the instantaneous value for a solar zenith

FIG. 26. Solar absorption by ozone for a solar zenith angle of 60° . A_s is the surface albedo.

FIG. 27. Solar absorption by NO_2 for a solar zenith angle of 60° .

angle of 60° . The radiative transfer model used to compute the solar absorption rate includes Rayleigh scattering and assumes a cloudless, plane-parallel atmosphere above an isotropically scattering ground (Luther, 1976). The solar absorption by NO_2 is shown in Fig. 27 also for a solar zenith angle of 60° .

Ambient and perturbed species concentration profiles were computed using the LLL one-dimensional transport-kinetics model. The model chemistry is listed in Table A-1, except for a few reactions. The rates used for the reactions $\text{O}_3 + \text{HO}_2$, $\text{O}_3 + \text{H}$, $\text{HO}_2 + \text{HO}_2$, and $\text{Cl} + \text{HO}_2$ are given in Table A-2. The rate of 9.0×10^{-12} was used for the reaction $\text{NO} + \text{HO}_2$, and a rate of $5.0 \times 10^{-13} \exp(-1238/T)$ was used for $\text{ClO} + \text{ClO}$. The reactions $\text{O}(\text{D}) + \text{O}_3$ and $\text{HO}_2 + \text{HO}_2 + \text{H}_2\text{O}$ were not included. Two perturbation cases were considered: NO_x injections at 17 or 20 km at the rate of 1000 molecules $\text{cm}^{-2}\text{s}^{-1}$ uniformly distributed over a 1-km-thick layer. This corresponds to a hemispheric injection rate of 6.2×10^8 kg/yr of NO_2 . Changes in the O_3 and NO_2 column densities and solar absorption rates for a solar zenith angle of 60° and a surface albedo of 0.25 are summarized in Table 6. The unperturbed column densities are 9.730×10^{18} molecules/ cm^2 (0.382 atm.cm) for O_3 and 3.506×10^{15} molecules/ cm^2 for NO_2 .

Table 6. Increases in total atmospheric solar absorption by O_3 and NO_2 due to NO_x injections at the rate of 6.2×10^8 kg/yr. Calculations are for a solar zenith angle of 60° and a surface albedo of 0.25.

Quantity	NO_x injection altitude	
	17 km	20 km
ΔO_3	1.06%	0.39%
ΔNO_2	6.87%	15.60%
$\Delta\text{Abs}(\text{O}_3)$	0.16 W/m^2	0.06 W/m^2
$\Delta\text{Abs}(\text{NO}_2)$	0.06 W/m^2	0.13 W/m^2

In both cases the injection of NO_x resulted in a small increase in total O_3 . Although the changes in the O_3 column density are small, the change in the local O_3 concentration (Fig. 28) may be several percent. The change in column density reflects the net difference between regions of O_3 increase (below 22 km) and O_3 decrease (above 22 km). Consequently, although the change in the net heating may be small, the redistribution in altitude of where this heating occurs may be significant. The change in the local concentration of NO_2 is shown in Fig. 29.

FIG. 28. Change in local ozone concentration due to NO_x injections (as NO_2) of 6.2×10^8 kg/yr.

FIG. 29. Change in local NO_2 concentration due to NO_x injections (as NO_2) of 6.2×10^8 kg/yr.

Changes to the Solar Radiation Budget and Heating Rates

In addition to the two NO_x injection cases already described, we also considered the steady-state O_3 reduction due to CFM's at the 1975 release rate. The change in O_3 column density computed at steady state was -14.4%. For a solar zenith angle of 60° and a surface albedo of 0.25, there is a reduction

in solar absorption by O_3 of 2.45 W/m^2 . The change in the local O_3 concentration is shown in Fig. 30. There is a reduction in O_3 concentration at all altitudes with the largest percent reduction occurring at 40 km.

In addition to affecting the gaseous absorption of solar radiation in the stratosphere, changes in stratospheric composition also affect solar absorption in the troposphere by changing the atmospheric transmissivity. A decrease in O_3 column density, for example, allows more solar radiation to reach the troposphere, thereby increasing both the amount of solar absorption and the amount of radiation scattered back to space. Changes to the solar radiation budget are presented in Table 7 for the three perturbation cases. The net solar flux at the top of the atmosphere is defined as the incoming flux minus the outgoing flux. The values for the change in solar absorption in the troposphere include the change in gaseous absorption and the change in absorption by the earth's surface. The changes in the instantaneous

solar absorption rates for the NO_x injection cases are small compared with the unperturbed values. The CFM perturbation case, on the other hand, represents a significant perturbation to the solar radiation budget. There is a significant reduction in the solar absorption in the stratosphere and an increase in the troposphere.

The changes in the O_3 and NO_2 solar heating rates are presented in Fig. 31 for the 17-km NO_x injection and in Fig. 32 for the 20-km NO_x injection. The O_3 and NO_2 both contribute to an increase in the heating rate in the lower stratosphere. Consequently, the change in solar heating tends to increase the temperature in the upper stratosphere.

The change in the solar heating rate due to a CFM perturbation is shown in Fig. 33. The reduction in the solar heating rate in the lower stratosphere is approximately the same magnitude as the increase in heating rate computed for the NO_x injection cases. The change in the solar heating rate is -0.07 K/day at 24 km, -0.02 K/day at 20 km, and -0.01 K/day at 18

FIG. 30. Change in ozone concentration at steady state due to CFM's at the 1975 release rate.

FIG. 31. Change in the instantaneous solar heating rates for a solar zenith angle of 60° and $A_s = 0.25$ due to an NO_x injection at 17 km.

Table 7. The perturbed solar radiation budget (solar zenith angle = 60° , surface albedo = 0.25).

Quantity	Perturbation case			Unperturbed value
	NO_x , 17 km	NO_x , 20 km	CFM	
Δ Net solar flux at top of atmosphere	0.1 W/m^2	0.0 W/m^2	-1.0 W/m^2	470 W/m^2
Δ Stratospheric solar absorption	0.13	0.08	-2.35	34.1
Δ Troposphere/surface solar absorption	-0.1	-0.1	1.3	436

FIG. 32. Change in the instantaneous solar heating rates for a solar zenith angle of 60° and $A_0 = 0.25$ due to an NO_x injection.

FIG. 33. Change in the solar heating rate of ozone at steady state for a solar zenith angle of 60° and $A_0 = 0.25$ due to CFM's at the 1975 release rate.

km. In this case there is cooling at all altitudes with the largest effect in the upper stratosphere.

Potential Climatic Impact

The climatic impact of changes in stratospheric composition depends upon both the solar and longwave effects of the perturbation. Changes in temperature, in addition to affecting the transfer of longwave radiation, also affect atmospheric stability and transport. Here we will consider only the global impact of the solar and longwave effects and neglect any potential feedback on transport.

A previous assessment of the effect of changes in O_3 and NO_2 on surface temperature by Ramanathan *et al.* (1976) showed a cooling at the surface associated with a reduction in O_3 due to an NO_x injection. Only reductions in O_3 were considered (not increases), and it was assumed that the changes in O_3 and NO_2 were uniform (percentagewise) between 12 and 40 km. Our present results differ from these modeling assumptions in that the changes in O_3 and NO_2 concentrations are not uniform with altitude, and there is a net increase in O_3 column density rather than a decrease. Nevertheless, the work of Ramanathan *et al.* (1976) is useful because it demonstrates the importance of the longwave effect of the perturbation. The reduction in total O_3 tended to warm the troposphere by increasing the transmissivity of the stratosphere for solar radiation. The reduction in stratospheric temperature due to reduced O_3 , however, had a greater effect on the longwave radiation emitted downward from the stratosphere. The net result was a slight reduction in surface temperature.

A similar calculation using our current modeling results would predict an increase in temperature in the lower stratosphere (Luther and Duewer, 1978). It is possible that the longwave effect would also dominate in this case. Although the net change in temperature is uncertain, it is clear that the longwave effect would tend to warm the troposphere, whereas the solar effect would tend to cool.

In attempting to assess the effect of changes in stratospheric composition on the global mean surface temperature, it is desirable that the same model be used throughout the study. Since we do not have a climate model that may be applied to this study, we will rely on the results of other researchers. The two methods used here are the published results of Ramanathan's radiative equilibrium model and Budyko's (1969) empirical formulation relating the change in outgoing longwave flux at the top of the atmosphere to the change in surface temperature.

According to Ramanathan's model (Ramanathan *et al.*, 1976), the change in surface temperature is related to the change in ozone by

$$\Delta T_s = (0.009 \text{ to } 0.014 \text{ K}) \Delta \text{O}_3,$$

where ΔO_3 is the percent change in ozone concentration applied uniformly over the altitude region 12–40 km. The first coefficient applies to the assumption of constant cloud top altitude whereas the second coefficient applies to the assumption of constant cloud top temperature. A similar expression relates the change in surface temperature to the percent change in NO_2 concentration between 12 and 40 km:

$$\Delta T_s = (3 \times 10^{-4} \text{ to } 6 \times 10^{-4} \text{ K}) \Delta \text{NO}_2$$

The expressions are not applicable directly to our results, but they may be used to estimate an approximate upper limit on ΔT_s .

The present changes in O_3 and NO_2 averaged over various altitude ranges between 12 and 40 km are given in Table 8. Since the change in species concentrations in the lower stratosphere will have a greater effect on the downward longwave flux into the troposphere than changes at higher altitudes, we can get a rough estimate of ΔT_s by using the values of ΔO_3 and ΔNO_2 for the 12-22 km region. Using these values tends to overestimate ΔT_s because it assumes that the ozone concentration has increased by the same percentage at higher altitudes when the calculation indicates that smaller changes occur at higher altitudes.

Table 8. Percent change in O_3 and NO_2 concentrations averaged over various altitude ranges.

Perturbation	Quantity	Average over altitude range, km		
		12-22	22-40	12-40
NO_x injection at 17 km at rate of 6.2×10^8 kg/yr	$\Delta \text{O}_3, \%$	4.3	-0.7	0.7
	$\Delta \text{NO}_2, \%$	30	6.0	8.7
NO_x injection at 20 km at rate of 6.2×10^8 kg/yr	$\Delta \text{O}_3, \%$	4.9	-2.0	0.0
	$\Delta \text{NO}_2, \%$	56	15.6	20.1

Values of ΔT_s computed using the relations above and values of ΔO_3 and ΔNO_2 for the 12-22 km region are given in Table 9. The change in surface temperature is estimated to be less than 0.1 K for both the 17- and 20-km injection altitudes. For comparison, values are also given in Table 4 for ΔT_s using Budyko's empirical formulation

$$\Delta T_s = 0.701 \text{ K } \Delta F,$$

where ΔF is the change in the outgoing longwave flux in W/m^2 at the top of the atmosphere. The value for ΔF is obtained by dividing in half the change in net solar flux at the top of the atmosphere given in Table 7 to account for day-night averaging. At equilibrium the change in the outgoing longwave flux equals the change in the net incoming solar flux. Again the computed values of ΔT_s are significantly less than 0.1 K.

The same methods were applied to the CFM perturbation results. In this case, however, the value

Table 9. Estimated change in surface temperature using different assessment methods.

Perturbation	Change in surface temperature, K	
	Ramanathan	Budyko ^a
NO_x injection at 17 km		
ΔO_3	0.04 to 0.06 ^b	
ΔNO_2	0.01 to 0.02 ^b	
$\Delta \text{O}_3 + \Delta \text{NO}_2$		0.04
NO_x injection at 20 km		
ΔO_3	0.04 to 0.07 ^b	
ΔNO_2	0.02 to 0.03 ^b	
$\Delta \text{O}_3 + \Delta \text{NO}_2$		0.02
CFM's at 1975 release rate		
ΔO_3	-0.13 to -0.21	-0.35
$\Delta \text{CFCl}_3, \Delta \text{CF}_2\text{Cl}_2^c$	0.44	0.44

^a $\Delta T_s = 0.701 \text{ K } \Delta F (\text{W/m}^2)$.

^bThe method used to determine these values tends to overestimate the change in surface temperature.

^cFrom Wang *et al.* (1976), $\Delta T_s = 0.38$ to 0.57 K .

of ΔO_3 averaged over 12-40 km (Table 8) was used to estimate ΔT_s . The resulting values of ΔT_s are presented in Table 9. In this case the change in the global mean temperature is on the order of several tenths of a degree, which may be a significant climatic perturbation since regional changes in temperature might be several times greater than the global mean. Pollack *et al.* (1976) suggest that 0.1 K is a threshold value for considering the change in global mean surface temperature to be significant. Computing values of ΔT_s associated with past major changes in climate, they infer that values below 0.1 K would not have major consequences.

In the case of a CFM perturbation, there is the additional effect of the longwave properties of CF_2Cl_2 and CFCl_3 . At steady state we compute the tropospheric concentrations of the CFM's to be larger than present day levels by 0.6 ppbv for CFCl_3 and 1.52 ppbv for CF_2Cl_2 . The greenhouse effect of CFM's has been studied by Ramanathan (1975), and he finds the following relationships between the change in surface temperature and the change in tropospheric CFM concentration:

$$\Delta T_s = 0.215 \text{ K } \Delta \text{CF}_2\text{Cl}_2 (\text{ppmv})$$

$$\Delta T_s = 0.180 \text{ K } \Delta \text{CFCl}_3 (\text{ppmv}).$$

Ramanathan's model results therefore imply an increase in surface temperature of 0.44 K due to

CFM's, which is the same magnitude as predicted using Budyko's empirical formulation. A similar calculation has been performed by Wang *et al.* (1976) in which an increase in surface temperature of 0.38 to 0.57 K due to these CFM concentrations is predicted. This result brackets the value of 0.44 K obtained by the other methods.

We now consider the potential climatic effect of the water vapor injected into the stratosphere along with the NO_x from SST engine emissions. Assuming an emission index of 1250 g/kg fuel for water vapor and 18 g/kg fuel for NO_x , the associated water vapor injection rate would be 4.3×10^{10} kg/yr. According to our model calculations in which the stratospheric water vapor profile is computed, this would lead to an increase in the stratospheric water vapor mixing ratio of 0.1 ppmv for a 17-km injection and an increase of 0.31 ppmv for a 20-km injection. Ramanathan's model was also used in the CIAP study to estimate the change in surface temperature resulting from a change in stratospheric water vapor mixing ratio (Grobecker *et al.*, 1974):

$$\Delta T_s = (0.2 \text{ to } 0.3 \text{ K}) \Delta \text{H}_2\text{O} \text{ (ppmv)}.$$

The estimated change in surface temperature due to these changes in stratospheric water vapor are given in Table 10. These values of ΔT_s are larger than those due to ΔO_3 and ΔNO_2 resulting from SST engine emissions, but they are still less than 0.1 K.

In addition to NO_x and water vapor, SST engines also emit SO_2 , which is converted to sulfate aerosols. Assuming an emission index of 1.0 g/kg fuel, the SO_2 injection rate would be 3.4×10^7 kg/yr when the NO_x injection rate is 6.2×10^8 kg/yr. The change in surface temperature due to increased stratospheric aerosols (75% H_2SO_4) has been computed by Pollack *et al.* (1976). Using a radiative-convective model, they find

$$\Delta T_s = (-6.3 \text{ to } -10 \text{ K}) \Delta \tau,$$

where $\Delta \tau$ is the increase in the stratospheric optical depth. Pollack *et al.* find that $\Delta \tau$ is related to the mass density (m) of sulfate aerosols in $\mu\text{g}/\text{m}^3$ averaged over a 10-km thick layer by the expression $\Delta \tau = 0.031 m$. The expression $\Delta \tau = 0.038 m$ was used in the CIAP Report of Findings (Grobecker *et al.*, 1974). The aerosol mass density is obtained from the expression

$$m = HFtc M_a/M_e,$$

where H is the fraction of the aerosols deposited in a given hemisphere, F is the SO_2 emission rate, t is the residence time, c is the conversion efficiency, M_a is the molecular weight of the aerosol, and M_e is the molecular weight of SO_2 . For a sulfuric acid solution that is 75% H_2SO_4 by weight, $M_a/M_e = 1.6$. Values for the various quantities used by Pollack *et al.* (1976) and used in the CIAP Report of Findings are shown in Table 11. The resulting values for $\Delta \tau$ are considerably smaller (by nearly a factor of 3) using Pollack *et al.*'s values. In both cases the values for ΔT_s are estimated to be less than -0.01 K for a 17-km injection altitude and less than -0.02 for a 20-km injection altitude.

Conclusions

Changes in O_3 and NO_2 concentrations due to an NO_x injection lead to increases in the total solar absorption of both species. These increases are small, however, when compared to the total energy absorbed by the stratosphere, and the climatic effect is estimated to be negligible. Using the criterion that changes in surface temperature less than 0.1 K would not have major consequences, none of the SST engine emissions (NO_x , H_2O , and SO_2) are estimated to have a major climatic effect. The largest individual effect on surface temperature is that of water vapor, which is estimated to cause a temperature increase of 0.06–0.09 K for a 20-km injection at 4.3×10^{10} kg/yr. The combined effect of all engine emissions on climate is likely to be an increase in global mean temperature of less than 0.1 K.

In the case of a CFM perturbation, there is a significant impact on the solar radiation budget leading to a decrease in the solar heating of the stratosphere and an increase in solar heating of the troposphere and earth's surface. There is also an increase in the solar flux scattered back to space. There is considerable uncertainty about the change in surface temperature at steady state caused by the reduction of O_3 due to CFM's released at the 1975 rate. Our estimates range from -0.13 K to -0.35 K. The greenhouse effect of CFCl_3 and CF_2Cl_2 , on the other hand, tends to warm the surface by an estimated 0.44 K. The net effect on surface temperature is

Table 10. Change in surface temperature due to an increase in stratospheric water vapor.

Altitude of injection, km	H_2O in stratosphere, ppmv	ΔT_s , K
17	0.11	0.02–0.03
20	0.31	0.06–0.09

Table 11. Factors used in calculating the change in surface temperature due to an SO₂ emission rate of 3.44×10^7 kg/yr in the Northern Hemisphere.

Source	Altitude of injection, km	Residence time, years	Conversion efficiency	Fraction in hemisphere	$\Delta\tau$	ΔT_s^2 , K
Pollack <i>et al.</i> , 1976	17	0.978	0.869	0.7	3.9×10^{-4}	-0.002 to -0.004
$\Delta\tau = 0.031 \text{ m}^b$	20	1.715	0.945	0.7	7.6×10^{-4}	-0.005 to -0.008
CIAP Report of Findings, 1976	17	1.70	0.83	1.0	1.1×10^{-3}	-0.07 to -0.011
$\Delta\tau \approx 0.038 \text{ m}$	20	3.00	0.93	1.0	2.3×10^{-3}	-0.014 to -0.023

^a $\Delta T_s = (-6.3 \text{ to } -10 \text{ K}) \Delta\tau$.

^b m is the mass density of sulfate aerosols in g/m^3 averaged over a 10-km thick shell.

uncertain, but it may be in excess of ± 0.1 K, which would be considered significant. The potential climatic effect of a CFM perturbation needs further study to reduce the large uncertainty associated with these results.

3.6 Effect of Ozone Reductions on Erythema Dose

Because reductions in total ozone would permit greater amounts of uv radiation to reach the surface of the earth (Cutchis, 1974; Halpern *et al.*, 1974), a number of studies have been performed with the goal of assessing biological sensitivity to ozone-induced changes in uv radiation (National Research Council, 1973). One approach has been to correlate skin cancer incidence data directly with ozone layer thickness. The possible influence of such factors as duration of sunlight, clothing and exposure habits, and optical path length have been considered (McDonald, 1971; van der Leun and Daniels, 1975). Another approach has been to explicitly consider the dose of uv radiation received as a function of ozone amount and other climatic variables (Green and Mo, 1975). The radiation dose is then related to cancer incidence after weighting by a wavelength-dependent function accounting for variation in radiation efficacy. This second approach, though less direct, is appealing because the mechanism of cancer production is more fully represented, and it allows for experimentation with combinations of independent variables outside the rather narrow range of reliable observation.

As the first step in this approach, Green and co-workers developed a semi-empirical model for calculating uv radiation at the surface of the earth in the spectral region 280-340 nm (Green *et al.*, 1974a,b; Mo and Green, 1974). They have calculated erythema (sunburn) dose as a function of total ozone, solar zenith angle, latitude, season, and cloud amount. Their model was also used in the Climatic Impact Assessment Program's analysis of ozone depletion (Green *et al.*, 1975).

One feature of this model, and uv dosimetry in general (Berger *et al.*, 1975), is that the receiver is assumed to be horizontal. The geometry of humans, however, is such that the majority of exposed skin would normally be in a nonhorizontal position. In fact, the horizontal projection of an upright person amounts to only a few percent of total surface area (Fanger, 1970).

The report of the National Research Council (1976a) summarizes the specific sites of origin of primary melanoma skin cancer. The data show the predominant localization of sites of origin to areas of the skin that are constantly exposed, such as the trunk and legs of males. These are, in general non-horizontal surfaces, which suggests that receiver orientation should be considered in the study of uv dose.

In last year's annual report (Luther *et al.*, 1977), we reported the results of a study of the effect of receiver orientation on erythema dose. The work reported here expands upon that earlier effort. Although the same numerical model is used for the current study, we will repeat the description of the model.

Model Description

The procedure employed here involves using the Green model (Green *et al.*, 1974a) to obtain total local uv radiation ($Q_h + q_h$) as a function of wavelength (λ) and solar zenith angle (θ). Valid for clear sky conditions, it is essentially a Beer-Bouguer formulation for both direct beam (Q_h) and diffuse (q_h) radiation. It is assumed that the latter is isotropically distributed. These fluxes are determined using the relationships

$$Q_h(\theta, \lambda) = H(\lambda) V^2 \exp[-A_i(\theta, \lambda)] \cos \theta \quad (1)$$

and

$$q_h(\theta, \lambda) = H(\lambda) V^2 \exp[-D_i(\theta, \lambda)] \quad (2)$$

where $H(\lambda)$ is the extraterrestrial solar irradiance at the mean earth-sun distance (taken from Howard *et al.*, 1960). The symbol V , which does not appear in the Green model, is the ratio of mean earth-sun distance to that distance on a particular day. It thus allows for eccentricity in the earth's orbit, which causes variations in the extraterrestrial flux of $\pm 3.5\%$.

The terms A_i and D_i are optical thickness functions accounting for the presence of ozone, air, and particulate matter, and they are given by Green *et al.* (1974a). For the spectral region considered here, the total ozone optical depth is of special interest.

To calculate the direct beam radiation incident on an inclined surface (Q_p), it is necessary to replace θ in Eq. (1) with the angle between the position of the sun and a line normal to the surface (i).

$$Q_p(\theta, \lambda) = H(\lambda) V^2 \exp[-A_i(\theta, \lambda)] \cos i \quad (3)$$

where

$$\cos i = \cos \alpha \cos \theta + \sin \alpha \sin \theta \cos(a - a') \quad (4)$$

Here a' is the solar azimuth (relative to north), a is the azimuth of the receiver, and α is the angle of the receiver's inclination (relative to horizontal). For a horizontal receiver, $\alpha = 0$. Equations required to find θ and a' as a function of latitude, season, and time of day may be found in Dave *et al.* (1975), Sellers (1965) or the Smithsonian Meteorological Tables (List, 1958). The last reference also contains tabled values of V .

Diffuse radiation incident on an inclined surface has two components: that arriving from the sky as

scattered radiation (q_s) and that reflected from the earth's surface (q_p). Under the assumption of isotropic reflection and the earlier assumption of isotropic atmospheric scattering, these quantities are given by (Dave *et al.*, 1975):

$$q_s(\theta, \lambda) = \frac{1}{2} q_h(\theta, \lambda) (1 + \cos \alpha) \quad (5)$$

and

$$q_p(\theta, \lambda) = \frac{r}{2} [Q_h(\theta, \lambda) + q_h(\theta, \lambda)] (1 - \cos \alpha) \quad (6)$$

The ground reflectivity r is small for surfaces other than snow and ice at uv wavelengths (Kondratyev, 1973). A value of 0.1 was chosen here for r .

The sum $Q_p + q_s + q_p$ represents the total radiation incident per unit area on a plane inclined at an angle α and with azimuth a . Because radiation is not equally efficient at all wavelengths in producing a biologic response, it is not possible to integrate incident radiation directly over wavelength and obtain a meaningful measure of skin tissue insult. It is necessary to know the relative response of skin to uv radiation as a function of wavelength. In the case of sunburn the so-called action spectrum (or erythema efficiency) has been studied using uv lamps (e.g., Coblenz and Stair, 1934; Mangus, 1964; Cripps and Ramsey, 1970) and can be represented by (Green *et al.*, 1974b):

$$\epsilon(\lambda) = \left[4 \exp \left(\frac{\lambda - 297}{3.21} \right) \right] \times \left[1 + \exp \left(\frac{\lambda - 297}{3.21} \right) \right]^{-2} \quad (7)$$

The action spectrum for skin cancer in humans is not known; it is usually assumed to be the same as for erythema or similar to the DNA action spectrum (Setlow, 1974).

Procedure and Results

Equations (4) through (7) may be used to calculate the instantaneous erythema dose for any time of day, date, latitude, ozone amount and receiver position. In analyzing the effects of receiver orientation, we have numerically integrated over wavelength and time to produce daily erythema doses for Northern Hemisphere latitudes assuming the receiver is stationary. Integrations were performed for the 15th day of each month using a time step of

approximately 20 minutes. The total ozone was specified as a function of latitude based on data from the Nimbus III satellite reported by Lovill (1972). The values of total ozone used in the calculation are shown in Table 12. Ozone reductions of 10 and 20% were also considered in the calculations.

The azimuth of the receiver was specified in two ways. First, to obtain a measure of the upper bound on erythema dose at middle latitudes in the Northern Hemisphere, the receiver was held fixed in a south-facing position. Second, to estimate the average dose for a population where there is random orientation (i.e., no preferred orientation), calculations were made while averaging over azimuth angle (a rotated receiver). Doses were computed at 20° intervals in the azimuth angle, and the average of these was used for integration. The inclination angle α was held fixed at values of 0, 45, and 90 degrees. Introducing time dependence for this term would require modeling specific body sites and activities; we have chosen to present more general calculations.

Figure 34 shows the daily total erythema dose for a south-facing surface as a function of latitude in the Northern Hemisphere for different ozone amounts and receiver inclinations for the 15th day of June, September, and December. The relationship between dose magnitude and inclination is such that inclined surfaces generally receive less daily integrated dose than a horizontal surface at the same latitude. Exceptions to this occur in some low sun situations (large θ) where the dose on the inclined, south-facing surface slightly exceeds that of the horizontal surface (e.g., $\alpha = 45^\circ$, 50-60°N in September and $\alpha = 45^\circ$, 20-30°N in December). This result is in contrast to the study of Dave *et al.* (1975) using the full solar spectrum where the total radiation on south-facing surfaces was shown to grow larger than that received by a horizontal surface at high latitudes. At the wavelengths contributing to erythema, the radiation is predominantly diffuse. Consequently, the angle of incidence does not exert as strong an influence as it would when the radiation is predominantly in the direct beam, as was the case in the study by Dave *et al.* (1975).

Figure 34 also indicates that the daily erythema does not change uniformly with inclination angle. For example, changing α from 0 to 45° results in less change in the daily erythema dose than results from changing α from 45 to 90°.

Variations in α affect the latitudinal gradient of erythema dose. Increasing α decreases the latitudinal gradient in erythema dose poleward of the peak dose. There is a small reduction in the gradient for $\alpha = 45^\circ$ as compared to $\alpha = 0^\circ$, but the gradient is reduced by approximately half for $\alpha = 90^\circ$.

For a horizontal surface, the latitude of the peak daily erythema dose corresponds closely to the solar declination angle. As α increases there is a poleward shift in the latitude of the peak dose. In June, for example, as α is changed from 0 to 90°, the latitude of peak dose moves from 20°N to approximately 40°N. A shift of similar magnitude occurs in September. This shift is the result of several factors.

The inclination angle affects the amount of direct solar flux received by the inclined surface. At latitudes toward the equator from the latitude of solar declination, increasing α results in a decrease in the direct solar flux. At higher latitudes there may be either an increase or a decrease depending on the value of α .

As already mentioned, the contribution to erythema dose due to diffuse radiation has two components: that arriving from the sky (Eq. 5) and that reflected from the earth's surface (Eq. 6). An inclined surface receives less diffuse radiation from the sky with increasing angle of inclination because less sky is visible. For example, a vertical surface receives half the flux of that received by a horizontal surface, assuming isotropic diffuse radiation. On the other hand, as α increases there is an increase in the diffuse flux component from the earth's surface. This flux component is generally small, however, because of the low surface albedo assumed.

The net result of the various factors just discussed is that there is a change in the partitioning of the direct and diffuse flux contributions to erythema dose as α is varied. This is illustrated for a south-facing surface in Fig. 35 which shows the

Table 12. Values of total ozone in atm-cm.

Months	Latitude (degrees north)								
	EQ	10	20	30	40	50	60	70	80
June	0.256	0.259	0.274	0.295	0.326	0.362	0.391	0.400	0.410
September	0.249	0.246	0.262	0.295	0.316	0.344	0.364	0.372	0.378
December	0.256	0.256	0.273	0.303	0.334	0.366	0.393	0.399	0.402

FIG. 34. Daily total erythema dose for a south-facing surface as a function of latitude, inclination angle α , and ozone amount: (a) June 15, (b) September 15, and (c) December 15.

FIG. 35. The fraction of the total daily erythema dose for a south-facing surface due to diffuse radiation (sky plus ground reflection): (a) June 15, (b) September 15, and (c) December 15.

fraction of the total erythema dose due to the diffuse flux (sky plus ground reflection). In low sun situations (e.g., at high latitude), increasing α causes a decrease in the diffuse fraction of the total erythema dose, whereas the opposite is true in the case of a high sun (small θ).

Figure 36 shows the daily erythema dose for a rotated, inclined surface as a function of latitude for

FIG. 36. Daily total erythema dose, same as Fig. 34 except for a rotated surface.

the same values of total ozone as used in Fig. 34. The dose received by the rotated surface never exceeds that for a horizontal surface, whereas it is possible at times for a south-facing, inclined surface to receive a slightly greater dose than the horizontal surface.

There is not a poleward shift in the latitude of the peak erythema dose with increasing α as was the case for the south-facing surface. Under the assumption of isotropic diffuse radiation, the contribution to erythema dose due to the total diffuse flux is the same for both the south-facing and rotated surfaces for a given α and latitude. Consequently, differences between Figs. 34 and 36 are due to differences in the direct flux component. The direct flux component is generally larger for the rotated surface than for the south-facing surface at latitudes near the equator, and the converse is true at high latitudes. In middle latitudes (30-50°N) the daily erythema dose is smaller for the rotated surface than for the south-facing surface.

Figure 37 shows the daily erythema dose averaged over a year for a south-facing surface assuming cloudless conditions. In middle latitudes the daily average erythema dose on a surface with $\alpha = 45^\circ$ ranges from 90 to 96% of the dose on a horizontal surface. The dose is significantly less for inclination angles greater than 45° .

Figure 38 shows the daily erythema dose averaged over a year for a rotated surface. In this case the daily average erythema dose in middle latitudes on a surface with $\alpha = 45^\circ$ is approximately 83% of the dose on a horizontal surface. At higher latitudes the dose on the rotated surface is significantly less than that on the south-facing surface.

FIG. 37. Daily erythema dose averaged over a year for a south-facing surface.

FIG. 38. Daily erythema dose averaged over a year for a rotated surface.

A semilog scale is used in Figs. 37 and 38 to demonstrate the effect of inclination angle on the doubling distance for erythema dose. In middle latitudes the computed erythema dose on a horizontal surface doubles over 16° of latitude moving toward the equator. The angle of inclination has very little effect on the doubling distance as evidenced by the similar slopes of the curves in Figs. 37 and 38.

The computed doubling distance is consistent with measurements of annual-average erythema dose (Urbach and Davies, 1975), but it differs from the doubling distance for the incidence of skin cancer. Data on the incidences of skin cancer in middle latitudes show a doubling over 8 to 12° of latitude (National Research Council, 1976b), indicating that there are other factors contributing to the incidence rate. Consequently, predicting the effect of a reduction in total ozone on the skin cancer incidence rate is more complex than just assessing the change in erythema dose and scaling proportionately.

The effect of a reduction in total ozone of 10% on the annual-average daily erythema dose for a rotated surface is shown in Fig. 39. The results were almost identical for the south-facing surface. The amplification factor on erythema dose ($\Delta \text{dose} / \Delta O_3$) varies from 1.3 to 1.4 at low latitudes, from 1.6 to 2.0 at middle latitudes, and is approximately 3 at high latitudes. It is a property of atmospheric transmission that a 10% reduction in the ozone column causes the greatest percent change in transmission for the largest optical depth. Because the ozone column and solar zenith angle both increase with latitude, the amplification factor is largest at high latitudes. While

FIG. 39. The percent change in daily erythema dose for a rotated surface averaged over a year due to a 10% reduction in ozone.

the percent increase in daily erythema dose at high latitudes is much greater, the total amount of radiation is very small compared to lower latitudes. Since the majority of the world's population lives south of 55°N , amplification factors in the range 1.3 to 2.0 are most realistic.

Reducing the ozone column increases both the direct and diffuse flux components, but by different factors. Since the relative contribution of the direct and diffuse flux components to erythema dose depends upon α , the amplification factor also depends upon α . This dependence is lessened at high latitudes where the flux is almost entirely diffuse.

As mentioned earlier, the action spectrum for skin cancer is an unknown function. However, van der Leun and Daniels (1975) argue that the peak in the action spectrum should occur near 270 nm. This is shifted considerably in wavelength from the location of the peak in the erythema action spectrum described by Eq. (7), which occurs at 297 nm. In order to test the sensitivity of dose to action spectrum position, the preceding calculations were repeated substituting 270 nm in Eq. (7). Aside from the expected decrease in dose magnitude, very little changed from the results obtained. An important exception concerns the percent change in the annual-average daily erythema dose produced by a 10% reduction in ozone, which is shown in Fig. 40. Dose amplification factors are significantly higher at middle and low latitudes compared to the results in Fig. 39. The amplification factor ranges from 1.8 to 2.0 at low latitudes and from 1.9 to 2.3 at middle latitudes. The reason for the larger amplification factors is related to the ozone absorption cross

FIG. 40. The percent change in daily erythema dose for a rotated surface averaged over a year with the peak in the action spectrum shifted to 270 nm.

section, which in the region near 300 nm is a rapidly decreasing function of wavelength. Shifting the action spectrum to shorter wavelengths, where the uv fluxes are more sensitive to variations in ozone amount, leads to larger amplification factors.

Figure 41 shows the distance moved south, which is equivalent to a 10% reduction in ozone based on the annual average data for a rotated surface shown in Fig. 38. The shaded area indicates the range of values as α is varied from 0 to 90°, the largest values corresponding to $\alpha = 90^\circ$. In middle latitudes the increase in daily average erythema dose due to a 10% ozone reduction is roughly equivalent to moving south a distance of 350 to 450 km with no ozone perturbation. The equivalent distance is much greater at latitudes toward the equator from 30°N. There is no equivalent distance for latitudes less than 15°N, because the erythema dose at these latitudes with a 10% ozone reduction is greater than the unperturbed erythema dose at the equator.

FIG. 41. The distance moved south equivalent to a 10% ozone reduction computed for a rotated surface. The shaded area indicates the range of values as the inclination angle is varied from 0 to 90°.

Summary

According to the simplified model used here, erythema doses have a significant dependence upon receiver orientation. Although it is possible at times for an inclined surface to receive a larger erythema dose than a horizontal surface, in general the highest doses are received by horizontal surfaces. In middle and high latitudes, inclined surfaces (south-facing or rotated) with inclination angles up to 45° receive at least 80% of the daily erythema dose received by a horizontal surface. Much larger reductions in daily erythema dose occur for $\alpha > 45^\circ$, which can result in a significant reduction in the latitudinal gradient of erythema dose. In the case of a south-facing surface, the inclination angle affects the latitude of the peak erythema dose. Varying the inclination angle, however, does not have a significant effect on the doubling distance for average daily erythema dose. Finally, if the skin cancer action spectrum peaks near 270 nm as argued by van der Leun and Daniels (1975), skin cancer rates may be more sensitive than erythema to variations in total ozone.

4. WORK IN PROGRESS

We are developing a new solution technique for the one-dimensional model. The new code is being designed so that certain species or species families can be held constant while other short-lived species are calculated. We may then use the program to study how latitudinal variations in species concentrations and temperature feedback control OH concentrations in the troposphere. We expect to use this program to test the sensitivity of global budget analyses to latitudinal variations.

The new solution method is also being designed to allow either steady-state or time-dependent calculations. It may be possible to extend the method to the two-dimensional model. The basic solution scheme is as follows (this is subject to change, since the method has not been tested):

1. Predict values of individual species concentrations at next time step, $t + \Delta t$.
2. Predict values of species family concentrations (e.g., NO_x , ClO_x , etc.).
3. Use the concentrations from (1) to estimate the time derivative and flux terms of the species conservation equation. Scale each specie's time derivative by the predicted time derivative for its family from (2). This

will damp fluctuations in short-lived species concentrations and allow a full solution of the stiff system of equations we wish to solve. As a fully consistent solution is approached, the scaling factor becomes equal to unity and the true solution will be approached.

4. Solve the system of linear algebraic equations that result from using the fixed terms estimated in (3) and the individual production and loss terms for each species. The result is a new set of species concentrations at time $t + \Delta t$.
5. Check to see if the concentrations from (4) are the same as those from (1). If not, use the new values from (4) and repeat the procedure starting with step (2).

A special code is being written that will enable the model's vertical grid structure to be easily changed. The first utilization of this code will be to develop a more detailed model of atmospheric chemical and dynamical processes in the troposphere. This model will be used to derive a global distribution of OH to be compared with recent measurements by Doug Davis.

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APPENDIX A. CHANGES TO THE ONE-DIMENSIONAL TRANSPORT-KINETICS MODEL DURING THE PAST YEAR

The chemical reactions incorporated in our current model are given in Table A-1 along with the rate expressions. Nearly all of the rate expressions come from Hampson and Garvin (1978). Most of the exceptions reflect recently reported measurements, although a few minor reactions not treated by Hampson and Garvin (1978) come from other compendia.

We have adopted the measurements of Howard *et al.* (1978) for the reactions

and

Table A-1. Chemical reactions and rate coefficients currently used in the one-dimensional transport-kinetics model.

Reaction	Rate coefficient ($k = Ae^{B/T}$)		Ref.
	A	B	
$O + O_2 + M \rightarrow O_3 + M$	1.1×10^{-34}	510	1
$O + O_3 \rightarrow 2O_2$	1.9×10^{-11}	-2300	1
$O_3 + NO \rightarrow NO_2 + O_2$	2.1×10^{-12}	-1450	1
$O + NO_2 \rightarrow NO + O_2$	9.1×10^{-12}	0	1
$N_2O + O(^1D) \rightarrow N_2 + O_2$	5.5×10^{-11}	0	1
$N_2O + O(^1D) \rightarrow 2NO$	5.5×10^{-11}	0	1
$N + O_2 \rightarrow NO + O$	5.5×10^{-12}	-3220	1
$N + NO \rightarrow N_2 + O$	8.2×10^{-11}	-410	1
$O(^1D) + H_2O \rightarrow 2OH$	2.3×10^{-10}	0	1
$O(^1D) + CH_4 \rightarrow OH + 2HO_2 + CO^a$	1.3×10^{-10}	0	1
$O_3 + OH \rightarrow HO_2 + O_2$	1.5×10^{-12}	-1000	1
$O + OH \rightarrow O_2 + H$	4.2×10^{-11}	0	1
$O_3 + HO_2 \rightarrow OH + 2O_2$	1.4×10^{-14}	-590	2
$O + HO_2 \rightarrow OH + O_2$	3.5×10^{-11}	0	1
$H + O_2 + M \rightarrow HO_2 + M$	2.08×10^{-32}	290	1
$O_3 + H \rightarrow OH + O_2$	1.42×10^{-10}	-478	3
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	Note 1		4
$HO_2 + OH \rightarrow H_2O + O_2$	3.0×10^{-11}	0	1
$OH + NO_2 + M \rightarrow HNO_3 + M$	Note 2		1
$OH + HNO_3 \rightarrow H_2O + NO_3$	8.9×10^{-14}	0	5
$H_2O_2 + OH \rightarrow H_2 + HO_2$	1.0×10^{-11}	-750	1
$N_2 + O(^1D) + M \rightarrow N_2O + M$	3.5×10^{-37}	0	1
$N + NO_2 \rightarrow N_2O + O$	2.0×10^{-11}	-800	1
$NO + O + M \rightarrow NO_2 + M$	1.6×10^{-32}	584	1
$NO + HO_2 \rightarrow NO_2 + OH$	3.3×10^{-12}	254	2
$H_2 + O(^1D) \rightarrow OH + H$	9.9×10^{-11}	0	1
$OH + OH \rightarrow H_2O + O$	1.0×10^{-11}	-550	1
$N + O_3 \rightarrow NO + O_2$	2.0×10^{-11}	-1070	1
$NO_2 + O_3 \rightarrow NO_3 + O_2$	1.2×10^{-13}	-2450	1
$OH + CH_4 \rightarrow H_2O + 2HO_2 + CO^a$	2.36×10^{-12}	-1710	1
$OH + OH + M \rightarrow H_2O_2 + M$	1.2×10^{-32}	900	1

Table A-1. (Continued)

Reaction	Rate coefficient ($k = Ae^{B/T}$)		Ref.
	A	B	
$H_2O_2 + O = OH + HO_2$	2.75×10^{-12}	-2125	1
$O + CH_4 = OH + 2HO_2 + CO^a$	3.5×10^{-11}	-4550	1
$CO + OH = H + CO_2$	Note 3		6
$O(^1D) + M = O + M$	2.2×10^{-11}	99	1
$Cl + O_3 = ClO + O_2$	2.7×10^{-11}	-257	1
$Cl + OClO = 2ClO$	5.9×10^{-11}	0	1
$Cl + CH_4 = HCl + 2HO_2 + CO^a$	7.3×10^{-12}	-1260	1
$Cl + NO_2 + M = ClNO_2 + M$	6.9×10^{-34}	2115	7
$Cl + ClNO_2 = 2Cl + NO_2$	3.0×10^{-12}	0	1
$ClO + O = Cl + O_2$	7.7×10^{-11}	-130	1
$NO + ClO = NO_2 + Cl$	1.0×10^{-11}	200	1
$ClO + O_3 = Cl + O_2 + O_2$	1.0×10^{-12}	-4000	1
$ClO + O_3 = OClO + O_2$	1.0×10^{-12}	-4000	1
$ClO + NO_2 + M = ClONO_2 + M$	Note 4		1
$ClO + ClO = Cl + OClO$	2.1×10^{-12}	-2200	1
$ClO + ClO = 2Cl + O_2$	1.5×10^{-12}	-1238	1
$HCl + O(^1D) = Cl + OH$	1.4×10^{-10}	0	1
$OH + HCl = H_2 + Cl$	3.0×10^{-12}	-425	1
$O + HCl = OH + Cl$	1.14×10^{-11}	-3370	1
$O + OClO = ClO + O_2$	2.0×10^{-11}	-1100	1
$NO + OClO = NO_2 + ClO$	3.4×10^{-13}	0	8
$N + OClO = NO + ClO$	6.0×10^{-13}	0	8
$H + OClO = OH + ClO$	5.7×10^{-11}	0	1
$Cl + OH = HCl + O$	1.0×10^{-11}	-2970	1
$Cl + HO_2 = HCl + O_2$	4.1×10^{-11}	0	9
$Cl + HNO_3 = HCl + NO_3$	1.0×10^{-11}	-2170	1
$CFCl_3 + O(^1D) = 2Cl^b$	2.3×10^{-10}	0	1
$CF_2Cl_2 + O(^1D) = 2Cl^b$	2.0×10^{-10}	0	1
$Cl + H_2 = HCl + H$	4.7×10^{-11}	-2340	10
$Cl + H_2O_2 = HCl + HO_2$	1.6×10^{-12}	-384	1
$ClONO_2 + O = ClO + NO_3$	3.0×10^{-12}	-808	1
$CH_3Cl + OH = Cl + H_2O + HO_2^b$	2.2×10^{-12}	-1142	1
$NO + NO_3 = 2NO_2$	8.7×10^{-12}	0	11
$NO_2 + O + M = NO_3 + M$	1.0×10^{-31}	0	1
$NO_2 + NO_3 = NO + O_2 + NO_2$	2.0×10^{-13}	-2000	1
$NO_2 + NO_3 + M = N_2O_5 + M$	Note 5		6
$N_2O_5 + M = NO_2 + NO_3 + M$	Note 6		6
$N_2O_5 + O = 2NO_2 + O_2$	1.0×10^{-14}	0	12
$N_2O_5 + H_2O = 2HNO_3$	1.0×10^{-20}	0	1
$O(^1D) + O_3 = 2O_2$	1.2×10^{-10}	0	1
$HO_2 + HO_2 + H_2O = H_2O_2 + O_2 + H_2O$	Note 7		4

Table A-1. (Continued)

Photolysis reactions

Note 1:
$$\frac{3.25 \times 10^8 + M \times 4 \times 10^{-10}}{(1 + 3.5 \times 10^{-16} \times M \times e^{-2060/T}) (8M + 4 \times 10^{+20})}$$

Note 2: Tsang (1977) as given by Hudson (1977).

Note 3:
$$1.4 \times 10^{-13} + M \times 7.3 \times 10^{-33}$$

Note 4:
$$\frac{3.3 \times 10^{-23} T^{-3.34}}{1. + 8.7 \times 10^{-9} T^{-0.6} \times (M)^{1/2}}$$

Note 5:
$$\frac{2.9 \times 10^{-12}}{7.0 \times 10^{+21} e^{-2670/T} + M}$$

Note 6:
$$\frac{6 \times 10^{-14} e^{-10970/T}}{7.0 \times 10^{+21} e^{-2670/T} + M}$$

Note 7:
$$\frac{1.1 \times 10^{-34} e^{+3730/T}}{1 + M \times 3.5 \times 10^{-16} e^{-2060/T}}$$

^a Methyl radical production is assumed to yield $2HO_2 + CO$.

^b Products such as F, H₂, CO, COF₂, etc. are not followed when produced from halocarbons.

We have adopted the pressure, temperature and water-vapor-dependent expression for

as given by Cox (1978) in his errata. We have adopted values given by Watson (1978) for

and Thrush (1978) for

A privately communicated estimate by Johnston (1977) is used for

Several minor reactions involving OCIO were retained based on expressions cited by Watson (1975). None of these has any effect on model predictions. Simple pressure-dependent rate expressions for

were developed from data cited by Hampson and Garvin (1978).

It should be noted that we do not use a detailed mechanism for the oxidation of methyl radicals. Instead we assume that a methyl radical is oxidized in such a way as to release two HO_2 radicals and CO .

Rate coefficients were changed for several reactions during the past year. These reactions are listed in Table A-2 along with the rate coefficients that were used previously. The most significant changes are the new rate for $\text{HO}_2 + \text{O}_3$, the new temperature dependence for $\text{HO}_2 + \text{NO}$, and a pressure- and water-vapor dependent rate for $\text{HO}_2 + \text{HO}_2$.

Water-vapor concentration is now computed at altitudes greater than 12 km in the model. The water-vapor distribution in the troposphere (0-12 km) is specified based on the global average distribution given by Oort and Rasmusson (1971). The derived ambient water-vapor distribution increases in concentration from 3.5 ppmv at the tropopause to 5.4

Table A-2. Chemical rate coefficients used in the 1977 model chemistry. Only those reactions that were changed during the past year are listed.

Reaction	Rate coefficient ($k = A e^{B/T}$)	
	A	B
$\text{O}_3 + \text{HO}_2 \rightarrow \text{OH} + 2\text{O}_2$	1.0×10^{-13}	-1250
$\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$	3.0×10^{-11}	0
$\text{O}_3 + \text{H} \rightarrow \text{OH} + \text{O}_2$	1.23×10^{-10}	-562
$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	1.7×10^{-11}	-500
$\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	2.0×10^{-11}	0
$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$	4.28×10^{-11}	-500
$\text{N} + \text{O}_3 \rightarrow \text{NO} + \text{O}_2$	4.0×10^{-12}	-650
$\text{CO} + \text{OH} \rightarrow \text{H} + \text{CO}_2$	1.4×10^{-13}	0
$\text{NO} + \text{ClO} \rightarrow \text{NO}_2 + \text{Cl}$	2.2×10^{-11}	0
$\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}$	5.1×10^{-33}	1030
$\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2$	3.0×10^{-11}	0

ppmv in the upper stratosphere. Water vapor is produced in the upper stratosphere by the reactions $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ and $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$.

A new scheme was developed to calculate the multiple scattering factors used in the calculation of photodissociation rates. A computationally fast method for calculating the multiple scattering factor was needed for the diurnal model, and this method is also used in the diurnal-averaged model. Multiple scattering factors are no longer read in but are computed internally for the given solar zenith angle and species distributions. A detailed description of the method will be prepared in the near future.

An effort has been made to program the model to run as efficiently as possible, to use a minimum amount of storage, and to exist in a modular form for ease of future modifications. To minimize the use of storage, the model was divided into sections with the use of overlays so that at runtime all coding used to initialize the problem is released. There is now more space to add future chemistry. A significant reduction in running time was accomplished by using machine language versions of two subroutines. The user now has the option of running either diurnal or diurnal-averaged versions of the model with or without including the effect of temperature feedback.

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*Annual Report of Lawrence Livermore Laboratory to
FAA on the High Altitude Pollution Program—1979*

F. M. Luther et al.

Lawrence Livermore National Laboratory
report UCRL-50042-79, 1979
Livermore, California

PREFACE

Since July 1, 1975, Lawrence Livermore Laboratory (LLL) has been participating in the High Altitude Pollution Program sponsored by the U.S. Department of Transportation's Federal Aviation Administration. This report describes the major accomplishments and significant findings during the fiscal year ending September 30, 1979, for work performed at LLL under Reimbursable Agreement DOT-FA79WAI-034. Two major research areas are covered by this agreement: (1) numerical modeling of the atmospheric response to stratospheric perturbations, and (2) the processing, archiving, and analysis of satellite ozone data. Each of these research areas has been divided into a number of subtasks, and the successful accomplishment of these subtasks has required contributions and cooperation from many participants. The work reported here should be considered the collective effort of all those listed below.

Scientific Administration

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Numerical Modeling

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Annual report of Lawrence Livermore Laboratory to the FAA on the high altitude pollution program—1979

1. INTRODUCTION

This annual report documents the progress made on research in support of the High Altitude Pollution Program (HAPP) during FY-1979. Work performed during previous years at Lawrence Livermore Laboratory (LLL) is described in our earlier annual reports (Luther *et al.*, 1976, 1977, 1978). A review of progress made during previous years of effort on HAPP is also included in this year's report.

During the past decade, a great deal of effort has been devoted to understanding the potential environmental impact of high-altitude aircraft flights. In 1970, the Climatic Impact Assessment Program (CIAP) was created to evaluate the impact of the future operation of supersonic transport aircraft (SST's) in the stratosphere. This research program was sponsored by the U.S. Department of Transportation and was completed in 1975 with the publication of a series of monographs that assessed the potential chemical, climatic, biological, and economic effects of stratospheric aircraft emissions. Additional assessments were prepared by the Climatic Impact Committee of the National Academy of Sciences (National Research Council, 1975), by the British (COMESA, 1976), and by the French (COVOS, 1976).

The High Altitude Pollution Program was initiated in 1975 by the Federal Aviation Administration to extend the investigations carried out during CIAP so as to ensure that stratospheric aircraft emissions would not result in unacceptable environmental effects. The environmental issues that were raised relative to SST's pertain to all types of aircraft operating in the stratosphere. Consequently, the flight regimes of interest to HAPP include subsonic, supersonic, and hypersonic aircraft. The aircraft engine effluents of primary concern in terms of impact on ozone are oxides of nitrogen (NO and NO₂) and water vapor. Perturbations other than aircraft emissions have also been proposed as having a potentially significant impact on ozone (e.g.,

Cl and ClO from chlorofluoromethanes). The HAPP research effort also considers these other perturbations in order to address the overall problem of the combined effects of stratospheric perturbations.

Lawrence Livermore Laboratory has participated in HAPP since July 1975 under interagency agreements DOT-TSC-76-1, DOT-FA76WAI-653, and DOT-FA79WAI-034. Primary research emphasis at LLL is on numerical modeling of the atmospheric response to stratospheric perturbations. The modeling effort at LLL covers four major research areas: photochemical kinetics, coupled kinetics and transport, radiative transfer, and meteorological analysis.

Photochemical kinetics modeling spans gas-phase reaction processes and heterogeneous (i.e., gas-particle) reaction processes, constant and diurnally (and seasonally) varying photochemical reaction rates, a wide range of ambient temperatures and pressures, neutral and ionized species, processes with both accurately and poorly known rates of reaction, and species of both acknowledged and questionable importance in the stratosphere. Considerable attention has been directed toward evaluation of the sensitivity of reaction mechanisms to deficiencies in our knowledge of reaction rates, quantum yields, and reaction mechanisms.

The transport-kinetics models are intended for time-dependent calculations of the response of the atmosphere to stratospheric perturbations. These models incorporate interactive radiative and chemical processes coupled with transport, which must be parameterized in one- and two-dimensional models. These models are designed to facilitate perturbation and sensitivity studies.

Radiative transfer modeling includes: application of highly detailed models to assessment of the effect on the radiation budget of perturbations to the stratospheric composition, and development of

simplified radiative transfer models for inclusion in the transport-kinetics models. Considerable attention has been directed toward including interactive radiative processes in the transport-kinetics models in order to assess possible feedback mechanisms.

Meteorological analysis provides guidance and support for the modeling effort through in-depth studies of atmospheric processes and phenomena. A primary responsibility of this research is to develop test situations to validate various aspects of the numerical models.

In August 1976, LLL's participation in HAPP was extended to include a feasibility study to determine whether good quality total ozone data could be derived from infrared radiance measurements by a multi-channel filter radiometer (MFR) sensor carried aboard a series of satellites operated by the U.S. Air Force. These satellites are a part of the Defense Meteorological Satellite Program Block 5D series. The first four satellites in this series carry MFR sensors from which total ozone data may be derived. The MFR sensor is the first cross-track scanning sensor capable of measuring ozone, and it has a higher spatial resolution and lower noise level than previous instruments. The first satellite began transmitting MFR measurements in March 1977, and MFR data will be received from these satellites into the early 1980's. These MFR data should be useful for determining the temporal and spatial variability of ozone over this period of time.

The feasibility study was completed in May 1978, with the successful processing of 20 days of data taken during 1977. The quality of the derived total ozone data was demonstrated by comparison with corresponding ozone data obtained at selected stations in the world surface network of Dobson spectrophotometer observatories. A description of the methodology used and global maps of the total ozone data for the 20 days are contained in the report by Lovill *et al.* (1978).

Following completion of the feasibility study, LLL's effort has been directed toward archiving and processing the MFR data. Before routine data processing could begin, an automated data-basing system had to be developed. Each MFR sensor is

capable of taking up to 67,500 observations (each observation consisting of 16 radiance measurements) per day, and as many as three satellites were taking data concurrently, so several million pieces of data are included in the data base for each day of coverage. Consequently, the archiving and processing of the data would be difficult without an automated data base. We have also been evaluating various aspects of the ozone retrieval methodology and making refinements. Thus, the methodology used for regular data processing will be improved over that used in the feasibility study.

The satellite data processing task has three major areas of effort: (1) radiative transfer and ozone retrieval methodology, (2) data processing, archiving, and distribution, and (3) data analysis, interpretation, and quality assurance. Work on these tasks is supported in part by the National Aeronautics and Space Administration (NASA).

The first area of effort involves detailed transmittance and simulated radiance calculations, comparisons between models and laboratory measurements, and ozone retrieval model development using regression analysis. Sensitivity studies, error analysis, and special studies with satellite radiances are also included.

The second area of effort involves MFR data calibration, optimization of data processing methodology, design and implementation of an automated data base, data processing, mapping of ozone data, and data distribution. In addition, satellite overflight times are predicted and distributed to over 36 Dobson observatories each month so that special Dobson spectrophotometer measurements can be taken for comparison with the MFR ozone data.

The third area of effort involves development of the Dobson and ozonesonde data bases, development of quality-assurance techniques and statistical analyses, comparison of the MFR ozone data with other data sources, and analyses of the data on various temporal and spatial scales. The data will be analyzed for both anthropogenic and non-anthropogenic effects.

2. ATMOSPHERIC MODELING

A fundamental tool in the LLL effort in atmospheric modeling has been the one-dimensional transport-kinetics model. This model includes as complete a set of the important chemical and photochemical reactions as is feasible and is designed for time-dependent perturbation and sensitivity studies. This model currently includes 39 chemical species and 134 chemical and photochemical reactions. Species concentrations are computed at 44 levels in the atmosphere, extending from the ground to 55 km. Vertical transport is parameterized using a one-dimensional diffusion formulation that describes hemispheric-average net vertical transport. The model can include temperature coupling between changes in composition and reaction rate coefficients and hydrostatic adjustment of pressure and density as user options, but these options are not utilized in our standard model calculations. The one-dimensional transport-kinetics model is described in more detail in Appendix A.

In addition to the one-dimensional transport-kinetics model, we have used radiative transfer codes of varying complexity for several studies. We are also in the process of developing a two-dimensional transport-kinetics model.

Since the beginning of the HAPP program, LLL has completed the following major research studies and activities:

- Sensitivity of NO_x catalytic ozone destruction to uncertainties in rate coefficients.
- Sensitivity of ozone reduction from chlorofluoromethanes to parameter uncertainties.
- Effects of changes in O_3 and NO_2 on atmospheric solar absorption.
- Effect of NO photolysis on NO_y mixing ratios.
- Analysis of chemical rate data.
- Effect of multiple scattering on species concentrations and model sensitivity.
- Effect of changes in stratospheric water vapor on ozone reduction estimates.
- Effect of atmospheric nuclear testing during the 1950's and 1960's on ozone.
- Effect of agriculture on stratospheric ozone.
- Calculation of global tropospheric OH distributions.
- Tropospheric lifetimes and potential effects on ozone of halocarbons.

- Analysis of global budgets of halocarbons.
- Effects of changes in total ozone and receiver orientation on received erythema dose.
- Effect of possible variations in solar ultraviolet flux on stratospheric ozone.
- Effects of a solar eclipse on stratospheric chemistry.
- Potential effects of space shuttle emissions.
- Potential effects of solar power satellite launch vehicles.
- Effects of a massive pulse injection of NO_x into the stratosphere.
- Effects of stratospheric perturbations on the earth's radiation budget and the climatic implications.

In addition to the listed special studies, we have continued to work on model improvements and comparisons between model calculations and observations. These comparisons are important to the verification of various aspects of the model. We have compared computed species profiles with observations for the ambient atmosphere as well as simulations of natural and man-made perturbations. Several basic types of data have proven to be useful: height and latitudinal distributions of individual species and groups of species, partitioning of related species, and local diurnal and seasonal variations of individual species. Interpretation of the results from such comparisons is not always simple because of the significant level of local variability of species concentrations. It is the overall reasonableness of the models and their predictions that provide a high level of confidence in their basic correctness. Of course, this is often a matter of judgment.

The one-dimensional transport-kinetics model has been used to assess the potential chemical effects of several man-made perturbations to the stratosphere. Whenever significant changes occur to the model chemistry or to the treatment of physical processes, the assessment studies are repeated in order to assess the effect of the changes on the model sensitivity.

The research activities that were completed during the past year are described in the following sections. One of the major accomplishments during the past year was the preparation of a detailed assessment report on the potential effects of aircraft emissions (Luther *et al.*, 1979). The reader should

refer to that report for additional material and a more detailed discussion of the topics presented here.

2.1 MODEL SIMULATIONS OF STRATOSPHERIC OBSERVATIONS

Stratospheric Composition

Comparison with observational data on trace species concentrations is an important aspect of validating the performance of numerical models of the stratosphere. Although comparisons with observations are a necessary part of model validation, these comparisons alone are not sufficient to validate the performance of the model because we know from past experience (Duewer *et al.*, 1977) that models with significantly different chemistry and sensitivity can predict very similar ambient species profiles.

Two somewhat different sets of chemical reaction rate coefficients and photolysis cross sections were used in the calculations presented in this report. Most of the calculations were performed prior to the NASA Workshop at Harpers Ferry, West Virginia (June 1979), and utilized chemical rates based primarily on JPL (1979). After the NASA Workshop, we repeated several of the perturbation calculations using chemical rates based on the recommendations of the chemistry panel at the NASA Workshop. These two chemistries are described in Appendix A as 1979a and 1979b chemistries.

In this section, we compare the results of our current one-dimensional model using 1979b chemistry with measured trace species concentrations. Much of the measurement data used in the comparisons was derived from LLL-supplied information communicated at the NASA Harpers Ferry Workshop. As such, some is preliminary in nature. The evaluation of measurements is strongly influenced by that of the NASA panels as reflected at the Workshop. Our discussion in this section closely parallels some of that in the NASA document, reflecting, in part, our participation in writing parts of that document.

O(³P). There is good agreement between model-calculated distributions and the few available measurements. However, the O(³P) concentration is near photoequilibrium with O₃, and the ozone used in the calculations is calculated for

equinox conditions whereas the measurements are winter measurements. Because O₃ was not measured at the same time that O was, there is some danger that the apparent good agreement is fortuitous.

O₃. Ozone profiles vary significantly with latitude and season. Total column ozone ranges from about 200 m · atm · cm in the tropics to about 400 m · atm · cm near the poles. The altitude of the peak concentration is lower near the poles than at the equator. The model-derived O₃ profile resembles observations of O₃ taken at middle latitudes.

OH, HO₂. Within the plausible error in the measurements, there appears to be reasonable agreement between theoretical calculations and the few available measurements of OH and HO₂ in the stratosphere. Data are available only between 28 and 38 km for HO₂. The point-to-point variability of the measurements for both species exceeds measurement precision. This suggests that the different air masses measured may have significantly different histories. It would be desirable if, in the future, concurrent measurements of various species (OH, HO₂, O₃, H₂O, etc.) would be made. If such concurrent measurements become available, it may be possible to explain local variability, as well as to usefully examine ratios (e.g., HO₂/HO) in relation to those expected theoretically. Comparison of the total OH column calculated by current one-dimensional models with the observations of Burnett and Burnett (1979) does not indicate significant differences in average column content.

NO. When measurements taken at middle latitudes and near noon are compared to calculated noon profiles, the calculated profiles are significantly larger than the observations above 30 km. The maximum difference occurs in the upper stratosphere where NO is the dominant NO_x species. One contribution to the difference between models and observations is the overprediction of the total NO_x content by current models. The apparent NO maximum near 40 km lends some credibility to the hypothesis that the treatment of NO photolysis may underestimate the actual upper stratospheric NO sink.

Recent measurements of NO (discussed by H. Schiff and others at the N.A.T.O. Advanced Study Institute on Atmospheric Ozone held in Portugal in October 1979) find higher concentrations in the upper stratosphere than previous measurements. These measurements agree better with model

calculations. However, the reason for disagreement with previous observations (whether it is due to natural variability or measurement errors) must be resolved.

HNO₃. Current models predict more HNO₃ than is observed above about 25 km. In part this may simply reflect the higher-than-observed NO_x concentrations currently calculated. However, this does not appear to be sufficient to explain the entire difference, nor is it likely that model overprediction of OH between 25 and 35 km is responsible for the difference, since model OH and observations are in good agreement between 28–35 km.

Total NO_y. Our theoretical model presently calculates approximately a factor of 2 more NO_y (NO + NO₂ + HNO₃) than has been measured. However, it should be noted that *in situ* measurements of all three species are not available with readily comparable techniques to permit an unambiguous comparison between theory and measurements.

Part of the reason for the difference between model and observation may be that the model predicts too much N₂O in the upper stratosphere, since reaction of N₂O with O(¹D) is the primary source for NO_x in the stratosphere. More measurements of N₂O in the upper stratosphere would be necessary to confirm this hypothesis. The N₂O content in one-dimensional models is sensitive to the choice of vertical transport coefficient used in the calculation.

Other possible factors that might cause the models to overpredict NO_y would include: (1) A lower rate coefficient for O(¹D) + N₂O → 2NO than is currently recommended. The data for this process are not in good agreement. However, if anything, they suggest a faster rate coefficient. (2) O(¹D) may be overestimated. This could happen if the quantum yield for O(¹D) production from O₃ photolysis has a stronger temperature dependence than is used in the models. (3) The rate at which NO photolysis occurs may be underestimated in the models. Frederick and Hudson (1979) estimate their results to be uncertain by a factor of 3. Adoption of their treatment decreased the photolysis rate by a factor of about 3 from the previous value in the model which resulted in an increase of the model-calculated NO_x by about 40%.

HNO₃/NO₂. The ratio of HNO₃/NO₂ currently calculated by models is much higher than is observed by Evans *et al.* (1976) but is within the error bounds of other measurements. In none of

these measurements were both species measured by similar techniques. Concurrent measurements taken at a given point with the same technique are needed to establish whether a discrepancy actually exists. Even then, because of the difference in chemical lifetimes, it would be difficult to determine the time history of both NO₂ and HNO₃ that led to the ratio observed. If a discrepancy does exist, one possible explanation would be that current estimates of OH in the lower stratosphere (below approximately 30 km) are too large. Another possibility would be that the sinks for HNO₃ are underestimated.

N₂O₅. We currently calculate a N₂O₅ concentration of approximately 2.5 ppb near sunrise. This can be compared to the value of 2 ppb deduced for N₂O₅ by Evans *et al.* (1978) based upon measurements of other species a few hours after sunrise. It should be noted that the measurement was not made at the latitude and season the model most nearly approximates. Until further measurements are made, the comparison is inconclusive.

Cl, ClO. The single observed Cl profile (and one additional Cl observation at a single altitude) and calculated Cl profiles agree within the measurement uncertainty of ±35%. However, the measurements suggest a larger vertical gradient in Cl mixing ratio than is predicted. More Cl measurements are needed to determine whether any seasonal or spatial variations exist and, if so, whether these are consistent with model predictions.

For ClO, at the mixing ratio maximum, with the exception of the 14 July 1977 measurement by Anderson *et al.* (1979), the resonance fluorescence measurements are within a factor of about 2 of the predicted ClO abundances. The September through December ClO measurements show a significantly sharper than predicted gradient below the mixing ratio peak. Except for the summer of 1979, summer measurements give more ClO than the September through December measurements. The 14 July 1977 measurement gives six times more ClO than is predicted near the mixing ratio peak, and exceeds by about a factor of 3 the total chlorine mixing ratio believed to be present in the stratosphere. Predicted variations of the Cl and ClO profiles with season are very small compared to the range of observed profiles. A broader data base is needed to explain the difference in these results as well as the large (factor of 10) variation in the ClO profiles observed but not predicted by one-dimensional models.

The differences between theoretical calculations and observations of the ClO gradient below

34 km also require attention. At present, speculations for explaining these differences range from the possibility of a missing chemical reaction or an incorrect rate constant in present theory to the possibility of it being an artifact of the transport parameterization used in current models, or an artifact of the measurement techniques.

Cl/CIO Ratio. The Cl/CIO ratios from the 28 July 1976 resonance fluorescence measurements (Anderson *et al.*, 1979) agree to within measurement uncertainty with most calculations. It is difficult at present to make any conclusions regarding this comparison because of the experimental uncertainties, the limited amount of data, the apparent variability of CIO, and the poor agreement between models and observations for CIO.

HCl. Although there may be significant disagreement (as large as 30–40% when compared with the IR spectra data, much larger if compared to the filter or radiometer data) above 30 km, the uncertainty in the observational data in this altitude range is such as to probably encompass the model predictions.

CIONO₂. The only observational data for CIONO₂ are from one flight by Murcray (1979). There is excellent agreement if the fast production rate for CIONO₂ is used in the calculations, whereas there is a factor of 3 difference if the slower production rate is used (see Section 2.4 discussion regarding the rate of production of CIONO₂).

Until further data are available, it is difficult to make any conclusive statements regarding this species. However, the limited amount of data available does not indicate any gross discrepancies between theory and observations.

Total ClX. There now exist a limited number of measurements for Cl, CIO, HCl, and CIONO₂ in the stratosphere. Except for three measurements of CIO taken in summer (Anderson, 1979; Menzies, 1979), there does not appear to be any large discrepancy between the total amount of ClX predicted and that observed. However, the summer measurements of CIO are so large as to require much more total ClX than known sources are capable of producing. This implies the possibility of an unknown source for ClX in the atmosphere, an error in the observation, or some unusual episodic event.

Model Simulations of Past Perturbations

Possible Long-Term Solar Variations and Effects on Temperature and Ozone. In the study of

potential anthropogenic influences on the stratospheric ozone budget it is necessary to first understand the natural variations of ozone. In order to achieve early detection of anthropogenic trends and to establish the magnitude of such effects, we must differentiate the natural stratospheric ozone variations from the man-made effects that are of comparable time scales. The suggested correlation between ozone and sunspot number is of primary interest. If this relation is real, then for the next few years the theoretically predicted effect of CFM's on ozone may not be directly detectable unless the effect of this ozone-solar cycle relation can be quantified and removed from the ozone data. At this time, the most plausible mechanism coupling the sunspot cycle and atmospheric ozone is the change in solar flux between 180 and 340 nm from solar maximum to solar minimum (Heath and Thekaekara, 1977; Callis and Nealy, 1978; Penner and Chang, 1978). Theoretically, a variation in solar flux between 180 and 340 nm of approximately 30% (maximum to minimum) can lead to local ozone changes as large as 10% near 35 km, and total ozone column changes of approximately 5% (Penner and Chang, 1978). This is comparable to the predicted CFM effect of ozone decreases of up to 5% around the year 1990. Consequently, the possible influence of periodic or aperiodic changes in solar UV flux intensities tends to obscure changes due to the present levels of CFM's, and this may continue for the next decade. The same is also true for the local ozone concentrations in the upper stratosphere.

The data that support a variation in solar UV fluxes during a solar cycle are limited (Heath and Thekaekara, 1977) and need to be confirmed with other independent measurements. Simon (1978) has pointed out the difficulty in the absolute calibration of the measuring instruments, especially those aboard a satellite.

Since the direct monitoring of solar UV fluxes and ozone are both of limited use in establishing the ozone-solar cycle relation, we are left with the monitoring of trace species other than ozone as a possible independent method for validating the effects of solar UV flux variations. We examined the possible variations of 31 trace species that result from hypothetical solar UV variations with the LLL time-dependent model of stratospheric chemistry, including self-consistently calculated stratospheric temperature and atmospheric adjustment to hydrostatic equilibrium (Penner and Chang, 1979).

From this study we identified N_2O as a most likely candidate for monitoring to study coupling between variations in solar UV and atmospheric composition. Furthermore, there remains the question of the effect of transport-related variability that can only be resolved with a set of upper stratospheric data.

The Atmospheric Nuclear Tests of the 1950's and 1960's. Past atmospheric tests of nuclear devices larger than about one megaton (TNT) yield provide a potentially significant source of NO_x to the stratosphere. During the late 1950's and early 1960's, large numbers of such tests were carried out, and the NO_x released to the stratosphere in 1961 and 1962 should have been comparable to the amount that would be released by about 2.7 years operation of a large SST fleet (i.e., one emitting ap-

proximately 10^8 molecules $cm^{-2}s^{-1}$). The paper by Chang, Duewer and Wuebbles (1979) gives an account of the predicted effects through early 1978. Figure 1 gives the computed ozone column change as a function of time. For computations made with 1979b chemistry (see Appendix A), the two curves give the ozone depletion calculated for injection altitudes based on a parameterization by Foley and Ruderman (1972) or on the lower altitude observations of Seitz *et al.* (1968). The two treatments are thought to bound the plausible range of injection altitudes.

Both treatments predict maximum ozone depletions of less than 2% for the largest annual-average change. The largest change is only about 1.25% if a 1-2-1 smoothing function is applied to annual perturbations. The computed changes are

FIG. 1. Computed change in total ozone resulting from atmospheric nuclear testing during 1950's and 1960's.

clearly within the observed variability in the ozone record as analyzed by Angell and Korshover (1978).

Figure 2 gives the computed changes at selected altitudes. The ozone concentration decreases at all altitudes above 25 km. However, at lower altitudes the concentration of ozone was computed to increase significantly, which accounts for the net increase in total ozone prior to 1962 shown in Fig. 1. Some of these computed changes are much larger than the change in the ozone column. However, the predicted ozone variations at specific altitudes are still only about the same magnitude as the variations in ozone concentrations determined by the Umkehr technique.

Thus, the model-predicted response to the atmospheric nuclear tests does not lead to conflict with the ozone record, but it also does not seem to explain much of the observed ozone variation. The predicted effect on ozone of the nuclear tests should be considered in any attempt to model ozone variations during the 1960's since the predicted changes in ozone at specific altitudes are comparable to both the observed variations and to the variations calculated for such phenomena as the hypothesized variation of ultraviolet light tied to the solar cycle, or the predicted change in ozone from CFM production through 1978.

Polar Cap Absorption Events. Crutzen *et al.* (1975) noted that large polar cap absorption (PCA) events should produce significant quantities of NO_x in the middle and upper stratosphere, especially at high latitudes. Indeed the PCA events of August 1972 were estimated to have produced several times as much NO_x as the ambient content of the atmosphere in the region above 40 km. In a comparison with Nimbus 4 ozone data, Heath *et al.* (1977) found that the agreement between predicted ozone change and observation was quite good north of 75° latitude and above 4 mb (the model underpredicted the perturbation by roughly 30%). Since those calculations were made, several important changes in model chemistry have occurred. However, these changes have had only a modest effect on the sensitivity of the model to large injections of NO_x at high altitude and high latitude. There are two recent recalculations of the effect of the August 1972 PCA event in the literature. Fabian *et al.* (1979) found that their computed ozone change was in excellent agreement with observation if more recent estimates of the NO production per

ion-pair are used. However, the agreement between observation and computation at lower latitudes was less satisfactory, although still qualitatively encouraging. Borucki *et al.* (1978) report similar findings, and also find that their model substantially underpredicts the ozone perturbations at altitudes near 30 km.

The August 1972 PCA events seem to provide a useful test of the short-term (several days) response of stratospheric ozone to NO_x increases above about 40 km. Unfortunately, the test is not directly applicable to lower altitude, midlatitude NO_x perturbations occurring over long (several-year) time periods. The nature of the NO_x injection and of the O_3 data do not permit resolution of questions about the adequacy of model simulations of transport phenomena or of the chemistry of the lower stratosphere. Thus, PCA events provide the only phenomenon for which models forecast an observable and observed stratospheric ozone perturbation in response to an NO_x change, but the nature of the perturbation and the response differ from the problems associated with SST operations to an extent that precludes its direct use as a calibration point for SST predictions of column ozone changes. Nonetheless, the good agreement above 40 km is encouraging since it suggests at least that models are adequately representing the short-term response of ozone to NO_x injections at higher altitudes.

The Solar Eclipse on February 26, 1979. In addition to ozone observations, measurements of other minor constituents during a solar eclipse could provide validation of the short time constant chemistry in atmospheric models. Consequently, experiments for upcoming solar eclipses, when properly supported by theoretical analysis, could contribute significantly to our understanding of atmospheric chemistry. In fact, given the proper data on trace species concentrations during an eclipse, such measurements could provide a direct demonstration that the currently proposed major reactions of NO_x , HO_x , and Cl_x species are indeed concurrently functioning in the stratosphere in the manner suggested by laboratory chemistry. However, the measurements yield little information about slower processes that can have large effects on model sensitivity to perturbations.

We have examined theoretically (Wuebbles and Chang, 1979) the expected effect of a solar eclipse on stratospheric minor constituents. Primary emphasis was given to the total eclipse that occurred

FIG. 2. Computed change in local ozone concentration at various altitudes resulting from atmospheric nuclear testing during 1950's and 1960's.

over North America on February 26, 1979. Variations similar to those computed for this particular case should be expected for other total eclipses. Totality was the longest (approximately 3 minutes) at 50°N latitude for the February 1979 eclipse.

While ozone, tropospheric water vapor, and temperature were held fixed in the model for most of our eclipse calculations, the model was also run with calculated ozone to examine the expected response of ozone to an eclipse. Our analysis has shown that fixing the ozone distribution does not significantly affect the temporal variations calculated for other species during the eclipse. Solar flux variations during the eclipse were based on Hunt (1965).

Those species having chemical lifetimes less than a few hours are expected to vary significantly from normal diurnal behavior during a solar eclipse. Local concentrations of the species could be quite variable, and therefore we should focus on relative changes rather than absolute magnitudes.

The model-calculated response of ozone during an eclipse essentially agreed with Hunt (1965). A significant increase in O_3 is to be expected in the upper stratosphere and in the mesosphere as a result of the conversion of $O(^3P)$ to ozone through the reaction $O(^3P) + O_2 + M \rightarrow O_3 + M$ accompanied by decreased photolysis of O_2 and O_3 . The maximum increase in O_3 , found at the end of totality, was computed to be 15% and 45% at 50 and 55 km, respectively. Larger fractional changes are expected in the mesosphere. Since most of the atmospheric ozone is at lower altitudes in the stratosphere, an insignificant change in the total ozone column is expected. Significant changes were also predicted to occur in NO , NO_2 , Cl , ClO , OH , and HO_2 concentrations.

The results of this study suggest that significant and detectable variations are expected for some of the important stratospheric minor constituents during a solar eclipse. Such observations, particularly simultaneous observations of trace species, would demonstrate clearly the simultaneous functioning of the various important photochemical catalytic cycles in the stratosphere.

The model calculations were completed prior to the eclipse. Measurements during the solar eclipse of February 26, 1979, were made with NASA's aircraft. This plane carried instruments to measure NO , O_3 , and temperature at 20 km (instrument of Starr, Craig, and others of NASA-Ames) and to measure the NO and NO_2 columns above

20 km (by David Murcay of University of Denver). Preliminary results by Starr and Craig show no change in O_3 at 20 km during the eclipse (as was predicted), and they show excellent agreement with the theoretically expected change in NO . A detailed comparison between this measurement and model calculations is being made. In any case, the results demonstrate that the reactions $NO + O_3$ and $NO_2 + h\nu$ occur in the stratosphere at rates similar to those computed theoretically.

2.2 POTENTIAL CHANGES IN OZONE CAUSED BY AIRCRAFT EMISSIONS

Emission Indexes and Fleet Projections

We consider the potential effects on atmospheric ozone of several different aircraft emissions scenarios. These emission scenarios were developed for three basically different applications: (1) the projected 1990 fleet, (2) a commercially viable fleet of supersonic transports, and (3) a commercially viable fleet of hypersonic transports. In all of the perturbation calculations discussed, the "ambient" or "unperturbed" atmospheric conditions refer to the model-calculated initial state rather than to atmospheric measurements.

1990 Fleets. We developed emission profiles for both high and low projected 1990 aircraft fleet sizes. In the case of the projected 1990 high fleet, we adopted the emissions factors and fleet projections used by Oliver *et al.* (1977) in their Table 2.33. The projection used by Oliver *et al.* (1977) was based on A. D. Little, Inc. (1976) with corrections to the mean flight altitude of the projected SST fleet of 142 Concorde and TU 144's and an emissions factor four times larger than used by A. D. Little, Inc. (1976) for CF6 engines (which Oliver *et al.*, 1977, treated as having the same emissions indexes as JT9D engines). The NO_x emission index for SST's was assumed to be 20 g NO_2 /kg fuel.

In converting the projected emissions in Table 2.33 of Oliver *et al.* (1977) to a format compatible with the one-dimensional model, we treated the model as a Northern Hemisphere model, summed emissions over all latitudes between zero and 90°N at a given altitude, and converted kg/year at each altitude to molecules $cm^{-3} s^{-1}$ over a 1-km-thick layer centered at even-kilometer altitudes. Table 1 gives the emission rates used in our calculation.

TABLE 1. Projected 1990 aircraft emissions of NO_x (Oliver *et al.* (1977) high estimate); low estimate of emission rates equals 0.633 times high estimate.

Injection altitude (km)	NO_x injection rate total fleet (molecules $\text{cm}^{-3} \text{s}^{-1}$)	NO_x injection rate subsonic only (molecules $\text{cm}^{-3} \text{s}^{-1}$)
6	90	90
7	179	179
8	265	265
9	665	665
10	1167	1167
11	1161	1161
12	520	520
13	75	75
14	18 ^a	12
15	18	—
16	33	—
17	43	—
18	29	—
19	8	—

^aEmissions from the SST fleet are included at 14 km and above.

We also examined the effects of the projected subsonic fleet without the SST contribution using the emissions given in Table 1 for the subsonic fleet only. We generated a 1990 low estimate by multiplying the 1990 high estimate emissions by 0.633, the ratio of the 1990 low estimate fuel usage to the 1990 high estimate fuel usage given in Table 2.25 of Oliver *et al.* (1977).

SST Fleets of Commercially Viable Size. In treating hypothetical SST fleets of commercially viable magnitude, we have considered a fleet emitting 1000 molecules of NO_x $\text{cm}^{-3} \text{s}^{-1}$ and 1.77×10^5 molecules of H_2O $\text{cm}^{-3} \text{s}^{-1}$ over a 1-km-thick layer in the Northern Hemisphere, which is equivalent to 6.2×10^8 kg of NO_x (as NO_2) and 4.3×10^{10} kg of H_2O per year. These emission rates correspond to a fuel usage of 3.5×10^{10} kg yr^{-1} by SST's, assuming the emission indexes are 18 g NO_2/kg fuel and 1.25 kg $\text{H}_2\text{O}/\text{kg}$ fuel. The NO_x emissions index for currently realizable SST engines has been estimated to be as high as 22 g NO_2/kg fuel or as low as 15.6 g NO_2/kg fuel. A still unresolved discrepancy exists between spectroscopic and probe sampling methods of determining NO_x in aircraft exhaust (Oliver *et al.*, 1977). If the spectroscopic analyses are correct, the above-cited emission index should be increased by a factor of 2 to 3 for SST operations.

Future technologies may be capable of reducing the NO_x emission index by several fold. A three-fold reduction in the NO_x emission index is projected for some existing design concepts (Popoff *et al.*, 1978). We consider NO_x emission indexes of 18 g NO_2/kg fuel for current technology and 6 g NO_2/kg fuel for future technology.

The number of SST's corresponding to a fuel usage of 3.5×10^{10} kg yr^{-1} is difficult to determine on an absolute scale. The number of SST's corresponding to a given fuel usage is inversely proportional to the expected hours/day of flight and the fuel usage per hour. Estimates of the hours per day of flight at cruise altitude have varied from 4.4 to 7.5 hr. Estimates of fuel usage have ranged from 16,800 to 19,100 kg/hr for the Concorde; from 52,000 to 60,000 kg/hr for the B2707; and as low as 44,000 kg/hr for a hypothetical advanced design similar to the B2707 (Popoff *et al.*, 1978). Thus, more than a two-fold variation in engine emissions from a projected SST fleet is possible based on different estimates of aircraft operation and fuel consumption rate. A fuel usage of 3.5×10^{10} kg yr^{-1} , therefore, corresponds to about 750–1000 Concorde, or 180–660 advanced SST's. Thus, our standard emissions rates are compatible with a large fleet of SST's.

Hypersonic Transport Emissions. In addition to the effects of subsonic and supersonic fleets, we projected a range of emissions and environmental impacts of a possible hypersonic transport (HST) fleet. For this purpose, we adopted the emissions indexes given in CIAP Monograph 2 (1975), Chapter 6 for a fleet of research HST's of gross takeoff weight 2.27×10^5 kg operating at Mach 8 and cruise altitude of "36.68" km. According to data in CIAP Monograph 2, the hypothesized HST operations would consist of an initial acceleration to hypersonic speeds (and cruise altitude) using rocket engines, followed by about five minutes of SCRAMjet operation, followed by a cruise-mode during which most emissions would consist of liquid hydrogen boil-off for cooling. The SCRAMjet would use 670 kg/flight of liquid H_2 ; the rocket engines would use 2450 kg/flight of liquid H_2 , and 14,650 kg/flight of liquid oxygen (CIAP Monograph 2, p. 6–7); but it would only release a total of 1650 kg/flight of water vapor and 615 kg/flight of H_2 (CIAP Monograph 2, p. 6–8). Thus, the fuel use and emissions estimates given in CIAP

Monograph 2 for rocket operations are incompatible, with not enough mass being emitted. This difficulty would be resolved by increasing the water-vapor emissions by a factor of 10. Cooling at cruise altitude would consume an additional 309 kg of liquid hydrogen per flight.

The emissions consist of H_2O , H_2 , H , OH , NO , and O as given in Table 2. In analyzing the effects of HST emissions, only cooling and SCRAMjet emissions were treated, and these were based on the data presented in Table 6-9 of CIAP Monograph 2. Rocket emissions were neglected since much of the rocket emissions would occur in the troposphere. In order to approximate a commercially viable fleet, we increased the emissions to correspond to an HST fleet with 1000 flights/day. Because even these emissions are relatively small, and the CIAP-Monograph-2-based emissions estimates may not apply to commercial-scale fleet operations (they are based on research flights), we also examined the effects of a 10-fold larger emission, perhaps interpretable as longer flights or flights of heavier aircraft. The emissions of H_2O , H_2 , NO , and OH were treated simply as a source of the molecules in question. Emissions of H -atoms (the code calculates H -atoms as an equilibrium species) were treated as emissions of an equivalent number of HO_2

molecules, while the small emissions of O atoms were ignored.

Because NO_x emissions are responsible for the major portion of the predicted change in total ozone, it might be attractive to use more than the stoichiometric amount of OH in the SCRAMjets in order to reduce NO_x emissions. According to CIAP Monograph 2, operating at a stoichiometric ratio of 1.5 instead of 1 would reduce NO_x emissions by more than a factor of 3 while increasing H_2O and H_2 emissions by factors of about 1.1 and 3, respectively. The net effect of these changes in emissions should be a smaller ozone perturbation.

We wish to emphasize that we performed no independent calculations of HST emissions indexes, and that the fleet projections are no more than crude parametric estimates of the approximate level of activity that might be associated with a mature, commercially successful fleet of HST's. If specific aircraft designs were to be proposed, the emissions should be independently projected.

Aircraft Assessment Results

The LLL one-dimensional transport-kinetics model has been used to assess the potential chemical effects of aircraft engine emissions in the troposphere and the stratosphere. Calculations were

TABLE 2. HST emissions on a per-flight basis. Data from CIAP Monograph 2, Ch. 6, assuming cruising speed of MACH 8, cruise altitude of 36.68 km, and $H_2:O_2$ ratio of 1.

	Emissions per flight		Altitude (km)	Emission rate for 1000 flights/day (molecules cm ⁻³ s ⁻¹) ^a
	(kg)	(moles)		
SCRA:				
H ₂ O	5705.0	317,000	36.68	8504
H ₂	136.7	68,350	36.68	1820
H	13.1	13,100	36.68	350
OH	132.3	7,800	36.68	210
NO	137.4	4,500	36.68	123
O	34.4	2,150	36.68	58
Rocket (not included in calculation)				
H ₂ O ^b	16,500	917,000	0-36 mostly tropospheric	—
H ₂	615	307,500	0-36	—
Cooling in flight				
H ₂	308.5	154,200	36	4130

^aEmissions in a 1-km-thick layer.

^b H_2O emissions from rockets have been increased by a factor of 10 to permit mass balance.

made using projected fleet sizes for subsonic and supersonic aircraft as well as for a range of emission rates at particular injection altitudes. In order to determine the effect of uncertainties in various input parameters on the assessment calculations, several sensitivity studies were also performed and are reported in the following section.

Subsonic and Supersonic Aircraft Fleets. The altitude of injection has a significant effect on the computed change in ozone because of the increase in residence time with altitude and because of the variation with altitude of the dominant chemical reactions and cycles. Table 3 shows the effect on total ozone at steady state of the same NO_x injection rate at different injection altitudes. An injection rate of 1000 molecules $\text{cm}^{-3}\text{s}^{-1}$ over a 1-km-thick layer was used for NO_x , and there was no injection of H_2O .

Injections of NO_x over the altitude range of 7 to 20 km resulted in a net increase in total ozone in each case. The change in total ozone increased with increasing injection altitude for the troposphere and lower stratosphere. Throughout this region HO_x chemistry is the dominant chemical destruction process for ozone. When HO_x chemistry is more efficient than NO_x catalytic destruction of ozone, injections of NO_x lead to a net increase in odd oxygen production through the reaction sequences:

TABLE 3. Change in total ozone resulting from NO_x injection of 1000 molecules $\text{cm}^{-3}\text{s}^{-1}$ distributed over a 1-km-thick layer centered at injection altitude. Calculations were made using 1979a chemistry (Appendix A).

Injection altitude (km)	Change in total ozone (%)
7	0.25
9	0.40
11	0.64
13	0.84
17	1.34
20	1.31

and

The reaction sequence in Eq. (1) acts to shift HO_x more toward OH, thereby increasing the conversion of OH and HO_2 to H_2O by the reaction $\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$. Reaction sequence in Eq. (2) acts to reduce HO_x as OH and HO_2 are converted to H_2O and HNO_3 . Conversion to H_2O , and to a lesser extent HNO_3 , acts as a sink for HO_x , since the chemical lifetimes of these reservoir species can be long compared to the time for transport into the troposphere. Injections of NO_x act to increase the rates of the above reactions. The net effect of reaction sequences (1) and (2) is a reduction of HO_x and an increase in odd oxygen production, both of which contribute to an increase in ozone. Of course, the odd-hydrogen species may have been generated through reaction of $\text{O}(^1\text{D})$ with H_2O . If this is the case, the odd oxygen produced via (1) or (2) only regenerates that used in the initiation of a catalytic cycle. It is important, nonetheless, because these sequences compete for HO_x with odd-oxygen destroying sequences.

Increases in NO_x concentration in the upper stratosphere lead to a reduction in ozone concentration in this region due to the greater importance of the NO_x catalyzed ozone destruction at these altitudes. The 20-km injection of NO_x resulted in a smaller net increase in total ozone than did the 17-km injection case, since more NO_x reached the upper stratosphere causing a greater reduction in ozone concentration at high altitudes relative to the increase at lower altitudes. This effect was found to be sensitive to the shape of the K_z profile used, however.

The standard model uses fixed-value boundary conditions for all species (except CCl_4) at the ground. Using flux boundary conditions for the species N_2O , CH_4 , CH_3Cl , and HCl , resulted in slightly larger increases in total ozone (approximately 0.1% in absolute change) when compared to the fixed boundary condition case. Consequently, the choice of boundary condition has only a very small effect on the assessment results. Fixed-value

boundary conditions are used in the model calculations unless otherwise noted.

The model was tested for interference effects by comparing the effect of simultaneous injections at the various injection altitudes given in Table 3 with the sum of the changes in ozone for individual injection altitudes. Table 4 shows that there is a destructive interference. That is, the simultaneous injections resulted in less change in total ozone than the sum of the changes caused by individual injections. This implies that summing the results of separate calculations for subsonic and supersonic fleets will not give the same answer as considering the effect of the two fleets simultaneously.

The effect of NO_x emissions by subsonic and supersonic fleets projected for 1990 are given in Table 5. Using the high estimate of the fleet sizes, the effect of subsonic and supersonic aircraft combined is estimated to be an increase in total ozone of 2.01%. This number represents the steady state change in ozone due to constant NO_x emission rates at the rates estimated for 1990. The subsonic fleet alone (injection altitudes up to 14 km) is estimated to cause an increase in total ozone of 1.86%. The small effect of the supersonic fleet is due primarily to the small fleet size projected for 1990. Using the lower estimate for fleet emissions, the corresponding numbers for ΔO_3 are 1.39% for the combined fleets and 1.29% for the subsonic fleet alone.

It should be noted that the effects of the existing 1979 subsonic fleet are of the order of a 0.5% increase in total ozone. This effect is not negligible when compared to the estimated present-day effects of CFM's. Thus, an accurate assessment of the effects of subsonic aircraft will be important in interpreting ozone data for trends due to other anthropogenic influences.

The changes in ozone concentration for the high and low estimates of subsonic and supersonic fleet emissions are shown in absolute concentration in Fig. 3. The largest absolute increase in ozone concentration occurs near 12 km, and the region of increasing ozone extends up to about 26 km. Be-

TABLE 5. Computed change in total ozone at steady state using NO_x emission estimates for 1990 subsonic and supersonic fleets (1979b chemistry).

Case	Change in total ozone (%)	
	Subsonic and supersonic	Subsonic only
Oliver <i>et al.</i> (1977) high 1990 fleet estimate	2.01	1.86
Low 1990 fleet estimate	1.39	1.29

tween 26 and 39 km there is a small decrease in ozone concentration.

It should be recognized that the bulk of the ozone change calculated for the subsonic fleet occurs in the upper troposphere. As a result, it is sensitive to the treatment of such poorly understood phenomena as wet and dry removal processes and surface boundary conditions for rarely measured species. The tropospheric pressures differ from the pressure conditions used in most direct measurements of chemical rate coefficients (to a greater degree than stratosphere pressures). Heterogeneous reactions, which might have a significant effect on the calculations, are not included, and the one-dimensional treatment is not as good an approximation for the troposphere as it is for the stratosphere because of the strong latitudinal and longitudinal gradients in many trace species. Thus, the results for the 1990 fleet estimates are suggestive but are not definitive.

Assessments of potential changes in ozone due to future large fleets of supersonic transports have focused on injection altitudes of 17 and 20 km. In updating these assessments, we have assumed an emission index of 18 g/kg fuel for NO_x and 1250 g/kg fuel for H_2O . These emission indexes are based on current engine technology. It may be possible through future advances in technology that the NO_x emission index could be reduced to 6 kg (one-third of present value). Calculations of ΔO_3 given a constant fuel consumption rate at cruise altitude (3.5×10^{10} kg/yr in a hemispheric shell) are shown in Table 6 for different emission indexes. The NO_x emission rate of 1000 molecules $\text{cm}^{-3}\text{s}^{-1}$, which roughly estimates the emissions from a commercially viable fleet, was chosen as a reference case. The equivalent annual hemispheric injection rates of NO_x and H_2O are given in Table 7.

TABLE 4. Synergism test using fixed boundary conditions and 1979a chemistry.

Case	ΔO_3 (%)
Simultaneous injections	3.68
Sum of individual injections	4.78

FIG. 3. Change in ozone concentration expressed as molecules cm^{-3} (1979b chemistry) computed for 1990 high and low fleet estimates.

TABLE 6. Change in total ozone due to NO_x and H_2O emissions distributed over a 1-km-thick layer centered at injection altitude.

Injection altitude (km)	Injection rate (molecules $\text{cm}^{-3} \text{s}^{-1}$)		Change in total ozone (%)	
	NO_x	H_2O	1979a Chemistry	1979b Chemistry
17	1000	0	1.34	1.25
17	1000	177,000	1.18	—
17	333	177,000	0.32	—
20	1000	0	1.31	1.14
20	1000	177,000	0.91	—
20	333	177,000	0.07	—

For each of the perturbations considered, there was an increase in total ozone. When the water vapor injection is included with the NO_x injection, there is less of an increase in total ozone because of the additional ozone destruction caused by HO_x which is produced from dissociation of H_2O . Even for the advanced technology case (reduced NO_x emission), the increase in total ozone due to the NO_x injection is greater than the reduction due to the H_2O injection, the net effect being a very small increase in total ozone.

TABLE 7. Equivalent annual hemispheric injection rates for various NO_x and H_2O emissions.

Species	Injection rate	
	(molecules $\text{cm}^{-3} \text{s}^{-1}$)	(kg/yr) ^a
NO_x	333	2.1×10^8
NO_x	1,000	6.2×10^8
H_2O	177,000	4.3×10^{10}

^aHemispheric injection assuming uniform injection over a 1-km-thick layer.

Hypersonic Transport Fleet. The hypothesized hypersonic transport fleet making 1000 flights per day was calculated to cause a -0.218% change in the ozone column. Emissions from a fleet ten times larger were calculated to cause a -2.06% change in the ozone column. The NO_x emissions from the latter fleet by themselves caused an ozone change of -2.13% .

Figure 4 shows the local percentage changes in ozone vs altitude for the 10,000 flight per day HST emissions and the NO_x emissions alone from 10,000 flights per day of HST's. (Because ΔO_3 is roughly

linear in emissions rate over the range considered, large fleets were chosen to avoid comparing very small local changes that might contain significant numerical noise.) As is evident, the NO_x emissions dominate the ozone changes below approximately 40 km, while H_2O and H_2 emissions are responsible for most of the ozone change at higher altitudes. Because most of the ozone column is below 40 km, the integral column change is largely a result of the NO_x emissions.

Effect of Variations in Background Cl_x . The effect of aircraft engine emissions on stratospheric

FIG. 4. Change in ozone concentration caused by HST emissions for a fleet with 10,000 flights per day (1979 chemistry).

composition is coupled with other stratospheric perturbations. As chlorofluoromethanes (CFM's) continue to be released to the atmosphere, there will be a gradual increase in the background concentration of ClX (Cl + ClO + HCl). Model calculations indicate a present day stratospheric ClX concentration of more than 1 ppbv. Assuming CFM releases at the 1976 release rate indefinitely into the future, the background ClX concentration is projected to increase to 2 ppbv around 1990 and to 4 ppbv around 2020. To assess the effect of changes in background ClX concentration on the model sensitivity, several NO_x perturbation calculations were repeated using a range of ClX concentrations. The results are shown in Table 8. In each case the ClX concentration was held constant. So the change in total ozone is the steady state value for a constant injection rate (i.e., the ΔO_3 value does not pertain to any particular year) relative to a natural atmosphere with the same ClX concentration.

Table 8 shows that the change (increase) in total ozone resulting from an NO_x injection increases as the ClX concentration increases. The reason for the increase in ΔO_3 is related to the mechanism by which an NO_x injection leads to an increase in total ozone. The increase in total ozone comes about because for these magnitudes of NO_x injections, NO_x interferes with the more efficient ozone destruction by HO_x and ClX. Increasing the background ClX concentration means that there is more ozone destruction by ClX in the ambient case, so there is more that can be interfered with by the injected NO_x.

Effects of Uncertainties in Chemical Rate Coefficients. Probably the best method for assessing the sensitivity of model predictions to errors in the inputs that describe fairly well understood quantities (e.g., rate constants for which experimental precision is the dominant source of error) is a Monte

Carlo calculation (e.g., Stolarski *et al.*, 1978). As yet, no such calculation has been carried out for a perturbation resulting from aircraft operations. In part this reflects the hypothesis that prediction error is dominated by systematic error in poorly understood reactions.

Even a full sensitivity analysis (like that of Butler, 1979) has not yet been performed. The most recent sensitivity study on the NO_x system was a partial sensitivity analysis carried out in 1975 by Duewer *et al.* (1976, 1977). The major conclusions of that study were that large prediction errors were possible, and that a few reactions dominated the error. Subsequent events have shown these conclusions to be valid. The large changes in model sensitivity to NO_x injection that have occurred have been dominated by changes in the rate coefficients for the five reactions that were identified as plausible sources of error in the 1975 and 1977 reports. In the intervening years, many rate coefficients have been determined or redetermined with substantially improved accuracy. For the majority of the reactions in the model, experimental precision is probably a reasonably good estimate (as well as a lower bound) to the actual error in the measured rate, and model predictions are only weakly sensitive to modest errors in most rate coefficients. Nonetheless, the composite error in prediction caused by such errors could be significant, although, since it is unlikely that random errors will reinforce each other, this is not too likely to be realized.

Table 9 gives the change in O₃ calculated for several perturbations using the structure of our current model but using the rate coefficients recommended in NBS 866 (1975) and NBS 513 (1978) as well as the current results. In calculating the response for 1975 and 1977 chemistries, we excluded species (such as HOCl or HNO₄) that the LLL

TABLE 8. Effect of variations in background ClX on computed change in total ozone (1979a chemistry).

Injection altitude (km)	NO _x injection rate (molecules cm ⁻³ s ⁻¹)	Change in total ozone (%)		
		1.14 ppb ClX	1.83 ppb ClX	3.76 ppb ClX
17	500	0.65	0.72	0.89
17	1000	1.22	1.34	1.69
17	2000	2.14	2.37	3.03
20	500	0.61	0.75	1.12
20	1000	1.04	1.31	2.03
20	2000	1.42	1.91	3.28

TABLE 9. Effect of choice of rate coefficients on model sensitivity using structure of current LLL model.

Chemistry	1950 ambient O ₃ (DU)	Change in total ozone (%)				
		1990 high subsonic	17-km SST ^a	20-km SST ^a	CFM 1978	CFM steady-state ^b
1975 (NBS 866)	288	-0.31	-3.94	-9.12	-0.76	-7.5
1977 (NBS 513)	366	1.43	1.20	-0.52	-0.98	-12.7
1979a (JPL, 1979 ^c)	324	2.01	2.57	2.18	-1.92	-19.4
1979b (NASA, 1979)	327	1.86	2.00	1.06	-1.30	-14.2

^aNO_x injection rate of 2000 molecules cm⁻³s⁻¹ over a 1-km-thick layer. Contribution to ClX due to CFM's is not included in calculations.

^bCFM's released at 1976 rate.

^cRate of OH + ClO → HCl + O₂ is set to zero.

model contemporary with the rate compendium in question did not include. In addition, we include the results of calculations made using the 1979a chemistry with the rate coefficient for the reaction OH + ClO → HCl + O₂ set to zero.

The conclusion to be drawn from Table 9 is that over the last five years, changes in evaluated recommendations for chemical rate coefficients have resulted in substantial changes in the model predicted response to perturbation, and that even recent recommendations appearing a few months apart carry a significant amount of uncertainty. (However, the differences between model predictions are not such as to change any qualitative conclusions if one restricts one's self to post-1976 models with consistent physics.)

A comparison of the results in Table 9 with the results of LLL calculations in earlier years given in Fig. 5 for some of the perturbations demonstrates that other changes in model structure have had quantitatively significant effects, but would have had little effect on the qualitative conclusions drawn from model predictions of aircraft effects. The results in Fig. 5 demonstrate the combined effects of the evolution of our understanding of stratospheric chemistry and evolution of the treatment of physical phenomena such as multiple scattering of light, the averaging of reaction rates over diurnal cycles, the treatment of boundary conditions, and the transport parameterization. Although many different factors have contributed to the variation described in Fig. 5, the evolution of model chemistry has been the most important single factor.

The uncertainty limits for reactions in the various evaluations [NBS 513 (1978), NBS 866 (1975), NASA 1010 (1977), JPL (1979), NASA 1049 (1979)] have generally become smaller when individual reactions are considered. However, over the same period, new and often highly uncertain reactions have been recognized, and it is far from obvious that the error that might be associated with rate coefficients actually included in models has gotten smaller over the last decade. Moreover, "new" reactions have been introduced to the modeling community at a fluctuating but not obviously decreasing rate.

Effect of Temperature Feedback and Hydrostatic Adjustment. In the calculations up to this point, the *U.S. Standard Atmosphere* (1976) temperature profile was used, and temperature was not allowed to change. Changes in the concentrations of species that are radiatively important (either solar or longwave) will affect the temperature profile by changing radiative fluxes and heating or cooling rates. At a given pressure level, as the temperature changes, the air density will also change as defined by the equation of state. Since chemical reaction rates are affected by changes in temperature and air density, it is important to assess the magnitude of these effects on the assessment calculation.

Air density can be computed in a one-dimensional model by assuming hydrostatic equilibrium (i.e., the pressure at any height is determined by the weight of the column of air above that point, and the air density is determined by the equation of state given the temperature). Expressed mathematically,

FIG. 5. Historical evolution of LLL model calculations of change in total ozone due to an NO_x injection of $3000 \text{ molecules cm}^{-3} \text{ s}^{-1}$ over a 1-km-thick layer centered at either 17 km (open circles) or 20 km (solid circles). This injection rate was a standard for assessment and comparison purposes and did not pertain to any particular fleet estimate. Values for 1978 are approximate.

$$dP = -\rho g dz \quad (3)$$

and

$$P = \rho RT \quad (4)$$

where P is pressure, ρ is density, g is the acceleration of gravity, z is altitude, R is the gas constant and T is temperature. The temperature is computed using a radiative transfer model assuming radiative equilibrium in the stratosphere (see Appendix A). In our calculations, the temperature profile is computed above 13 km, and is specified below this altitude. Changes in surface temperature may be imposed, but they are not calculated in this version of the model. The model includes solar absorption and

longwave exchange by O_3 , H_2O and CO_2 along with solar absorption by NO_2 (Luther *et al.*, 1977).

We assume that the change in surface temperature is negligible. Ozone reductions of up to 30% due to NO_x injections were computed to cause less than a 0.1 K change in surface temperature by Ramanathan *et al.* (1976). An increase in the stratospheric water vapor mixing ratio of 2 ppmv is estimated to cause an increase in surface temperature of $<0.2 \text{ K}$ (Grobeck *et al.*, 1974, p. F125). Increasing the surface temperature in our model by 0.2 K causes a change in total ozone of -0.06% . Neglecting changes in surface temperature of this magnitude has no significant effect on the results.

In studying the effect of temperature feedback and hydrostatic adjustment on model sensitivity, we

considered four calculation alternatives: (1) temperature feedback with hydrostatic adjustment, (2) temperature feedback without hydrostatic adjustment, (3) constant temperature using the ambient computed temperature and pressure profiles, and (4) constant temperature using the *U.S. Standard Atmosphere* (1976) temperature and pressure profiles. The results are presented in Table 10.

The constant temperature calculation using the ambient computed temperature profile (consistent with hydrostatic adjustment) is the reference case with which to compare the effects of temperature feedback and hydrostatic adjustment. Table 10 shows that inclusion of temperature feedback leads to a larger increase in total ozone compared to the constant temperature calculation (ambient profile). When hydrostatic adjustment is included, the increase in total ozone is even larger. To understand these effects, we need to look at the change in temperature versus height.

For analysis purposes, we consider the results for an NO_x injection rate of 1000 molecules $\text{cm}^{-3}\text{s}^{-1}$ and an H_2O injection rate of 177,000 molecules $\text{cm}^{-3}\text{s}^{-1}$ at 20 km. The change in local ozone concentration is shown in Fig. 6 and the change in the temperature profile is shown in Fig. 7. The temperature increases below 20 km causing an increase in the chemical destruction rate of ozone. Thus, there is less of an increase in ozone concentration in this region when temperature feedback is included. Conversely, above 20 km the temperature decreases, thereby slowing the rates of reaction and leading to less ozone reduction in this region.

In the case with hydrostatic adjustment, the air in the 14–20 km region expands due to the rise in

temperature. As the air expands it lifts the atmosphere above so that a given pressure level is raised in altitude relative to the ambient profile. Conversely, where the temperature decreases, there is contraction.

The results with temperature feedback and hydrostatic adjustment represent the most complete model calculations in terms of physical processes and feedback mechanisms. The changes in ozone concentration computed with these processes included are shown in Fig. 8 for various injection rates of NO_x and H_2O at an injection altitude of 17 km. The results for an NO_x injection rate of 1000 molecules $\text{cm}^{-3}\text{s}^{-1}$ with and without a simultaneous H_2O injection are nearly identical below 26 km. The injection of H_2O only leads to noticeable differences in the computed change in ozone concentration above 26 km.

Given the same H_2O injection rate, the results for NO_x injection rates of 1000 or 333 molecules $\text{cm}^{-3}\text{s}^{-1}$ are quite different. The lower NO_x injection rate causes much less change in ozone concentration in the middle and lower stratosphere; the relative magnitudes of the change in ozone concentration being roughly proportional to the NO_x injection rate. This result indicates that the NO_x injection rate is a much more important (and sensitive) parameter than the H_2O injection rate in estimating the effects of projected aircraft fleets.

Another important conclusion from Table 10 is that the choice of temperature profile in a constant temperature calculation can have a significant effect on model sensitivity. The difference between the ΔO_3 values using the ambient or the *U.S. Standard Atmosphere* (1976) temperature profile is the same

TABLE 10. Effect of temperature feedback and hydrostatic adjustment on model sensitivity (1979a chemistry).

Injection altitude (km)	Injection rate (molecules $\text{cm}^{-3}\text{s}^{-1}$)		Change in total ozone (%)			
	NO_x	H_2O	Temperature feedback with hydrostatic adjustment	Temperature feedback without hydrostatic adjustment	Constant ambient temperature ^a	U.S. standard atmosphere temperature
17	1000	0	1.45	1.30	1.20	1.34
17	1000	177,000	1.37	1.24	1.04	1.18
17	333	177,000	0.43	0.40	0.26	0.32
20	1000	0	1.26	1.17	1.10	1.31
20	1000	177,000	1.29	1.03	0.70	0.91
20	333	177,000	0.33	0.27	-0.02	0.07

^aThe temperatures and pressures were computed at equilibrium using temperature feedback and hydrostatic adjustment; they then were kept fixed for the perturbation calculation.

FIG. 6. Change in ozone concentration due to NO_x injection of $1000 \text{ molecules cm}^{-3}\text{s}^{-1}$ and H_2O injection of $177,000 \text{ molecules cm}^{-3}\text{s}^{-1}$ at 20 km.

magnitude as the difference between including and not including temperature feedback.

2.3 POTENTIAL CHANGES IN OZONE RESULTING FROM OTHER PERTURBATIONS

Many potentially significant perturbations to stratospheric ozone have been proposed. In order to put the effects of aircraft engine emissions presented in Section 2.2 in perspective, we present assessments

for other anthropogenic perturbations. Just as the effects of aircraft emissions were shown to depend on the effects of other perturbing influences, such as the concentration of ClX and the atmospheric temperature structure, the changes in O_3 resulting from the other perturbations considered here also depend on the interference effects of multiple perturbations.

Our effort has been primarily directed toward the assessment of predicted changes for individual perturbations since future perturbation scenarios are often quite uncertain. Of the perturbation scenarios considered here, only the increases in the

FIG. 7. Change in temperature vs altitude for 20-km injection perturbation described in Fig. 6 (1979a chemistry).

concentrations of chlorofluoromethanes and CO_2 are well established. Increases in N_2O and increases in stratospheric HC_3CCl_3 are predicted on uncertain knowledge of budgets and, in the case of CH_3CCl_3 , uncertain tropospheric chemistry.

Chlorofluoromethanes

It has been firmly established that the chlorofluoromethanes, CFCI_3 and CF_2Cl_2 , have been increasing in the troposphere and stratosphere, and the observed increase is consistent with model estimates based on the historical production rates. The CFM's are photolyzed in the stratosphere to

yield free chlorine which may catalytically destroy ozone.

Quantitative estimates of the depletion of ozone have changed as models, physics, and chemistry have improved. In 1976 the predicted change in total O_3 due to steady-state production of CFM's at 1973 rates was estimated to be -7.5% (National Research Council, 1976b). In 1977 a major change in the model chemistry occurred when the rate for

FIG. 8. Change in ozone concentration, due to various NO_x and H_2O injection rate at 17 km. Injection rates have units of molecules $\text{cm}^{-3}\text{s}^{-1}$ over a 1-km-thick layer. Calculations include temperature feedback and hydrostatic adjustment (1979a chemistry).

was measured to be almost 40 times faster than previously thought (Howard and Evenson, 1977). In addition, some models at that time adopted diurnally-averaged reaction rates and multiple scattering effects. The depletion estimates in 1977 ranged from -10.8 to -16.5% for the various modeling groups (NASA, 1977); the LLL estimate was -15.0%. With 1979b chemistry, we predict a change of -14.2% in total O_3 at steady-state assuming constant CFM production at the 1976 rates. (The 1976 production rates are 3.2% smaller for CFCl_3 and 2.9% larger for CF_2Cl_2 than those for 1973.)

Many changes to chemical rate constants on the order of 30% or more occurred between our 1977 chemistry and our 1979b chemistry. One major change affecting the CFM perturbation calculation was the inclusion of HOCl . HOCl is formed by the reaction,

and is destroyed by photolysis,

Destruction of O_3 is more efficient at lower altitudes if HOCl is included in the model. When HOCl is included, ClX shifts to more Cl and less ClO. Also, a new catalytic ozone destruction cycle is created that does not depend on the limited amount of O atom,

Figure 9 shows a number of calculated time histories for ozone under various assumptions regarding the future release rates for CFM's. For curve A it was assumed that CFM production continued at the 1976 rate until 1982, then it was

lowered by 25%. In 1987, it was lowered again by 25%. The eventual steady-state ozone depletion for this case was 7.5%. For curve B, the 1976 production rate continued until 1982 and was then cut by 25%. The ozone depletion at steady state was 10.8% for this case. For curve C the 1976 production rate was used for the entire time, and the steady-state ozone depletion was 14.0%. For curve D the 1976 production rate was assumed to continue through 1980, then the CFM production was increased by 7%/year up to the year 2000. The steady-state depletion for this case is 37.9%. Case E is almost the same as case D except that the increased CFM production begins in 1978. The rate of increase is such that the production rate doubles by 1990 and doubles again by 2000. The steady-state ozone depletion is 38.6%. The 1979a chemical rates were used in all of these model calculations.

Increase in N_2O

Concern that human perturbations to the nitrogen cycle might lead to enhanced concentrations for atmospheric N_2O has stimulated interest in

FIG. 9. Change in total ozone as a function of time for various CFM release rate scenarios. Curve A: 1976 CFM release rate until 1982, reduced by 25%, and further reduced by 25% after 1987. Curve B: 1976 release rate until 1982 and reduced by 25% thereafter. Curve C: 1976 release rate constant throughout period. Curve D: 1976 release rate through 1980 followed by release rate increase of 7% per year up to year 2000 followed by being constant thereafter. Curve E: Same as D except the increase in release rate begins in 1978. All calculations were based upon 1979a chemical rates.

the budget for this gas. Tropospheric N_2O is the major source for stratospheric NO_x so perturbations in N_2O are expected to alter stratospheric chemistry.

The fertilizer source of fixed nitrogen is currently estimated to be about 4.2×10^7 tN/yr, which converts to a source of 1.5×10^6 tN/yr as N_2O (estimate of Logan *et al.*, 1978). Combustion provides about 1.5×10^6 tN/yr as N_2O directly (Weiss and Craig, 1976; Pierotti and Rasmussen, 1976). These anthropogenic sources are thus currently significant relative to the natural sources and could grow in the future and lead to a doubling of N_2O perhaps by the early part of the next century (Logan *et al.*, 1978). This doubling time is very uncertain due to the lack of detailed understanding of the cycle for N_2O .

The level of atmospheric N_2O determines the atmospheric response to chlorine changes, and vice versa, mainly because of the coupling of chemistry by $ClONO_2$. Figure 10 illustrates how the percentage change in total O_3 with increased N_2O depends on the level of background ClX and on the chemical rate constants in the model. The dashed curves were produced using chemical rate constants that were used in 1978 (see Luther, 1978). The solid line refers to results using the 1979a rate coefficients. The major differences between the 1978 and 1979 chemistries as they affect this perturbation are: (1) the NO photolysis rate is slower in the 1979 chemistries so that the background level of NO_x is approximately 40% higher, and (2) the $ClONO_2$ formation rate via $ClO + NO_2 \xrightarrow{M} ClONO_2$ is almost four times slower in the 1979a chemistry. Both

FIG. 10. Change in total ozone due to an increase in N_2O expressed in multiples of present ground level concentration which is 325 ppbv. Results produced using 1979a rate coefficients are indicated by the solid line. Results using chemical rate data that were used in 1978 (Luther, 1978) are shown by dashed curves. Dash-dot line refers to results using fast $ClONO_2$ formation rate (see text).

changes tend to diminish the predicted O_3 increase as N_2O is increased. Even for 1.95 ppbv ClX, ozone decreases for all N_2O perturbations with the 1979a chemistry. This remains true even for the fast rate of $ClONO_2$ formation as indicated by the dot-dash line in Fig. 10, so most of the qualitative change in results is due to the change in NO photolysis.

Doubling of CO_2

Systematic measurements of CO_2 since 1958 (Keeling *et al.*, 1976a and b) have shown a rise in atmospheric CO_2 concentrations that has been attributed primarily to the use of fossil fuels. The CO_2 levels were 315 ppm in 1958, 320 ppm in 1965, and 334 ppm in 1978. By the year 2000 atmospheric CO_2 is expected to be between 365 and 400 ppm. Detailed prediction of the doubling time depends on uncertain knowledge of the budget for CO_2 . Assuming that fossil fuel usage continues to increase at 4.3%/yr and that about half of the CO_2 released resides in the atmosphere, the atmospheric CO_2 concentration would double by about 2030, but estimates using other assumptions vary from 2015 to 2070. It is possible that the concentration could be limited to less than 500 ppm by shifting away from fossil fuels and relying more on solar and nuclear energy.

An increase in CO_2 is expected to lead to changes in the thermal structure of the atmosphere. In particular, a doubling of CO_2 has been estimated to increase the global mean surface temperature by 1.5 to 3 K due to the greenhouse effect (Schneider, 1975; Augustsson and Ramanathan, 1977). The temperature should decrease in the stratosphere, where the infrared opacity is smaller than in the troposphere.

We tested the effect of tropospheric temperature changes by increasing the specified temperature below 14 km by 2 K when CO_2 was doubled from 320 to 640 ppm. The calculated change in the ozone profile (Fig. 11) for this case was nearly the same as for the case where the tropospheric temperature remained unchanged (local ozone concentrations were within 2.6% at all altitudes). The calculated temperature changes above 14 km were also similar, differing by less than 0.7 K. In this test the background atmosphere remained fixed (no hydrostatic adjustment). When hydrostatic adjustment was included, the local ozone increase near 40 km was about 15%, which was larger than the perturbation for no tropo-

spheric temperature change but smaller than the calculated change when hydrostatic adjustment was neglected entirely. Without hydrostatic adjustment, the stratospheric temperature decrease leads to an increase in O_3 at all altitudes. The O_3 increase tends to offset the calculated temperature decrease due to CO_2 above 40 km by increasing solar absorption by O_3 . The calculated temperature decrease is a maximum near 42 km.

With hydrostatic adjustment, however, ozone decreased above 45 km even though the temperature decreased. This is due to the decrease in background air density. As a result of the ozone decrease, the temperature decreased further above 45 km.

The increase in total O_3 for a doubling of CO_2 was 5.06% with hydrostatic adjustment and 4.74% without. The larger change for the hydrostatic case reflects the behavior of O_3 near 25 km, as shown in Fig. 11. At this level, the photolysis rates for O_2 and O_3 both decreased for doubled CO_2 as a result of the larger optical depth (more O_3 above 25 km). The change in optical depth is larger for the case without hydrostatic adjustment, so the photolysis rate for O_2 decreases more for this case, causing a smaller increase in O_3 . When the surface temperature was increased 2 K, the change in total ozone was 4.17% without hydrostatic adjustment.

Increase in CH_3CCl_3

The use and release of methylchloroform, CH_3CCl_3 , which is used as a cleaning agent, has been increasing at a steady rate. Its presence in the atmosphere has been observed since 1974 (Cox *et al.*, 1976), and it has been suggested that its continued use will lead to a reduction of ozone (McConnell and Schiff, 1978). The sinks for CH_3CCl_3 are photolysis and reaction with OH in the stratosphere,

Stratospheric destruction of CH_3CCl_3 leads to release of Cl atoms which are able to destroy ozone. Reaction (10) is also effective in the troposphere, so the growth of stratospheric CH_3CCl_3 is limited. The effectiveness of reaction (10) for removing tropospheric CH_3CCl_3 , however, is fairly uncertain.

FIG. 11. Change in ozone concentration due to a doubling of CO_2 concentration (1979a chemistry).

The major uncertainties result from inadequate knowledge of the tropospheric OH distribution and the rate of reaction. The rate for reaction (10) is uncertain since there are several conflicting measurements of its rate at room temperature and of its temperature dependence (JPL, 1979). Comparison of the budget for CH_3CCl_3 with available measurements leads to an estimate for the tropospheric lifetime of between 8 and 11 years (Penner and Chang, 1978). Model calculated lifetimes are considerably shorter, implying larger tropospheric destruction rates, on average, than conform to the measurements. For example, using the historical

release rate data from Neely and Plonka (1978) in our one-dimensional model, we calculate an average abundance near the surface for January 1978 of 47.3 pptv using the 1979a chemistry. The rate coefficient for reaction (10) was $2.5 \times 10^{-12} \exp(-1450/T)$ (see JPL, 1979). We calculate 66.1 pptv using the 1979b chemistry and a rate coefficient of $5.4 \times 10^{-12} \exp(-1820/T)$ for (10). These rates differ by about a factor of 2 at temperatures characteristic of the upper troposphere and by about 50% near the surface. Measurements taken by R. Rasmussen (private communication, 1979) give an average concentration of 101 pptv for CH_3CCl_3 .

With CH_3CCl_3 , CFCl_3 , and CF_2Cl_2 releases included in our model, the calculated reduction in total ozone in 1978 was 1.7% (relative to 1950) using 1979b chemistry, whereas without CH_3CCl_3 , O_3 decreased by 1.3%. The total stratospheric chlorine burden increased by 7%. Figure 12 shows the time

history for O_3 depletion at constant 1976 production rates for CFCl_3 and CF_2Cl_2 . The CH_3CCl_3 release rate at the earth's surface is constant at 1.23×10^7 molecules $\text{cm}^{-2} \text{ s}^{-1}$ beyond 1978. At steady state ozone decreased 15.2%, whereas without CH_3CCl_3 it decreased 14.2%. Of course, the

FIG. 12. Enlargement of period from 1980 to 2000 for calculations presented in Fig. 9. Curve C' is same scenario as Curve C except 1979b model chemistry is used with exception that CH_3CCl_3 is added.

effects of CH_3CCl_3 could be much greater if its use were to continue to increase. Because of significant uncertainties in the model treatment of photochemistry in the lower troposphere, these results must be considered preliminary.

2.4. EFFECTS OF SPECULATIVE REACTIONS AND MECHANISMS

There are several reactions that have been suggested to be of possible importance in the stratosphere but have not been measured yet. Also, there are a few reactions for which anomalous pressure/temperature dependencies have been suggested but not demonstrated. We have examined the sensitivity of model predictions to a subset of such hypothetical reactions. The subset selected was based on the following criteria: (1) the hypothesized reaction or mechanism has at least some support from laboratory work, and (2) the hypothesized reaction appears to have the potential for causing a major change* in predicted effects of SST's or CFM's. The reasons for selecting these two criteria were to reduce the number of possible cases to be considered and to focus attention on mechanisms that appear to have a maximum potential for altering model predictions. It must be stressed that most of the mechanisms considered here have no more than a weak basis in actual measurement. The purpose of this section is to suggest experiments that might deserve some priority. It is not to suggest that the hypothesized mechanisms or their computed effects are particularly likely to be true.

In this section we will discuss the major effects on the computed ambient atmosphere and model sensitivity of the various mechanisms considered. Although the changes to the ambient species concentration profiles may tend to either improve or worsen the agreement with observations for various species, we have not established a criterion for agreement (or disagreement) upon which to evaluate the likelihood that the mechanism actually occurs or to eliminate it from consideration. By

combining the description of the effects on the ambient profiles discussed in this section with the comparison with observations discussed in Section 2.1, the reader can form his own opinion on this matter.

Chlorine Nitrate Formation

In terms of published evaluations of mechanistic data, perhaps the most plausible speculation is that roughly 75% of the reaction between ClO and NO_2 forms a relatively short-lived species isomeric with chlorine nitrate, and the effective rate of chlorine nitrate formation is only about one-fourth of the observed rate of reaction between ClO and NO_2 . In JPL (1979) (and NASA, 1979) no firm choice is made between the assumption that all of the reactions between ClO and NO_2 lead to chlorine nitrate and the assumption that only about 25% do, although most modelers have adopted the first assumption. The choice of treatment for this reaction is one of the major differences between the 1979a and 1979b chemistries. As can be seen from Table 11, if the slower rate of chlorine nitrate formation is assumed, the calculated effects of an SST fleet become more positive than in the base case, while the computed effects of CFM's become more negative. In each case, the fractional change is of the order of a factor of 1.3. Clearly, the correct treatment of chlorine nitrate formation is of substantial importance. It is also worth noting that if the isomeric products have greater photolytic stability than ClONO_2 , or if, as impurities, they account for some of the observed absorption spectrum of ClONO_2 , the effect of chlorine nitrate isomers on predictions might actually be reversed. This could happen if the mean rate of loss of some ClNO_3 products were to be slower than that presently assumed for ClONO_2 so that larger concentrations of ClNO_3 species would be generated.

When the low rate is assumed for chlorine nitrate formation, a significant ($>10\%$)* change in the ambient state is computed for Cl , ClO , HCl , HOCl , and ClNO_2 , all of which increase by nearly a factor of 2 at 25-30 km, while ClNO_3 is reduced by a factor of 3 to 4 at almost all altitudes. Thus, this hypothesis exacerbates the apparent disagreement between observation and calculation for the shape of the ClO vertical profile and destroys the apparent

*In this context a major change would consist of a change in the computed steady-state effect of chlorofluoromethanes at 1975 levels by at least 50% or a change in sign or two-fold increase in computed SST effects. Not all of the cases studied actually have such large effects and some mechanisms not studied might have larger effects.

*All percent changes reported in this section refer to fractional changes in the quantity relative to the standard (1979b model) ambient conditions or model sensitivity.

TABLE 11. Results of sensitivity calculations for speculative chemical reactions and mechanisms.

Model content	Ambient ozone column (Dobson units)	Change in total ozone (%)		CFM production ^b
		17-km NO injection ^a	20-km NO injection ^a	
Baseline Model (1979b)—NASA 1049 (1979) 2 ppb CLX	322	1.25	1.14	-14.6
Slower rate of ClONO ₂ formation	312	1.42	1.54	-19.3
Photolysis of XONO ₂ to XO + NO ₂ products	324	1.35	1.20	-12.2
Pressure- and temperature-dependent HO _x disproportionation reactions	339	0.47	-0.40	-8.9
HCl production from ClO + OH, ClO + HO ₂	334	0.74	0.02	-4.4
ClO ₃ production, K _{equilibrium} as for ClO ₂ from NASA 1010; no other reaction of ClO ₃	322	1.24	1.11	-14.0
OCIO ₂ production K _{equilibrium} as for ClO ₂ from NASA 1010; subsequent chemistry described in text	337	1.51	1.40	-6.91
OCIO ₂ production K _{equilibrium} as for ClO ₂ from JPL (1979); subsequent chemistry described in text	323	1.27	1.16	-14.0
OCIO ₂ production K _{equilibrium} as for ClO ₂ from NASA 1010; subsequent chemistry described in text and P,T-dependent HO _x disproportionation reactions	353	0.49	-0.51	0.73

^aRate of emission is 1000 molecules (NO) cm⁻³s⁻¹ over a 1-km-thick layer.

^bConstant release rate at 1976 levels.

agreement between calculation and the preliminary chlorine nitrate measurement reported by Murcray (1979).

Photolysis of XONO₂ Species

Almost equally uncertain are the products of the photolysis of species of the form XONO₂, where X = OH, Cl, NO₂. In the base case, it has been assumed that all of these reactions lead to X + NO₂. This assumption is largely based on the experimental results of Chang *et al.* (1979) for chlorine nitrate.

Other products are possible, perhaps the most distinct (in terms of model predictions) would be XO + NO₂ (or for N₂O₅, 2NO₂ + O). In a computation in which all of these photolyses were assumed to yield XO + HO₂ products (except N₂O₅, which was assumed to yield 2NO₂ + O), the computed effects of SST emissions became more positive by 5–10% (of the change computed for the base case) while the effects of CFM's became less negative by about 17%. Thus, resolving the question

of photolysis products of XOCIO species is of modest importance to perturbation calculations.

In terms of species concentrations, only NO₃ and N₂O₅ displayed large changes (both were reduced by a factor of two to three at the region of their largest mixing ratios, and by up to 90% at some (lower) altitudes). Several other species displayed changes on the order of 10–15% at some altitudes.

Pressure-Dependent Rates for HO_x Disproportionation Reactions

A significant pressure, inverse temperature and water vapor dependence has been reported for the reaction HO₂ + HO₂ $\xrightarrow{M, H_2O}$ H₂O₂ + O₂ (Cox, 1978; Hamilton and Lü, 1977; Cox and Burrows, 1979). Furthermore, while the measurements of the reaction HO₂ + OH at low pressures seem only mildly inconsistent with each other, the indirect values inferred at higher pressures (Hochanadel *et al.*, 1972; DeMore and Tschukov-Roux, 1974; DeMore,

1979) are substantially (two to four fold) faster than the values measured at low pressures. In this context, the poorly understood pressure, temperature, and water vapor dependence of $\text{HO}_2 + \text{HO}_2$ suggests the possibility that $\text{HO}_2 + \text{OH}$ may also be affected by similar phenomena. As can be seen in Table II, when we assumed that the expression given by Cox (1978) for $k_{\text{HO}_2 + \text{HO}_2}$,

$$k_{\text{HO}_2 + \text{HO}_2} = \frac{3.25 \times 10^8 + 4 \times 10^{-10} (M) / [1 + 3.5 \times 10^{-16} (M) e^{-2060/T}]}{8(M) + 4.08 \times 10^{20}} \quad (11)$$

and an expression for $k_{\text{OH} + \text{HO}_2}$ designed to yield a low-pressure value compatible with Chang and Kaufman (1978), and a high pressure value compatible with the larger rate constants reported at high pressure, i.e.,

$$k_{\text{HO}_2 + \text{OH}} = (5 \times 10^{-30} \times M + 3 \times 10^{-11}) \chi(300/T)^3, \quad (12)$$

there were major changes in model predictions for both SST's and CFM's. Here it should be emphasized that the expression used for the rate constant for reaction of HO_2 with OH is completely arbitrary. It was designed to approximately fit high- and low-pressure data. Had a Lindeman-Hinshelwood expression been fitted to the same data, or had a constant ratio to the $\text{HO}_2 + \text{HO}_2$ rate been assumed, the effects would have been different (probably larger) but equally plausible. The form chosen reflects the postulation of a pressure independent abstraction mechanism coupled with a pressure dependent enhancement reflecting complex formation (with a limiting value well above 1×10^{-10} at room temperature).

Elucidation of the pressure and temperature dependencies of the HO_x radical disproportionation reactions should be of high priority to those concerned with SST effects and of considerable importance to those concerned with CFM production effects. The assumed change in the $\text{HO}_2 + \text{OH}$ reaction is substantially more important than the change in the $\text{HO}_2 + \text{HO}_2$ reaction within the stratosphere. However, the $\text{HO}_2 + \text{HO}_2$ reaction is of significant importance in the troposphere, and the effects of subsonic aircraft operations are expected to be sensitive to it, as would be the effects of CH_3CCl_3 emissions.

When the above assumptions were made about the HO_x disproportionation reactions, many species changed by roughly a factor of 2 between approximately 10 and 20 km. Roughly two-fold reductions (between approximately 10 and 20 km) occurred for OH, HO_2 , Cl, ClO, and CH_2O , while H_2O_2 was reduced by roughly the square of the fractional reduction in HO_2 . Computed NO and NO_2 displayed two-fold increases over the same altitude range. Species that were only slightly changed included HNO_3 (<10% changes) and CH_4 (approximately 10% increase at high altitudes).

Thus, changes in the HO_x disproportionation rates akin to those considered here would cause substantial changes in computed profiles of short lived species in the region from 10 to 20 km. Some of these changes tend to improve agreement with observation, others tend to reduce it. Although CH_4 increases at higher altitudes, the increase is not large enough to demand a major revision in K_2 even if future experiments should suggest the pressure-dependent disproportionation rates used here to be fair approximations of reality. For CH_4 to increase substantially at higher altitudes, it would be necessary for an increase in $k_{\text{OH} + \text{HO}_2}$ to extend to substantially lower air densities.

All of the above speculations have at least some direct basis in laboratory measurements. The speculations that follow are even more tenuous than the above.

HCl Formation from $\text{HO}_x + \text{ClO}$

The reaction between OH and ClO could yield $\text{HO}_2 + \text{Cl}$ or $\text{HCl} + \text{O}_2$ at low pressures, or a three-body process might yield a moderately stable species of the form HOOC (a peroxide) or HOClO (an acid). Either of these last species might be expected to be unstable with respect to disproportionation in a condensed phase, but gas phase stability seems possible. In any case, the production of $\text{HCl} + \text{O}_2$ from $\text{HO} + \text{ClO}$ would seem likely to have the most drastic effect on model predictions. The overall reaction has a rate constant of 9.2×10^{-11} at room temperature, and the products $\text{HO}_2 + \text{Cl}$ account for at least 65% of the products (Leu and Lin, 1979). These products have little effect on model sensitivity.

An investigation of the effect of this reaction producing HCl assuming a rate constant of $2 \times 10^{-12} \text{ cm}^3/\text{s}$ suggested that model sensitivity to

a CFM perturbation could be reduced by approximately 40%; at 1×10^{-12} cm³/s the sensitivity would be reduced by roughly 20%.

A similar argument could be applied to the reaction:

The only evidence suggesting a plausible role for reaction (14) is that at temperatures below room temperature, the rate of the overall reaction increases substantially as the temperature is reduced (C. Howard *et al.*, NOAA Aeronomy Laboratory, Boulder, private communication, 1979). This suggests the possibility that a five-centered complex might be formed and HCl + O₃ eliminated. If the rate of HCl formation via this reaction were to be as large as 1×10^{-12} cm³/s, then the effect of CFM's would be reduced by approximately 50%, and, if the rate were to be even larger, increases might be computed from CFM releases.

Table II gives the sensitivities obtained when both $\text{HO} + \text{ClO} \rightarrow \text{HCl} + \text{O}_2$ and $\text{HO}_2 + \text{ClO} \rightarrow \text{HCl} + \text{O}_3$ were assumed to have rate constants of 1×10^{-12} cm³/s. As is evident, these reactions might have a major impact on both CFM and SST effects, and they might have a smaller but significant effect on computed CFM effects at rates as low as approximately 1×10^{-13} cm³/s.

The effect on the model sensitivity to an NO_x perturbation is largely a result of there being a lessened rate of ClX and HO_x catalytic destruction of ozone with which NO_x can interfere. Also, null cycle sequences involving ClX and HO_x are not as effective in competing with ozone-destroying sequences for NO. The reduced sensitivity to CFM perturbations results from both an increase in the rate at which HCl is formed and a transfer of ClO and HO_x radicals out of odd-oxygen destroying sequences and into null sequences.

There is the possibility that the reaction $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_3$ might occur to some extent. An analysis of available data (H. Johnston, University of California at Berkeley, private communication, 1979) suggests an upper limit of about 5% of the total rate for this reaction. If the similar reaction $\text{HO}_2 + \text{ClO} \rightarrow \text{HCl} + \text{O}_3$ had a branching ratio of less than 0.05, it would have no more than a modest effect on model sensitivity (based on calculations

made in 1978, the reaction $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_3$ would need to have a branching ratio of nearly 0.1 to be of even marginal significance in stratospheric perturbation studies).

The model-calculated ambient atmosphere with rates for both $\text{OH} + \text{ClO} \rightarrow \text{HCl} + \text{O}_2$ and $\text{HO}_2 + \text{ClO} \rightarrow \text{HCl} + \text{O}_3$ set to 10^{-12} cm³/s contained about half as much Cl, ClO, ClONO₂, ClNO₂ and HOCl as did the normal ambient, whereas HCl increases of about a factor of 2 were calculated near 30 km. No other measured species were significantly (>10%) affected, although H₂O₂ and CH₃OOH were reduced by about 30% between 25 and 35 km.

Although model predictions are indeed sensitive to these reactions, the likelihood that they occur is probably not very great. Thus, while an effort should be made to measure them, an upper limit less than approximately 10^{-13} cm³/s would resolve most of the issues they raise.

ClO₃ Chemistry

A final mechanism that was studied was the possibility that O₂ and ClO add to form a molecule with a binding strength comparable to that of ClOO, the complex formed from Cl and O₂. There is evidence for some such phenomenon from the effect of added O₂ on the quantum yield for ozone loss in systems containing Cl₂, O₃ and O₂ (Wongdontri-Stuper *et al.*, 1978; J. Birks, University of Colorado, private communication, 1979).

If it is assumed that the formation and decomposition rate constants for the process $\text{ClO} + \text{O}_2 \rightarrow \text{ClO}_3$ are those given in NASA 1010 (1977) for $\text{Cl} + \text{O}_2 \rightarrow \text{ClO}_2$ and no subsequent chemistry occurs (only the formation and thermal decomposition of the complex occur), then model sensitivities are virtually unaffected. Approximately 2 to 5% of the inorganic chlorine in the lower stratosphere is in the form of ClO₃, and all computed changes in ambient concentrations are small. Even though the coupling between ClO and ClO₃ is very rapid, and ClO₃ is computed to be larger than ClO between approximately 6 and 22 km, most of the ClO₃ apparently comes from the much more abundant HCl and ClONO₂. However, if the structure of the ClO₃ complex were OClO₂, then it is possible that the following reactions would occur:

and

Because ClO and OCIO have comparable heats of formation, the endoergicity of the photolysis would approximate 60 kcal plus the binding energy of the complex. This suggests an endoergicity for reaction (15) comparable to that for NO_2 photolysis. Thus, at least in principle, reaction (15) might have an effective J value as large as about 10^{-4}s^{-1} . The reaction $\text{OCIO} + \text{NO} \rightarrow \text{NO}_2 + \text{ClO}$ has a rate constant of about $3 \times 10^{-13} \text{ cm}^3/\text{s}$ at room temperature (JPL, 1979). Given the similarities in the reactions, a similar sort of rate constant might be estimated for $\text{OCIO}_2 + \text{NO}$. If one assumes that the J value for OCIO_2 photolysis is 10^{-4}s^{-1} , that the rate of reaction with NO is $1 \times 10^{-12} \text{ cm}^3/\text{s}$, and that the formation and decomposition rates are those given for ClO_2 in NASA 1010 (1977), then one estimates a moderate (20%) increase in the (small) ozone increase computed from SST operations and more than a 50% reduction in the effect of CFMs. If on the other hand one assumes the same subsequent chemistry but a lower stability for the complex, say that given for ClO_2 in JPL (1979), then no significant effect on model sensitivity is predicted.

Thus, for the formation of a complex between O_2 and ClO to significantly affect model sensitivity, the complex must have a binding energy approaching 6 kcal, and either photolysis or reaction with NO must be reasonably fast. However, if the complex were to be stable (bound by more than 8 kcal) and the subsequent chemistry were reasonably fast, one might even compute a decrease in ozone for NO_x injections and an increase in column ozone from CFM increases. Similarly, if the HO_x reactions were pressure-dependent and OCIO_2 were to have the chemistry discussed above, one would calculate a decrease in column ozone for the 20-km NO_x injection and an increase in column ozone from the CFM scenario (see Table 11). There is, of course, a lengthy chain of speculative assumptions required to achieve such results.

Even though the OCIO_2 chemistry discussed above is completely speculative, its potential for large effects may justify the attempt to study it by those chiefly interested in CFM effects.

Finally, it should be noted that the simplest (but probably not the most likely) route back to

computed effects of SST operations (like those obtained in CIAP Monograph 3 (1975) and National Research Council (1975a) would be for the HO_x disproportionation reactions to have fast rates (either via the pressure/temperature effects hypothesized above, or through an error in the post 1976 measurements) and for the reaction of $\text{HO}_2 + \text{NO}$ to be slower than is now thought to be the case. Although it seems unlikely that the growing body of experimental results involving HO_2 chemistry would all be wrong (at least at low pressures where many of the measurements have been direct and the data analysis reasonably straightforward), it cannot be denied that the new measurements have produced a startling number of unexpected negative temperature dependencies for apparently bimolecular reactions involving HO_2 (and ClO as well). While theories of reaction rates can no doubt be created to fit such data, the pre-existing theories do not easily lead to the observed rate constants. Although it seems very likely that the resolution of such problems will indeed come via a modification of theory, additional confirmatory measurements of some of the anomalous temperature dependences using independent, if perhaps less direct, techniques would still be welcomed.

2.5 STRATOSPHERIC WATER VAPOR

The review of our knowledge and observational data on stratospheric H_2O revealed several apparent paradoxes which remain to be resolved. These are illustrated by the data summarized in Figs. 13 and 14. These data indicate upward and poleward directed gradients of H_2O immediately downstream (in the Hadley flow) from the tropical tropopause source for air (and contained tracers including H_2O) entering the stratosphere. As pointed out previously (Elsaesser, 1974), these appear to require a sink for H_2O in the stratosphere. However, possible sinks proposed, such as the Antarctic winter freeze-out and the "cold finger" of overshooting cumulonimbi, do not appear adequate. An alternative possibility is that observational data have been accumulated mostly from the downwind edges of continents where cumulonimbi penetrations are most likely to be concentrated; thus the gradients indicated in Figs. 13 and 14 may exist only in such areas and not be representative of zonal averages as

FIG. 13. Summary of observations of the latitudinal gradient in stratospheric H_2O . Data sources identified by references.

they have been interpreted to be. If valid, disappearance of these gradients would obviate the need for an H_2O sink in the stratosphere.

An even greater paradox is indicated by two other observational phenomena: (1) the frequent occurrence of dry air with mixing ratios ≤ 3 ppmm (i.e., typical of the lower stratosphere) as much as 100 mb beneath the tropical tropopause in clearly tropospheric air (such mixing ratios are not only untypical of what has until now been our concept of tropospheric air, but they are actually lower than would be produced by passage through the overlying ambient tropical tropopause) and (2) on those

so-called "wet" days when soundings do conform to the Brewer-Dobson theory by showing saturated air at and below the tropical tropopause and/or when cumulonimbus penetrations of the tropopause are sighted, the mixings ratios at and just about the tropical tropopause are generally ≥ 6 ppmm.

These observations appear to imply that the aridity of the stratosphere is *not* controlled by freeze-drying at the tropical tropopause and that there exists in the troposphere a mechanism for drying the tropical tropospheric air above 200 mb to mixing ratios ≤ 3 ppmm typical of the lower stratosphere. As of now the only mechanism which

suggests itself is cirrus clouds. If there exist seeding agents, possibly including the cirrus ice crystals themselves, which at temperatures of -50 to -80°C and pressures below 200 mb, can condense vapor out of what is now regarded as unsaturated air and cause the resulting hydrometeors to fall to higher pressures and temperatures before re-evaporating, we could explain many currently puzzling observations. An additional strong argument for a tropospheric mechanism for drying the air to stratospheric mixing ratios is that it would open a new pathway for significant transfers of air from the troposphere to the stratosphere—and that is through the tropopause-gap. Many have suggested this pathway before based on tracers such as O_3 , but most have considered it as insignificant since it appeared to offer no way of maintaining the aridity of the stratosphere. However, if the air is dried by a mechanism operating in the troposphere, this objection goes away.

A third paradox is due to the H_2O believed to be added to the stratosphere by the oxidation there of CH_4 entering with the Hadley circulation from the troposphere. This should impose a downward directed gradient of H_2O in the middle and upper stratosphere with a total difference in H_2O mixing ratio somewhat less than 2 ppm and an equatorward directed gradient in the lower stratosphere since the return Hadley flow through the polar tropopauses presumably must carry more H_2O than is carried by the entering Hadley flux through the tropical tropopause. A downward directed gradient is shown by many soundings, but most of these show a total difference in mixing ratio of more than 2 ppm. Also, an equatorward directed gradient of approximately the right magnitude is shown by what are considered to be the two most reliable sets of observations of stratospheric H_2O , the MRF* and the Mastenbrook series. Such a gradient is also shown by the observations of McKinnon and Morewood (1970)

*MRF is the acronym for the series of British meteorological research flights.

FIG. 14. Summary of recent soundings of stratospheric and mesospheric H_2O .

(see Fig. 13). However, for the inferences drawn above to be correct requires that the data of most investigators of stratospheric H_2O are incorrect or unrepresentative.

3. SATELLITE OZONE DATA PROCESSING, ARCHIVING, AND ANALYSIS

3.1 OVERVIEW

Measurements of ozone have been made on a regular basis for several decades. The Dobson spectrophotometer instrument is the most widely used ground-based instrument. This instrument measures the differential attenuation of sunlight in adjacent spectral bands in the UV Huggins band of ozone from which the total column of ozone is determined. The Dobson instrument has been in use since 1929, and approximately 100 ozone observatories have used this instrument. Since 1960 the data from many of the Dobson sites have been compiled and published by the Atmospheric Environment Service of Canada. Presently, data from 61 Dobson sites are being published routinely. These sites are located principally on continents in the Northern Hemisphere. The largest data voids are over the oceans and in the Southern Hemisphere.

Global satellite measurements of total ozone were first made in 1969 using the infrared interferometer spectrometer (IRIS). Later, the backscatter ultraviolet spectrometer (BUV) and the IRIS sensors were both flown on the Nimbus 3 (launched in 1970) and Nimbus 4 (launched in 1972) satellites. The longest continuous satellite ozone data record is that of the Nimbus 4 BUV instrument that operated from April 1972 to July 1977. The multichannel filter radiometer (MFR) infrared sensor was first flown in 1977 on a Defense Meteorological Satellite Program (DMSP) Block 5D series satellite, which is operated by the U.S. Air Force. Four

satellites in this series have been launched, and the data from these satellites are expected to extend into 1980. The period covered by each of the four DMSP satellites is shown in Table 12.

In addition to the DMSP satellite, ozone data are being obtained by sensors aboard the NASA Nimbus 7 and NOAA TIROS N satellites that were launched in November 1978. The TIROS N satellite carries a high resolution infrared sensor and the Nimbus 7 satellite carries a solar BUV sensor and a TOMS* instrument. The series of NASA and NOAA satellites is expected to provide global ozone data into the late 1980's. The DMSP MFR sensors were the only satellite ozone monitoring systems operating between mid-1977 and November 1978.

All of the DMSP satellites are in polar, sun-synchronous orbits with basically the same orbital parameters. F4 is somewhat different in that it is in a nighttime ascending orbit (i.e., F4 ascends from southeast to northwest on the night side), whereas the others are in daytime ascending orbits. Consequently, although F2 and F4 are only about an hour apart in their overpass times, their flight-track (and site-scan) geometries are different, thereby better enabling F4 to fill data-void areas of F2 and F3. We receive the MFR radiance data on magnetic tape from the U.S. Air Force Global Weather Central, and the raw data are forwarded to the Environmental Data Service of NOAA where they are archived.

*Total Ozone Mapping Spectrometer.

TABLE 12. Data periods covered by MFR sensors^a on DMSP satellites.

DMSP satellite	Data period	Local overpass time
F1	March 1977 - July 1977	11-12 a.m. and p.m.
F2	July 1977 - Spring 1980 (estimated) ^b	9-10 a.m. and p.m.
F3	August 1978 - January 1980	6-7 a.m. and p.m.
F4	June 1979 - January 1980	10-11 a.m. and p.m.

^aThe F4 MFR sensor may be turned back on at a later time if satellite battery problems are solved or if there is a change in the power management plan.

^bF2 has already exceeded its designed lifetime.

The MFR sensor measures infrared radiances for 16 channels. The channel characteristics are given in Table 13. Total ozone amounts are determined from sets of radiance measurements using an empirical relationship that is developed using linear regression analysis. Total ozone is currently modeled as a linear combination of terms involving functions of the MFR radiances for four channels (1, 2, 7, and 16) and the secant of the zenith angle. The coefficients used in the retrieval model are determined by regression analysis using sets of simulated radiances derived from detailed radiative transfer calculations. Historical vertical temperature and ozone concentration profiles are used as input to the calculations, and calculations are made for various cloud amounts, surface temperatures, and instrument scan angles. Different sets of regression coefficients are derived for each latitude band (currently, we are using 11 bands) and for different times of the year.

Temperature-dependent molecular absorption coefficients for the 9.6- μm ozone band and the 15- μm carbon dioxide band are determined from high-resolution, line-by-line calculations. These coefficients are used to compute transmittance profiles for the various channels, given the temperature and optically active gas concentration profiles. Transmittances due to the water vapor continuum absorption in the atmospheric window are calculated with an "e-type" model. A regression model based on data from line-by-line calculations plus continuum effects is used for the tropospheric water vapor transmittance calculations in the 15- μm spectral region. A Goddy random band model is employed to calculate the transmittances due to the 14- μm ozone band. See Lovill *et al.* (1978) for more detail regarding the retrieval methodology as it was employed during the feasibility study.

The total column ozone data derived from the MFR measurements are compared with an independent set of ground-based measurements of total ozone in order to evaluate the MFR-retrieval methodology. This set of data consists of Dobson ozone measurements that are taken close in time to DMSP satellite overpasses. Currently, 36 Dobson observatories are providing special sets of ozone measurements for comparison purposes. We provide each observatory predictions of the daily overpass times for each DMSP satellite.* The North

*Special Dobson measurements are not being taken at F3 overpass times because its overpasses are near sunrise and sunset.

TABLE 13. Nominal MFR channel characteristics.^a

Channel number	Center		Half width (cm^{-1})	Species	NESR ^b
	(μm)	(cm^{-1})			
1	15.0	668.5	3.5	CO_2	0.30
2	14.8	676.0	10.0	CO_2	0.09
3	14.4	695.0	10.0	CO_2	0.10
4	14.1	708.0	10.0	CO_2	0.11
5	13.8	725.0	10.0	CO_2	0.11
6	13.4	747.0	10.0	CO_2	0.12
7	12.0	835.0	8.0	Window	0.11
8 ^c	18.7 ^d	535.0	16.0	H_2O	0.15
9	24.5 ^d	408.5	12.0	H_2O	0.14
10	22.7 ^d	441.5	18.0	H_2O	0.09
11	23.9 ^d	420.0	20.0	H_2O	0.12
12	26.7 ^d	374.0	12.0	H_2O	0.18
13	25.2 ^d	397.5	10.0	H_2O	0.16
14	28.2 ^d	355.4	15.0	H_2O	0.25
15	28.3 ^d	353.5	11.0	H_2O	0.33
16	9.8	1022.0	12.5	O_3	0.05

^aAfter Nichols (1975).

^bNESR = Noise Equivalent Spectral Radiance in $\text{mW}/(\text{m}^2 \text{ sr cm}^{-1})$.

^cNot on Flight Model 1.

^dNot used in this investigation.

American Air Defense Command (Colorado Springs) satellite tracking facility provides us with the orbital parameters for each of the DMSP satellites, which are input to the computer code that predicts the satellite overpass times.

In addition to the comparison with Dobson measurements, comparisons will also be made between the MFR-derived ozone measurements and total ozone data from TIROS N and Nimbus 7.

3.2 RADIATIVE TRANSFER AND RETRIEVAL METHODOLOGY

Several of the many investigations required to validate and document the physics, mathematics, and software as applied in the development of the total ozone retrieval model implemented in early 1978 have been completed or are in progress. The

assumptions made and shortcuts taken in developing the initial methodology and several items pointed out by various reviewers are also being evaluated.

Techniques and software were developed to compare line-by-line calculated absorption spectra against laboratory spectroscopic measurements. The laboratory data of Dr. Gryvnak and Dr. Burch at Ford Aerospace and Communications Corp. for the 15- μ m carbon dioxide bands were obtained, and software to read and display the data were developed. A version of the line-by-line software was modified to produce calculations for the homogeneous paths used in the laboratory investigation for direct high-resolution comparisons. Initial results indicated considerable disagreement. A spectral shift was obvious and the magnitude of the absorption was somewhat lower for the theoretical calculations. Discussions with Dr. McClatchey (Air Force Geophysics Laboratory) and Dr. Burch revealed that similar disagreements had also been found in their studies. Dr. McClatchey felt that the position of lines and bands in the spectrum were quite good in his theoretical line parameter data that are used as input to our line-by-line calculations. Our analysis indicated that the spectral shift was probably due to some instrument error in the spectroscopic data. Further discussions with Dr. Burch lead to the conclusion that the laboratory spectrum was observed through a "skewed" instrument slit function.

Software was developed to degrade our line-by-line calculations with a skewed slit function. Subsequent displays of the data using slit function widths appropriate for the laboratory data indicated that this was probably the cause for the apparent shift, since good agreement was obtained for the positions of lines and bands.

The disagreement in absorption magnitude has been investigated by adjusting two different input parameters which might be the source of error. One possible source of error in the laboratory data is in establishing the amount of carbon dioxide in the optical path of the spectrometer. An adjustment of approximately +8.6% in the reported concentrations produces results that are greatly improved. Dr. Burch felt that an error that large was highly unlikely. He suggested that a similar effect would result from a theoretical half-width error for the absorption lines, and that these parameters were not well known.

Calculations using a +8% adjustment in the half-widths produces results that give good agreement with the laboratory data. This was true for the data that were observed through a skewed slit function and for later higher-resolution data that were properly taken.

The results of our efforts were made available to Drs. Burch and McClatchey, and further discussions will be held in order to reach an agreement on the most probable cause for the discrepancies. If these questions can be resolved within the next few months, new line-by-line carbon dioxide calculations will be carried out including the necessary adjustments before regular data processing begins.

Comparisons similar to those for the carbon dioxide bands are also being made for the ozone bands in the near future. The laboratory data available for the ozone bands are not of high resolution, and the fine details of the spectra cannot be compared. However, the low-resolution absorption magnitudes will still be useful for evaluating the accuracy of our calculations. The comparison is accomplished by degrading the high-resolution line-by-line calculations by numerically applying an appropriate spectrally-weighted instrument slit function. Initial comparisons for ozone also indicate discrepancies in results for the 9.6- μ m bands.

The homogeneous path line-by-line calculations and laboratory measurement comparisons are critical evaluations, since measurements for inhomogeneous paths are very limited and of little use (because exact temperature, pressure, and concentration specifications are not well known). Transmittances for atmospheric paths, therefore, must be determined from accurate homogeneous calculations appropriately applied for atmospheric conditions specified during the simulation process.

The final step in the verification of the spectral calculations is to compare simulated space measurements against actual satellite radiometer measurements. Some data have already been collected for this purpose. Also, software is under development to perform the necessary calculations and to analyze the results.

We are preparing to process 45 days of MFR data to compare our ozone data with similar data for the same period using the TIROS N and Nimbus 7 sensors. The data period for comparison covers January 1 to mid-February 1979. In preparation for this comparison, several codes required for generating the simulated radiances and total ozone

retrieval models are being modified to implement changes to improve their accuracy and computational efficiency. For example, the running time of the codes used to generate simulated radiances has been reduced more than 50%. Additionally, recent ozonesonde data have been obtained from the World Ozone Data Center (Downsview, Canada) in order to bring our ozonesonde data base up to date. The ozonesonde data are used as input to the simulated radiance calculations. The ozonesonde data base includes nearly 6000 soundings from which representative sets of data are selected for the season for which the radiances are simulated.

Software has been developed to perform various analyses on retrieval results. Extraction of various parameters and data for specific regions and times from existing archives is now possible. These extractions can now be printed and displayed, and various manipulation options are being developed for performing analyses of various retrieval problems.

3.3 DATA BASING AND DATA PROCESSING

The major task for the past year has been the development of an automated data basing, archiving, and processing system. The computing capability at the Atmospheric Release Advisory Capability (ARAC) center at LLL will be used for data basing and data processing. We have purchased some additional hardware to supplement the capabilities of the DEC VAX 11/780 computer system which became operational in June 1979 at the ARAC center. A seven-track tape drive was added to enable the input data tapes from AFGWC to be handled, and a floating point accelerator was added to enhance the computation speed for MFR data processing. A 176 megabyte disc system was added to increase the online data storage capacity. One disc can hold one month of satellite and processed data, which is a convenient size for building the long-term archival data base and for data analysis purposes.

High density tape (6250 bpi) has been selected as the long-term storage medium for the data base. Disc packs had initially been considered as the storage medium, but they were rejected when investigation showed that there is a serious risk of catastrophic disc failure and head crashes when the

disc packs are handled frequently. The tape medium provides considerably less vulnerability, can be inexpensively duplicated, is cost effective over the data collection period even with the necessary additional hardware, and provides only slightly inferior accessibility to the data.

The presently available 1600 bpi tape technology will be used through the software development phase of this effort since the 6250 bpi tape technology has only recently become available for use on the VAX 11/780 computer system. The high density tape drive has been ordered and will arrive before regular data processing is scheduled to begin.

An LLL-developed scientific data management system called FRAMIS has been chosen for use with the SOAC/DMSP data base. This is a "relational algebra" approach at the forefront of current data base technology. LLL's Computation Department has already invested in a multi-man-year effort to develop this capability and plans considerable expansion and enhancement in the coming year. The system is currently available on the CDC 7600 computers, and we have completed most of the modifications necessary to transfer FRAMIS to the VAX 11/780 computer system. Testing of the initial capability is scheduled to begin in December 1979. Nearly 300 computer routines are being rewritten to run on the new system.

The codes that process and calibrate the raw DMSP radiometer data are being converted to the VAX 11/780 system. Part of the conversion involves the word size dependency problem (AFGWC = 36 bits, LLL 7600 = 60 bits, and VAX 11/780 = 32 bits), and part involves the development of a new quality control package to evaluate the sensor data stream continuously while processing the radiometer data and to provide a record of that performance for the data base archive quality assurance.

Significant progress has been made in how total ozone data are mapped and contoured. We completed the development of a computer code that generates an "intelligent fill" in data-void areas of the daily global ozone analysis. The code generates the fill-field by first mapping and averaging the satellite ozone retrievals in 2-deg latitude-longitude bins. The bins remaining empty after 24 hours of satellite data mapping require filling. Filling is accomplished by one of the following methods, which depends on the data available. The preference for

each method decreases in the order listed: (1) interpolate between the binned data of the day preceding and the day following, (2) use the binned data from the day preceding or the following, (3) use the zonal average values that are computed from the binned data for that day, or (4) use zonal average values that are taken from known climatology.

The resulting global fill-field is not combined with the binned data until it is smoothed. It is smoothed by applying an elementary filter that approximates a bivariate normal function three successive times. After each pass of the filter, the filtered fill-field is overlaid with the 2-deg binned data for that day. The overlaying and filtering process blends the fill-field in the data-void areas with the binned data outside the data-void areas for that day. Also, the filtering process removes small-scale features (e.g., 5-deg horizontal wavelength and smaller) but retains large-scale features (e.g., a wavelength of 60 deg is retained at 96% of its original amplitude) in the data-void areas. Thus only the large-scale features that change little in amplitude and position from day to day are used as an "intelligent fill."

The generated fill-field may be used with either the spline analysis code or the newly developed filter analysis code, which are used to generate ozone contour maps. In either code, the fill-field is used only to fill the data void regions of the global data-set.

The methodology of the filter analysis code is essentially to compute an average grid point value in each 2-deg latitude-longitude bin, fill the data-void bins using the fill-field, and filter the gridded data using a Lanczos filter (Duchon, 1979) having a preselected cutoff frequency. The methodology of the spline analysis is to divide the globe into 10-deg latitude-longitude regions, fit the data within a region in a least-squares sense with B-splines assuring continuity across region boundaries, and treating filled portions of the region as data points.

A study of the two methods has shown that the filter method requires 85% less computer time and fits the input data better than the spline method for all filter cutoff wavelengths (or cutoff frequency) smaller than 20-deg latitude-longitude. The smoothness of the analysis, generated using the filter method, can be varied by varying the cutoff wavelength; increasing the cutoff wavelength increases the smoothness. Two examples of analyses with cutoff wavelengths (λ_c) of 10 and 16 deg are

shown in Figs. 15 and 16, respectively. The shaded areas of each map indicate data-void regions. The analysis in Fig. 16 is aesthetically more pleasing than Fig. 15, but has less information content than the analysis in Fig. 15. We experimented with a number of values of λ_c ranging from 6 to 20 deg and selected 10 deg as a balance between aesthetics and information content.

We have also developed codes that generate analyses at 2.5-deg latitude-longitude grid intervals matching the National Meteorological Center (NMC) global temperature/pressure-height grid. This analysis requires 35% less computer time than the 2-deg analysis using the filter method. The 2.5-deg analysis is essentially the same as the 2-deg analysis except for a modulation of the minimum and maximum (L and H) values on the order of 1%. Figure 17 is an example of the 2.5-deg analysis using $\lambda_c = 10$ deg.

Our plan is to process the 45 days of data (January 1–February 15, 1979) for comparison with data from TIROS N and Nimbus 7 using the filter method at 2-deg latitude-longitude grid point intervals. When regular data processing begins, we will process the data at 2.5-deg grid intervals using the filter method.

3.4 DATA ANALYSIS

During the past year the number of Dobson observatories that have agreed to take special ozone measurements increased from 33 to 37. Also, measurements from the second Dobson instrument (which is automated) at Arosa are being sent to us. The locations of the participating Dobson observatories are shown in Fig. 18. Special observations are made daily at the time of DMSP satellite overpasses. The data that we receive are entered into a Dobson ozone data base for comparison with the MFR-derived ozone data. The Dobson data base extends from Spring 1977 to the present. All of the Dobson data that we receive are also forwarded to the NOAA Satellite Physics Branch, Silver Spring, Maryland, where they are in turn sent to other NOAA and NASA users. Quality assurance codes were developed to check the Dobson data for any obvious or suspected errors. Software was also written to provide information in a graphical format on the availability of ozone data in the Dobson data base for each individual station.

FIG. 15. Analysis for June 21, 1977 at 2-deg grid interval ($\lambda_c = 10^\circ$).

FIG. 17. Analysis for June 21, 1977 at 2.5-deg grid interval ($\lambda_c = 10^\circ$).

FIG. 18. Location of Dobson spectrophotometer observatories where special measurements of total ozone are taken for comparison with MFC-derived total ozone data.

Preliminary analyses have been made between the MFR ozone data that we processed during the feasibility study and conventional meteorological data fields. Upper-atmospheric data of temperature, pressure-height, wind velocity and humidity were obtained from the National Meteorological Center, Boulder, Colorado. Computer codes were built to access the upper-tropospheric and stratospheric data. Black and white and color graphics routines were used to display multi-parameter variability. A polar map projection is currently being used for displaying the data.

A comparison between the spatial variabilities of total ozone and 100-mb temperatures is shown in Fig. 19 for the Southern Hemisphere. The polar projection extends from the South Pole to 20°S latitude. The ozone data are the average of the 13 days of MFR data that have been processed from June 1977. The Southern Hemisphere was chosen for comparison because it is dynamically more active than the Northern Hemisphere at this time of year.

The total ozone isolines in middle latitudes indicate a dominance of wave number five. The 100-mb temperature data indicate a dominance of wave number five or six. At several locations the total

ozone and temperature waves are out of phase with each other. Examples of this may be seen over South America and near Africa. At these locations, relatively higher (lower) amounts of total ozone are associated with warmer (colder) lower-stratospheric temperatures. Total ozone maxima occurring near longitudes of 10°E, 170°E and 80°W at 50°S latitude are located near cores of warm stratospheric air. The relationships between temperature and total ozone just described are not apparent at all locations in the map. The region of high total ozone south of Australia corresponds well with the location of high ozone values for June indicated by London *et al.* (1976) for data from 1957–1967. The MFR total ozone data show more structure in this feature than is indicated by London *et al.* (1976).

Software is being developed that will be used to perform a power spectral analysis of the ozone field from MFR data. Also, work has begun on code development for spherical harmonic analyses of the MFR total ozone data. This line of research is one of several to be followed in later months. A number of methods of discerning relationships among various atmospheric variables are being tested and analyzed. Thus far the methods have been applied to a three-day period (in June 1977) in the Southern

FIG. 19. Southern Hemisphere June 1977 total ozone (units: M.atm.cm; solid line) from satellite MFR and 100-mb temperature ($^{\circ}\text{C}$; dashed line) from radiosonde.

Hemisphere. Several promising graphical display and data analysis tools have been developed which

should prove to be very useful when we begin regular data processing.

4. WORK IN PROGRESS

We are in the process of developing a two-dimensional transport-kinetics model which will be in the programming and initial validation stage during most of Fiscal Year 1980. This model will be used to study latitudinal and seasonal effects of various atmospheric perturbations.

A steady state version of the one-dimensional transport-kinetics code is under development which will significantly reduce the computation time needed for steady-state calculations. Most of our sensitivity studies involve computing the change in total ozone at steady state, so this code will be used extensively in the future.

Routine processing of the DMSP MFR data will begin in the spring of 1980 and will extend through Fiscal Year 1981. In all, data from four satellites with overlapping coverage over a three-year period will be processed. Daily maps of total ozone and monthly statistics and comparisons with Dobson data will be published for distribution to the scientific community. We will also be conducting studies of the spatial and temporal variability of ozone related to natural and man-made influences.

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APPENDIX A

DESCRIPTION OF LLL ONE-DIMENSIONAL TRANSPORT-KINETICS MODEL

(AS PRESENTED AT NASA HARPERS FERRY WORKSHOP 1979)

The local concentrations of trace species in an air parcel are determined by the chemical and photochemical processes and nonchemical sources and sinks occurring within the parcel, and by the transport and radiative fluxes into and out of the parcel. One-dimensional mathematical models of the chemical processes in the stratosphere are governed by the chemical species conservation equation

$$\partial c_i / \partial t + \frac{\partial}{\partial z} F_i(c_i, z, t) = P_i[c, J(z, t, c), k(z, t), \rho] - L_i[c, J(z, t, c), k(z, t), \rho] c_i + S_i(z, t) \quad (\text{A-1})$$

where $c_i = c_i(z, t)$ is the concentration of the i^{th} chemical constituent; c is the general representation of all constituents; P_i and $L_i c_i$ are the production and loss of c_i due to photochemical interactions; T is the ambient air temperature; ρ is the ambient air density; F_i is the vertical transport flux of c_i ; S_i represents any other possible sinks or sources of c_i ; J represents photodissociation coefficients; k represents chemical reaction rate coefficients; and all of these variables are defined at a given vertical position z at time t . The explicit display of the major interdependent relations of these variables in Eq. (A-1) illustrates the nonlinearity and general complexity of this mathematical system. Equation (A-1) is defined over a spatial domain D with appropriate boundary conditions. There is one conservation equation for each chemical species treated.

PHYSICAL DOMAIN

The LLL one-dimensional model extends from the ground to 56.25 km. The model currently calculates the vertical concentration distributions of 39 (2 of which are used only in sensitivity studies) atmospheric trace constituents. The model contains 134 (14 of which are used only in sensitivity studies) chemical or photochemical reactions. Table A-1 lists the species solved for in the model. Of these species, $O(^1D)$, H , and N are assumed to be in instantaneous equilibrium. The vertical grid structure is variable, but for the calculations reported here, we have a 0.5-km-thick layer at the surface, 1-km thick layers extending from 0.5 to 34.5 km, a 1.75-km thick layer between 34.5 and 36.25 km and 2.5-km thick layers extending to 56.25 km.

TRANSPORT REPRESENTATION

The net vertical transport flux, F_i , of any minor constituent c_i is represented through a diffusion approximation in which F_i is assumed to be proportional to the gradient of the mixing ratio of that trace species:

$$F_i = -K_z \rho \frac{\partial}{\partial z} (c_i / \rho) \quad (\text{A-2})$$

where K_z is the one-dimensional vertical diffusion coefficient. The LLL K_z profile (shown in Fig. A-1) used in the calculations for this report was originally based on an analysis of N_2O and CH_4 measurements (NAS, 1976) with considerations also given to measurements of radionuclide debris transport in the lower stratosphere.

The LLL one-dimensional model has been designed such that profiles of K_z utilized by other groups (or at previous times) can be easily incorporated. Such profiles have been utilized to test the sensitivity of the results to transport parameterization uncertainties.

TABLE A-1. Species calculated in LLL one-dimensional model.

O(³ P)	Cl	CH ₄
O ₃	ClO	HCO
NO	ClONO ₂	CH ₂ O
NO ₂	CINO ₂	CH ₃
N ₂ O	HCl	CH ₃ OOH
HNO ₃	OCIO ^a	CH ₃ O
OH	HOCl	CH ₃ O ₂
HO ₂	CH ₃ Cl	CO
H ₂ O ₂	CF ₂ Cl ₂	H ₂
NO ₃	CFCl ₃	O(¹ D)
N ₂ O ₅	CH ₃ CCl ₃	N
H ₂ O	ClO ₃ ^a	H
HONO	CCl ₄	
HNO ₄		

^aUsed only in sensitivity studies.

CHEMISTRY

We have used two 1979 versions of model chemistry in this report (see Tables A-2 through A-4). 1979a chemistry was based primarily on the rate recommendations in JPL (1979). However, several reactions discussed in JPL (1979) are omitted in the model, and several reactions not discussed in JPL (1979) are included. This chemistry was used for many sensitivity calculations carried out in the spring of 1979. 1979b chemistry was based almost exclusively on the draft chapter on chemical reaction rates prepared at the NASA Harpers Ferry Workshop (June, 1979). It has a few comparatively minor differences from the final draft of that report, and it includes a few reactions not assessed at the NASA Workshop.

Two reactions treated in the 1979a chemistry are controversial and are of some importance to our sensitivity studies. These are

and

In the 1979a chemistry, we used the slower of the two JPL-recommended rate constants for chlorine nitrate formation, and we adopted an expression for HCl formation from OH + ClO that is about half the upper limit for that reaction path. In the 1979b chemistry, we used the faster of the two recommendations for the chlorine nitrate formation rate coefficient. Three considerations inspired this choice: (1) the majority of the chemistry panel seemed to favor the faster expression, (2) even if the bulk of the reaction between ClO and NO₂ leads to other products (as suggested by those favoring the slower rate coefficient), the other products might easily have an effect on stratospheric chemistry similar to that of ClONO₂, and (3) it improved the comparison between calculation and observation for both ClO and ClONO₂.

FIG. A-1. Vertical transport coefficients currently being used by two modelling groups.

In our 1979b chemistry we omitted the reaction forming HCl from $\text{OH} + \text{ClO}$. The decision to include this reaction in the 1979a chemistry was based on privately communicated preliminary results that seemed to suggest that the reaction probably occurred, but they have since been interpreted as providing only an upper limit. Both of these controversial choices of rate coefficient have a significant impact on model sensitivities (especially for ClX) but they oppose each other. As a result, 1979a and 1979b chemistries yield qualitatively similar perturbational sensitivities for both NO_x and ClX perturbations. The 1979b chemistry is less controversial than the 1979a chemistry and is to be preferred for purposes of comparison with other workers. All primary assessments have been repeated using 1979b chemistry. However, several sensitivity studies were not repeated, since it seemed unlikely that the qualitative results of those sensitivity studies would differ if they were repeated, and because the 1979a chemistry is well within the limits of reasonable uncertainty in our present knowledge of the atmosphere. The two chemistries are also useful in emphasizing the existence of processes for which no clear recommendation is available.

TABLE A-2. Chemical reactions and rate coefficients where $k = A e^{B/T}$ used in 1979 model chemistry.

Reaction	A ^a	B	Note
1. $O + O_2 \xrightarrow{M} O_3$	See Table A-3	-	3
2. $O + O_3 \rightarrow 2O_2$	1.5×10^{-11}	-2218	1
3. $O_3 + NO \rightarrow NO_2 + O_2$	2.3×10^{-12}	-1450	1
4. $O + NO_2 \rightarrow NO + O_2$	9.3×10^{-12}	0	1
5. $N_2O + O(^1D) \rightarrow N_2 + O_2$	4.8×10^{-11}	0	1
	5.1×10^{-11}	0	2
6. $N_2O + O(^1D) \rightarrow 2NO$	6.2×10^{-11}	0	1
	5.9×10^{-11}	0	2
7. $N + O_2 \rightarrow NO + O$	4.4×10^{-12}	-3220	1
8. $N + NO \rightarrow N_2 + O$	3.4×10^{-11}	0	1
9. $O(^1D) + H_2O \rightarrow 2OH$	2.3×10^{-10}	0	1
10. $O_3 + OH \rightarrow HO_2 + O_2$	1.6×10^{-12}	-940	1
11. $O + OH \rightarrow O_2 + H$	4.0×10^{-11}	0	1
12. $O_3 + HO_2 \rightarrow OH + 2O_2$	1.1×10^{-14}	-580	1
13. $O + HO_2 \rightarrow OH + O_2$	3.5×10^{-11}	0	1
14. $H + O_2 \xrightarrow{M} HO_2$	See Table A-3	-	3
15. $O_3 + H \rightarrow OH + O_2$	1.4×10^{-10}	-470	1
16. $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	2.5×10^{-12}	0	1
17. $HO_2 + OH \rightarrow H_2O + O_2$	4.0×10^{-11}	0	1
18. $OH + NO_2 \xrightarrow{M} HNO_3$	See Table A-3	-	1
19. $OH + HNO_3 \rightarrow H_2O + NO_3$	8.5×10^{-14}	0	1,10
20. $H_2O_2 + OH \rightarrow H_2O + HO_2$	1.0×10^{-11}	-750	1
21. $N_2 + O(^1D) \xrightarrow{M} N_2O$	See Table A-3	-	3
22. $N + NO_2 \rightarrow N_2O + O$	2.1×10^{-11}	-800	1
23. $NO + O \xrightarrow{M} NO_2$	See Table A-3	-	3
24. $NO + HO_2 \rightarrow NO_2 + OH$	4.3×10^{-12}	200	1
	3.4×10^{-12}	250	2
25. $H_2 + O(^1D) \rightarrow OH + H$	9.9×10^{-11}	0	1
26. $OH + OH \rightarrow H_2O + O$	1.0×10^{-11}	-500	1
27. $N + O_3 \rightarrow NO + O_2$	2.0×10^{-11}	-3000	4
28. $NO_2 + O_3 \rightarrow NO_3 + O_2$	1.2×10^{-13}	-2450	1
29. $OH + OH \xrightarrow{M} H_2O_2$	See Table A-3	-	3
30. $H_2O_2 + O \rightarrow OH + HO_2$	2.8×10^{-12}	-2125	1
31. $CO + OH \xrightarrow{M} H + CO_2$	See Table A-3	-	3

^aWhen two entries are given, the lower one corresponds to 1979a chemistry and the upper one corresponds to 1979b chemistry.

TABLE A-2. (Continued)

Reaction	A ^a	B	Note
32. $O(^1D) + M \rightarrow O + M$	2.2×10^{-11}	99	5
33. $Cl + O_3 \rightarrow ClO + O_2$	2.8×10^{-11}	-257	1
34. $Cl + NO_2 \xrightarrow{M} ClNO_2$	See Table A-3	-	3
35. $ClO + O \rightarrow Cl + O_2$	7.7×10^{-11}	-130	1
36. $NO + ClO \rightarrow NO_2 + Cl$	7.8×10^{-12}	250	1
37. $ClO + NO_2 \xrightarrow{M} ClONO_2$	See Table A-3	-	3
38. $HCl + O(^1D) \rightarrow Cl + OH$	1.4×10^{-10}	0	1
39. $OH + HCl \rightarrow H_2O + Cl$	2.8×10^{-12}	-425	1
40. $O + HCl \rightarrow OH + Cl$	1.14×10^{-11}	-3370	1
41. $Cl + HO_2 \rightarrow HCl + O_2$	4.5×10^{-11}	0	1
42. $CFCl_3 + O(^1D) \rightarrow 3Cl$	2.2×10^{-10}	0	1,6
43. $CF_2Cl_2 + O(^1D) \rightarrow 2Cl$	1.4×10^{-10}	0	1,6
44. $Cl + H_2 \rightarrow HCl + H$	3.5×10^{-11}	-2290	1
45. $Cl + H_2O_2 \rightarrow HCl + HO_2$	8.9×10^{-12} 1.7×10^{-12}	-925 -384	11 2
46. $ClONO_2 + O \rightarrow ClO + NO_3$	3.0×10^{-12}	-808	1,10
47. $CH_3Cl + OH \rightarrow Cl + H_2O + HO_2$	2.2×10^{-12}	-1142	1
48. $NO + NO_3 \rightarrow 2NO_2$	2.0×10^{-11} 8.7×10^{-12}	0 0	1 3
49. $NO_2 + O \xrightarrow{M} NO_3$	See Table A-3	-	3
50. $HO_2 + NO_3 \xrightarrow{M} N_2O_5$	See Table A-3	-	3
51. $N_2O_5 \xrightarrow{M} NO_2 + NO_3$	See Table A-3	-	3
52. $N_2O_5 + H_2O \rightarrow 2HNO_3$	1.0×10^{-20}	0	7
53. $O(^1D) + O_3 \rightarrow 2O_2$	1.2×10^{-10}	0	1
54. $HO_2 + HO_2 + H_2O \rightarrow H_2O_2 + O_2 + H_2O$	See Table A-3	-	3
55. $O + NO_3 \rightarrow O_2 + NO_2$	1.0×10^{-11}	0	1
56. $HO_2 + NO_2 \xrightarrow{M} HNO_4$	See Table A-3	-	3
57. $HNO_4 \xrightarrow{M} HO_2 + NO_2$	See Table A-3	-	3
58. $OH + HNO_4 \rightarrow H_2O + NO_2 + O_2$	6.0×10^{-12}	-750	1,8
59. $Cl + HNO_4 \rightarrow HCl + NO_2 + O_2$	3.0×10^{-12}	-300	8
60. $HO_2 + ClO \rightarrow O_2 + HOCl$	7.0×10^{-13}	500	1
61. $Cl + HOCl \rightarrow HCl + ClO$	3.0×10^{-12}	-300	8
62. $OH + HOCl \rightarrow H_2O + ClO$	3.0×10^{-12}	-800	1

^aWhen two entries are given, the lower one corresponds to 1979a chemistry and the upper one corresponds to 1979b chemistry.

TABLE A-2. (Continued)

Reaction	A ^a	B	Note
63. $O + HOCl \rightarrow OH + ClO$	1.0×10^{-11}	-2200	1
64. $OH + CH_4 \rightarrow CH_3 + H_2O$	2.4×10^{-12}	-1710	1
65. $O + CH_4 \rightarrow CH_3 + OH$	3.5×10^{-11}	-4550	1
66. $O(^1D) + CH_4 \rightarrow CH_2O + H_2$	1.0×10^{-11}	0	1
67. $O(^1D) + CH_4 \rightarrow CH_3 + OH$	1.3×10^{-10}	0	1
68. $CH_4 + Cl \rightarrow HCl + CH_3$	9.9×10^{-12}	-1359	1
69. $Cl + CH_3Cl \rightarrow HO_2 + Cl + 2HCl$	3.4×10^{-11}	-1256	1,6
70. $CH_3O_2 + NO \rightarrow NO_2 + CH_3O$	7.0×10^{-12}	0	1
	8.0×10^{-12}	0	2
71. $Cl + CH_2O \rightarrow HCl + HCO$	9.2×10^{-11}	-68	1
72. $CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$	6.0×10^{-12}	0	1
	1.0×10^{-12}	0	2
73. $CH_3O + O_2 \rightarrow CH_2O + HO_2$	5.0×10^{-13}	-2000	1
74. $OH + CH_2O \rightarrow H_2O + HCO$	1.0×10^{-11}	0	1
	1.7×10^{-11}	-100	2
75. $O + CH_2O \rightarrow HCO + OH$	3.2×10^{-11}	-1550	1,10
	2.8×10^{-11}	-1540	2
76. $HCO + O_2 \rightarrow CO + HO_2$	5.0×10^{-12}	0	1
77. $OH + CH_3OOH \rightarrow CH_3O_2 + H_2O$	5.0×10^{-12}	-750	1,10
	6.2×10^{-12}	-750	2
78. $CH_3 + O \rightarrow CH_2O + H$	1.0×10^{-10}	0	1
79. $CH_3O_2 + O_3 \rightarrow CH_3O + 2O_2$	1.0×10^{-14}	-600	9
80. $CH_3O_2 + O \rightarrow CH_3O + O_2$	3.0×10^{-11}	0	9
81. $ClO + OH \rightarrow HO_2 + Cl$	9.2×10^{-12}	0	1
	2.0×10^{-11}	0	12
82. $CH_3 + O_2 \xrightarrow{M} CH_3O_2$	See Table A-3	-	3
83. $ClO + OH \rightarrow HCl + O_2$	Not used ($\sim 10^{-22}$)	-	12
	2.0×10^{-12}	-	
84. $H_2 + OH \rightarrow H_2O + H$	1.2×10^{-11}	-2200	1
	Not used	-	
85. $H + HO_2 \rightarrow H_2 + O_2$	4.2×10^{-11}	-350	1
	Not used	-	
86. $OH + CH_3OOH \rightarrow CH_2O + H_2O + OH$	5.0×10^{-12}	-750	1,10
	Not used	-	
87. $O + HNO_4 \rightarrow OH + NO_2 + O_2$	1.0×10^{-12}	-2200	1,10
	Not used	-	
88. $OH + ClONO_2 \rightarrow HOCl + NO_3$	1.2×10^{-12}	-333	1,10
	Not used	-	

^aWhen two entries are given, the lower one corresponds to 1979a chemistry and the upper one corresponds to 1979b chemistry.

TABLE A-2 (Continued)

Reaction	A ^a	B	Note
89. $\text{Cl} + \text{ClONO}_2 \rightarrow 2\text{Cl} + \text{NO}_3$	1.7×10^{-12} Not used	-607 -	1,10
90. $\text{HONO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_2$	6.6×10^{-12} Not used	0 -	1
91. $\text{OH} + \text{NO} \xrightarrow{\text{M}} \text{HONO}$	See Table A-3 Not used	- -	3
92-97. (not used; reactions used only in sensitivity studies)			
98. $\text{O} + \text{OCIO} \rightarrow \text{ClO} + \text{O}_2$	2.5×10^{-11}	-1166	1
99. $\text{NO} + \text{OCIO} \rightarrow \text{NO}_2 + \text{ClO}$	2.5×10^{-12}	-600	1

^aWhen two entries are given, the lower one corresponds to 1979a chemistry and the upper one corresponds to 1979b chemistry.

Notes to Table A-2

1. Draft report of NASA Harpers Ferry Workshop.
2. JPL (1979). Where only one entry is given for the rate coefficient, 1979a and 1979b are the same. Usually this means that the first two references at the end of this Appendix give the same recommendation.
3. The reaction is pressure-dependent. See Table A-3 for discussion.
4. Estimate designed to be compatible with upper limit given in the first reference at the end of this Appendix, and low enough to have no significant effect on model performance. Reaction is retained only to facilitate reintroduction if the evaluated upper limit should prove to be in error.
5. Weighted average of the rates of $\text{O}(^1\text{D}) + \text{N}_2$ and $\text{O}(^1\text{D}) + \text{O}_2$ from the first two references.
6. Product chemistry has been simplified.
7. Estimated reaction rate. This estimate is designed to include a possible heterogeneous contribution to the overall reaction. Important only in the lower troposphere.
8. Estimated reaction rate. This rate is estimated based on the assumption that HNO_4 and HOCl resemble H_2O_2 (as treated in JPL, 1979) in reactions with Cl and OH .
9. Estimated reaction rate. Rate is estimated based on the assumption that CH_3O_2 closely resembles HO_2 in reaction with O or O_3 .
10. Products are not given in the first two references at the end of this Appendix. The assumed products are based on the products that seem most plausible based on chemical considerations.
11. Rate based on a draft of the first reference that trivially differs from the final draft.
12. 1979a chemistry treated the reactions of HO and ClO based on privately communicated qualitative preliminary results. The treatment is nearly an upper limit to the plausible rate coefficients based on the recent results of Leu and Lin (1979).

Our treatment of photolysis reactions has also been modified. There is evidence for a moderate temperature dependence for many photoabsorption cross sections. With the exception of ozone, NO , and O_2 photolysis, we have not treated this temperature dependence explicitly, but have used cross sections measured at roughly 230 K for all temperatures. As a result our calculated trace species photodissociation rates should be more accurate for the stratosphere than for the lower troposphere.

For ozone photolysis we use quantum yields based on the recommendations of NASA (1979). Our treatment of O_2 photolysis is based on Hudson and Mahle (1972) while our treatment of NO photolysis is based on Frederick and Hudson (1979).

TABLE A-3. Rate coefficients used for pressure-dependent reactions.

Expression 1					
$k = \frac{A_0[M](300/T)^{n_0}}{1 + A_0[M](300/T)^{n_0}/A_1(300/T)^{n_1}} 0.06 \left\{ 1 + \left[\log_{10} \left(\frac{A_0[M](300/T)^{n_0}}{A_1(300/T)^{n_1}} \right)^2 \right]^{-1} \right\}$					
Reaction	A_0^a	n_0	A_1	n_1	Note
$\text{HO}_2 + \text{NO}_2 \xrightarrow{M} \text{HNO}_4$	2.1×10^{-31}	5.0	6.5×10^{-12}	5.0	1
$\text{OH} + \text{NO}_2 \xrightarrow{M} \text{HNO}_3$	2.6×10^{-30}	2.9	2.4×10^{-11}	1.3	1
$\text{ClO} + \text{NO}_2 \xrightarrow{M} \text{ClONO}_2$	1.6×10^{-31}	3.4	1.5×10^{-11}	1.9	1,2
	3.5×10^{-32}	3.8	1.5×10^{-11}	1.9	1,2
$\text{O} + \text{O}_2 \xrightarrow{M} \text{O}_3$	6.2×10^{-34}	2.1	-	0	1
$\text{CH}_3 + \text{O}_2 \xrightarrow{M} \text{CH}_3\text{O}_2$	2.2×10^{-31}	2.2	2.0×10^{-12}	1.7	1
$\text{O}(^1\text{D}) + \text{N}_2 \xrightarrow{M} \text{N}_2\text{O}$	3.5×10^{-37}	0.45	-	0	1
$\text{Cl} + \text{NO}_2 \xrightarrow{M} \text{ClNO}_2$	1.6×10^{-30}	1.9	3.0×10^{-11}	1.0	1
$\text{H} + \text{O}_2 \xrightarrow{M} \text{HO}_2$	5.5×10^{-32}	1.4	-	0	1
$\text{OH} + \text{NO} \xrightarrow{M} \text{HNO}_2$	6.7×10^{-31}	3.3	3.0×10^{-11}	1.0	1
$\text{OH} + \text{OH} \xrightarrow{M} \text{H}_2\text{O}_2$	2.5×10^{-31}	0.8	3.0×10^{-11}	1.0	1
$\text{NO}_2 + \text{NO}_3 \xrightarrow{M} \text{N}_2\text{O}_5$	1.4×10^{-30}	2.8	9.0×10^{-13}	-0.7	1
	$1.8 \times 10^{-32} e^{1316/T}$	0	$9.5 \times 10^{-13} e^{58/T}$	0	3
$\text{O} + \text{NO} \xrightarrow{M} \text{NO}_2$	1.2×10^{-31}	1.8	3.0×10^{-11}	-0.3	1
	$1.6 \times 10^{-32} e^{584/T}$	0	-		4
$\text{O} + \text{NO}_2 \xrightarrow{M} \text{NO}_3$	9.0×10^{-32}	2.0	2.2×10^{-11}	0	1
	1.0×10^{-31}	0	-	0	4
$\text{N}_2\text{O}_5 \xrightarrow{M} \text{NO}_2 + \text{NO}_3$	$1.18 \times 10^{-3} e^{-11180/T}$	2.8	$7.52 \times 10^{14} e^{-11180/T}$	-0.7	5
	$1.6 \times 10^{-5} e^{-9864/T}$	0	$7.94 \times 10^{14} e^{-11122/T}$	0	4
<hr/>					
$\text{HNO}_4 \xrightarrow{M} \text{HO}_2 + \text{NO}_2$			$k = \frac{5.2 \times 10^{-6} e^{-10015/T}}{1 + 4.86 \times 10^{-12} M^{0.61}}$		7
$\text{OH} + \text{CO} \xrightarrow{M} \text{H} + \text{CO}_2$			$k = 1.35 \times 10^{-13} \left(1 + \frac{M}{2.46 \times 10^{19}} \right)$		1
$\text{HO}_2 + \text{HO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O} + \text{O}_2$			$k = \frac{1.1 \times 10^{-34} e^{3730/T}}{1 + M \cdot 3.5 \times 10^{-16} e^{-2060/T}}$		6

^aWhen two entries are given, the lower one corresponds to 1979a chemistry and the upper one corresponds to 1979b chemistry.

Notes to Table A-3

1. Expression given in NASA (1979). 1979a chemistry differed from 1979b chemistry in that the parameter 0.6 in expression (1) was set equal to 0.8 in the expression used for 1979a chemistry.
2. Both expressions are recommended with no clear preference. The lower value is used in the 1979a chemistry and the upper one is used in the 1979b chemistry.
3. Private communication, D. Golden, SRI International, Inc. (1979).
4. Based on data in NBS 513 (1978).
5. Based on data in the first reference and the equilibrium constant from NBS 513 (1978).
6. Based on Cox (1978).
7. Based on Graham *et al.* (1978).

TABLE A-4. Photolysis reactions. Alternative products of reaction are shown in parentheses, but they were not used in either the 1979a or 1979b chemistry.

Reaction	Note	Reaction	Note
1. $O_2 \rightarrow 2O$	1,2	16. $CF_2Cl_2 \rightarrow 2Cl$	4,8
2. $O_3 \rightarrow O + O_2$	1,3	17. $CFCl_3 \rightarrow 3Cl$	4,8
3. $O_3 \rightarrow O(^1D) + O_2$	1,3	18. $CCl_4 \rightarrow 4Cl$	4,8
4. $NO_2 \rightarrow NO + O$	1,4	19. $N_2O_5 \rightarrow NO_3 + NO_2 (2NO_2 + O)$	4,6
5. $N_2O \rightarrow N_2 + O(^1D)$	4	20. $NO_3 \rightarrow NO + O_2$	4
6. $NO \rightarrow N + O$	5	21. $NO_3 \rightarrow NO_2 + O$	4
7. $HNO_3 \rightarrow OH + NO_2$	4	22. $H_2O \rightarrow H + OH$	9
8. $H_2O_2 \rightarrow 2OH$	4	23. $HNO_4 \rightarrow HO + NO_3 (HO_2 + NO_2)$	10,6
9. $HO_2 \rightarrow OH + O$	4	24. $HOCl \rightarrow OH + Cl$	4
10. $ClONO_2 \rightarrow Cl + NO_3 (ClO + NO_2)$	4,6	25. $CH_3OOH \rightarrow CH_3O + OH$	4
11. $HCl \rightarrow H + Cl$	4	26. $CH_2O \rightarrow HCO + H$	11
12. $ClO \rightarrow Cl + O$	7	27. $CH_2O \rightarrow CO + H_2$	11
13. $ClO \rightarrow Cl + O(^1D)$	Not used	28. $CH_3Cl \rightarrow CH_3 + Cl$	4
14. $ClNO_2 \rightarrow Cl + NO_2$	4	29. $HONO \rightarrow OH + NO$	4
15. $OCIO \rightarrow ClO + O$	7		

Notes to Table A-4.

1. Contributes to optical depth of model atmosphere.
2. Schumann-Runge bands are given special treatment based on Hudson and Mahle (1972).
3. Quantum yields of reactions (2) and (3) are given special treatment based on temperature-dependent treatment of JPL (1979).
4. Based on the data of JPL (1979). Where data for several temperatures is given, we have used the data at 230 K.
5. Nitric oxide photolysis is based on treatment of Frederick and Hudson (1979). We have used the photolysis rates averaged over the sunlit hemisphere for day time photolysis rates. 1979a chemistry used the treatment of Cieslik and Nicolet (1973).

6. The products used for XNO_3 ($\text{X} = \text{Cl}, \text{OH}, \text{NO}_2$) changed between our 1979a and 1979b chemistries. For 1979a they were based on the path of lowest endoergicity (except for N_2O_5 which was based on a recommendation of Johnston). For 1979b they are all based on analogy with ClONO_2 data of Chang *et al.* (1979). This treatment is highly uncertain.
7. Based on data in Watson (1974).
8. Product chemistry has been simplified.
9. Treatment based on Thompson *et al.* (1963).
10. Treatment based on Graham *et al.* (1978).
11. Treatment based on quantum yields of Moorjagat and Warneck (1979) and cross sections of McQuigg and Calvert (1969).

BOUNDARY CONDITIONS

The model now allows for either fixed concentrations or a flux condition at the surface as a lower boundary condition. For most of the calculations in this study, six species were assumed to have fixed concentrations (See Table A-5), while a surface flux was assigned to the other species. Zero flux was assumed except for those species shown in Table A-5. When those species with fixed boundary conditions in Table A-5 were given flux boundaries, a flux was determined to give an ambient concentration the same as those in Table A-5.

Zero flux was assumed for all species except NO and NO_2 at the upper boundary. NO and NO_2 are assumed to have a very small flux from the mesosphere into the stratosphere.

Water vapor concentrations are fixed in the troposphere and calculated in the stratosphere. All runs are made with fixed boundary conditions unless otherwise noted.

SOURCES AND SINKS

In addition to sources and sinks from the chemistry and boundary conditions described above, there are additional sinks due to dry and/or wet removal for many species in the model. A source for nitric oxide from cosmic ray dissociation of N_2 is also included based on the results of Nicolet (1974).

Wet removal processes are parameterized by a first-order loss rate. The wet removal of the trace species HNO_3 , H_2O_2 , HCl, ClO, ClONO_2 , ClNO_2 , HNO_4 , HOCl, CH_2O and CH_3OOH is assumed to vary with altitude as shown in Table A-6. NO_2 is assumed to have a loss rate half the above rate.

Dry deposition rates at the surface are also parameterized by a first-order loss rate as shown in Table A-7.

TABLE A-5. Boundary conditions.

Fixed concentrations (molecules cm^{-3})		Surface flux (molecules $\text{cm}^{-2} \text{s}^{-1}$)	
N_2O	8.25×10^{12}	NO	3.41×10^9
CH_4	4.03×10^{13}	NO_2	6.59×10^9
H_2	1.42×10^{13}	HNO_3	1.67×10^9
CH_3Cl	1.56×10^{10}	HCl	3.67×10^{10}
H_2O	4.30×10^{17}	CCl_4	1.40×10^6
CO	3.04×10^{12}	CF_2Cl_2	function of time and scenario
		CFCl_3	
		CH_3CCl_3	

TABLE A-6. Wet removal parameterization.

Altitude, km	Loss rate, sec^{-1}	Altitude, km	Loss rate, sec^{-1}
0	3.86×10^{-6}	6	1.93×10^{-6}
1	3.86×10^{-6}	7	1.93×10^{-7}
2	3.86×10^{-6}	8	9.58×10^{-7}
3	3.86×10^{-6}	9	4.78×10^{-7}
4	3.86×10^{-6}	10	0
5	3.86×10^{-6}		

TABLE A-7. Deposition rates in the lowest layer ($z = 0$).

Species	Loss rate, sec^{-1}	Species	Loss rate, sec^{-1}
$\text{O}(^3\text{P})$	2.0×10^{-5}	NO_3	2.0×10^{-5}
O_3	1.0×10^{-5}	N_2O_5	2.0×10^{-5}
NO	1.0×10^{-6}	H_2O	0
NO_2	3.0×10^{-6}	HNO_4	2.0×10^{-5}
N_2O	0	HOCl	2.0×10^{-5}
HNO_3	2.0×10^{-5}	HCO	2.0×10^{-5}
OH	2.0×10^{-5}	CH_2O	1.0×10^{-5}
HO_2	2.0×10^{-5}	CH_3	2.0×10^{-5}
H_2O_2	2.0×10^{-5}	CH_3OOH	2.0×10^{-5}
Cl	2.0×10^{-5}	CH_3O	2.0×10^{-5}
ClONO_2	2.0×10^{-5}	CH_3O_2	2.0×10^{-5}
ClO	2.0×10^{-5}	CO	5.0×10^{-7}
CH_4	0	ClO_3	2.0×10^{-5}
H_2	1.0×10^{-7}	OClO	2.0×10^{-5}
CH_3Cl	0	HONO	2.0×10^{-5}
ClNO_2	2.0×10^{-5}	CFCl_3	0
HCl	2.0×10^{-5}	CF_2Cl_2	0
CCl_4	0	CH_3CCl_3	0

MULTIPLE SCATTERING

In order to accurately compute photodissociation rates, it is important to describe radiative processes, such as multiple scattering, in addition to attenuation by gases such as O_2 , O_3 and NO_2 . The importance of molecular scattering varies significantly with wavelength over the spectral range 200-750 nm. At shorter wavelengths gaseous absorption dominates and very little solar flux reaches the lower atmosphere. The region 290-330 nm is a transition region where molecular scattering is very important, especially at the longer wavelengths in this interval. Beyond 330 nm, surface reflection is very important since the atmosphere is nearly transparent in this spectral region.

Multiple scattering is included in the model using a simplified method that is computationally fast so that it can be used for diurnal calculations. The method is similar to that of Isaksen *et al.* (1977) in terms of the numerical method but quite different in terms of the physical assumptions. The atmosphere is divided into optically thin layers and each layer can absorb and scatter radiation. The layer is assumed to scatter radiation isotropically with half of the scattered flux going upward and the other half downward at an average zenith angle of $\pm\theta$. The earth's surface is also assumed to scatter isotropically, and a surface albedo of 0.25 is used to approximate the effect of clouds on the upward scattered radiation. Using a high surface albedo and no clouds gives results that are nearly identical to those from dividing the atmosphere into clear and cloudy regimes and averaging the results (the exception being the region below the cloud layer, which is not important for the model applications considered here). For each atmospheric layer there is a contribution to the solar flux density from the direct flux and by the diffuse fluxes incident on the layer from above and from below. The flux density due to the various fluxes together can be much greater (depending on the wavelength and altitude) than the flux density computed considering only gaseous absorption (Luther and Gelinas, 1976; Luther and Wuebbles, 1976).

TEMPERATURE FEEDBACK

The temperature profile above 13 km is calculated using a stratospheric radiative transfer model, and the temperature profile is specified at lower altitudes. The model includes solar absorption and long-wave interaction by O_3 , H_2O , and CO_2 , along with solar absorption by NO_2 . The techniques adopted for treating long-wave radiative transfer are the same as those described by Ramanathan (1974). This formulation was chosen because it is computationally efficient, and its accuracy has been demonstrated (Ramanathan, 1974, 1976) by comparison with much more complex models. The effects of and justification for the simplifying assumptions used in the model are discussed by Ramanathan (1976).

A band absorbance formulation is used to treat the $9.6\text{-}\mu\text{m}$ band of O_3 and the fundamental and several hot and isotopic bands of CO_2 in the $15\text{-}\mu\text{m}$ region. An emissivity formulation is used to treat long-wave radiative transfer by H_2O . Solar absorption by O_3 is treated by using the empirical formulation given by Lindzen and Will (1973). The band absorbance formulation by Houghton (1963) is adopted for solar absorption by H_2O , and the band absorbance formulation by Ramanathan and Cess (1974) is adopted for solar absorption by CO_2 . The empirical formulation of Luther (1976) is used for solar absorption by NO_2 . Solar absorption by O_3 and NO_2 are treated independently because absorption by these species is weak in the region where their absorption bands overlap. Solar radiation scattered from the troposphere is included by assuming an albedo of 0.3. Doppler broadening effects are included for CO_2 and O_3 as described in Appendix B of Ramanathan (1976). The temperature dependences of the band absorbance and band intensity are included in the longwave calculations of CO_2 and O_3 .

A single cloud layer is included at 6.5 km with 42% cloud cover as was suggested by Cess (1974). The lapse rate within the troposphere is assumed to be -6.5 K/km , and the temperature at the earth's surface is specified to be 288 K.

NUMERICAL METHOD

Each of the 39 species in the model has its concentration calculated at each of 44 vertical levels extending from the surface to 55 km. The numerical technique used to solve the set of over 2000 differential equations (resulting from a continuity equation for each species at each grid level) is the method described by Chang *et al.* (1974). The main advantage of this method, which is a variable order, multistep, implicit method, is its ability to solve sets of mathematically stiff differential equations for almost any set of input parameters, initial and boundary conditions, in particular those resulting from the chemical kinetics system described in Table A-2.

DIURNAL AND DIURNAL-AVERAGED MODELS

We have developed a fully diurnal-averaged model that is consistent with our diurnal model. The diurnal model is used to generate species profiles for comparison with measurements and for perturbation studies involving short time integrations (e.g., solar eclipse effects). The diurnal-averaged model is used for perturbation and sensitivity studies involving longer time integrations.

The procedure that is used in developing the fully diurnal-averaged model is also applicable to two-dimensional models. If the continuity equation is averaged over a time period (24 hours in our case) that is very small compared to the time scale of the problem of interest, then one obtains averaged terms of the form $\overline{k_{ij} c_i c_j}$ and $\overline{J_i c_i}$ where c_i is the concentration of species i at time t and altitude z , k_{ij} is the two-body chemical rate coefficient, and J_i is the photodissociation rate coefficient for species i .

We define the diurnal weighting factors $\alpha_{ij}(z)$ and $\beta_i(z)$ by

$$\overline{k_{ij} c_i c_j} = \alpha_{ij} \overline{k_{ij} c_i c_j} \quad (\text{A-5})$$

and

$$\overline{J_i c_i} = \beta_i \overline{J_i c_i} \quad (\text{A-6})$$

Since k_{ij} is defined and is independent of time, we have

$$\alpha_{ij} = \overline{c_i c_j} / \overline{c_i c_j} \quad (\text{A-7})$$

and

$$\beta_i = \overline{J_i c_i} / \overline{J_i c_i} \quad (\text{A-8})$$

The computation of photodissociation rates can be an expensive part of stratospheric model calculations, hence evaluation of J_i 's in the diurnal-averaged model can be expensive. If we define β_i by

$$\beta_i = \overline{J_i c_i} / (\overline{J_i^{\text{noon}} c_i}) , \quad (\text{A-9})$$

then the computation in the diurnal-averaged model is greatly simplified. The diurnal model is used to determine $\overline{c_i c_j}$, $\overline{J_i c_i}$, $\overline{c_i}$, $\overline{c_j}$, and $\overline{J_i^{\text{noon}}}$ so that α_{ij} and β_i can be obtained for every chemical and photochemical reaction in the model.

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APPENDIX B

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*Potential Environmental Effects
of Aircraft Emissions*

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ABSTRACT

An assessment is provided of the potential environmental effects of fleets of subsonic, supersonic, and hypersonic aircraft. A general discussion of photochemical and transport modeling techniques is included along with a description of the LLL one-dimensional transport-kinetics model that was used in the assessment. Model simulations of the natural and perturbed stratosphere are used to compare theory with observations as a means of verification of model processes. A review is provided of engine emission indexes and 1990 fleet projections. Assessments of the potential effects of subsonic and supersonic aircraft fleets indicate a small increase in total ozone. However, the change in total ozone is the net difference between regions of ozone increase (in the lower stratosphere and upper troposphere) and ozone decrease (in the upper stratosphere). The percent change in the local ozone concentration is much larger than the change in total ozone. The effect of a proposed hydrogen fueled hypersonic transport fleet is a small reduction in total ozone. A study is made of the effect on these results of uncertainties in chemical rate coefficients, speculative chemical reactions, temperature feedback, hydrostatic adjustment, and various model parameters. The potential effect on ozone of aircraft emissions is compared with potential changes due to other anthropogenic perturbations.

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EXECUTIVE SUMMARY

The purpose of this report is to review the major changes in the aircraft emission assessments since the end of the Climatic Impact Assessment Program in 1975 and to provide a comprehensive discussion of the current modeling results. Assessments are made of the potential effects of subsonic and supersonic aircraft fleets and of a proposed hydrogen-fueled hypersonic transport fleet. Studies are made of the effects on the results of uncertainties in chemical rate coefficients, vertical transport coefficients, speculative chemical reactions, temperature feedback, hydrostatic adjustment, and various model parameters. A summary of the conclusions and recommendations resulting from these studies follows.

Assessment Results

- Subsonic aircraft fleets projected for the year 1990 are estimated to cause an increase in hemispheric mean total ozone of nearly 2%. Because of uncertainties in the treatment of poorly understood phenomena in the troposphere, these results are suggestive but not definitive.
- Supersonic transport fleets of commercially viable size are estimated to cause an increase in total ozone of less than 1.5%, depending on the altitude of injection, the NO_x emission index, and a number of model parameters (see below).
- Emissions from a hypothesized commercially viable fleet of hypersonic transports are estimated to cause up to a 2% reduction in total ozone.
- For subsonic and supersonic transport fleets, reductions in the NO_x emission rate have a greater effect on ΔO_3 than does a similar percent reduction of the H_2O emission rate.
- The increase in total ozone caused by an NO_x injection increases as the background CLX concentration increases.
- An analysis of the effect on model sensitivity of speculative reactions and photochemical mechanisms not included in the basic model shows that it is plausible that stratospheric injections of NO_x could lead to a slight decrease in total ozone rather than an increase as predicted with the

current model. These speculative reactions and mechanisms, although plausible, are not highly probable, but the fact that they have a significant effect on model sensitivity indicates that they are worthy of careful attention and further study.

- Changes in evaluated recommendations for chemical rate coefficients over the last five years have resulted in substantial changes in the model-predicted response to perturbations. Even recent rate recommendations appearing a few months apart carry a significant amount of uncertainty. The uncertainty limits for reactions in the various evaluations have generally become smaller when individual reactions are considered. However, over the same time period, new and often highly uncertain reactions have been recognized, and it is far from obvious that the error that might be associated with reactions actually included in models has gotten smaller over the last decade. Moreover, new reactions have been introduced to the models at a fluctuating but not obviously decreasing rate. Thus, past variations in model predictions may provide a reasonable estimator of the magnitude of possible future variations in similar predictions.
- Temperature feedback and hydrostatic adjustment have a small, but not insignificant, effect on the computed change in total ozone. Both of these feedback mechanisms tend to increase the value of ΔO_3 when the net effect is an increase in total ozone. Temperature feedback and hydrostatic adjustment have a much more significant effect on the computed change in local ozone concentration, particularly at higher altitudes (>35 km). This has important implications for monitoring programs that are directing their attention to certain altitude regions as a means of detecting early trends in ozone due to anthropogenic perturbations.

Model Comparisons with Observational Data

- There is good agreement between model-calculated distributions of $O(^3P)$ and the few available measurements.

- The unperturbed O_3 profile computed by the model falls within the range of rocket and balloon measurements at middle latitudes.
- There appears to be reasonable agreement between theoretical calculations and the few available measurements of OH and HO_2 in the stratosphere. Comparison of the total OH column does not indicate significant differences in annual-average column content.
- Theoretical models calculate approximately a factor of 2 more NO_y at high altitude than has been measured. Part of the reason for this difference (among others) may be that the model predicts too much N_2O in the upper stratosphere.
- The single observed Cl profile and calculated Cl profiles agree within the measurement uncertainty. However, the measurements suggest a larger vertical gradient in Cl mixing ratio than is calculated.
- At the ClO mixing ratio maximum, most measurements are within a factor of 2 of the model prediction. One resonance fluorescence measurement gives six times more ClO than is predicted. The measurements also show a sharper than predicted decrease in ClO below the peak.
- Except for three measurements of ClO taken in summer, there does not appear to be any large discrepancy between the total amount of ClX predicted and that observed. However, the summer measurements of ClO are so large as to require much more total ClX than known sources are capable of producing.
- Model simulations of various natural and man-made perturbations to stratospheric ozone give results that are not inconsistent with the observational record.
- Although there are individual disagreements between model-calculated species profiles and measurements that still need to be examined, on balance we believe the model adequately represents the stratosphere. The disagreements point to uncertainties in the model representation of the stratosphere. The large amount of data that agree indicates that the model is doing rather well. In doing assessments, we need to understand what effect the model uncertainties have on the predictions. Consequently, sensitivity studies are an important aspect of the overall effort.

- Calculations of the effect of a reduction in total ozone (ΔO_3) on the erythema dose at the earth's surface show an amplification factor ($\Delta \text{dose} / \Delta O_3$) of 1.3-1.4 at low latitudes (where the erythema dose is greatest), 1.6-2.0 at middle latitudes, and approximately 3 at high latitudes.
- An analysis of skin cancer incidence data from several countries (Cutchis, 1978) shows that the etiology of malignant melanoma is in a chaotic state. The anatomic site behavior, age dependence, geographical location, and relative rates of incidence in males and females suggest the existence of two carcinogen agents, neither of which is solar ultraviolet radiation.
- None of the SST engine emissions (NO_x , H_2O , and SO_2) are estimated to have a major climatic effect. Water vapor has the largest individual effect on surface temperature.

1. INTRODUCTION

In 1970 and 1971, the U. S. Congress conducted a major reassessment of the U.S. supersonic transport (SST) development program. There was considerable controversy over the potential environmental effects of SST fleet operations. The concerns were related to the effects stratospheric aircraft emissions might have on stratospheric ozone, which shields the earth's surface from harmful levels of ultraviolet solar radiation, and on the climate. Initial chemical and climatic concerns were related to water vapor emissions, but these concerns shifted to emphasize oxides of nitrogen (Crutzen, 1970), which were postulated to cause substantial catalytic destruction of ozone (Johnston, 1971; Crutzen, 1972). Estimates of the ozone depletion that might arise from large SST fleet operations ranged from 3 to 50%, depending on assumptions.

Although the U.S. SST development program was canceled, the issues and the scientific problems remained. Recognizing that SSTs were being developed in other countries and that new SSTs might be developed in the U.S. in the future, the Climatic Impact Assessment Program (CIAP) was implemented by the U.S. Department of Transportation to clarify the potential environmental effects of aircraft operation in the stratosphere. The goal of this three-year program was to assess, in a series of monographs to be prepared by 1975, the potential chemical, climatic, biological, and economic effects of stratospheric aircraft emissions.

The CIAP Report of Findings (Grobeck et al., 1974) was delivered to Congress in February 1975. In addition to the CIAP studies, a concurrent and independent study was conducted by the Climatic Impact Committee of the National Academy of Sciences, and their report was distributed in April 1975 (National Research Council, 1975a). Independent studies were also carried out in Europe by the British (COMESA, 1976) and by the French (COVOS, 1976).

The conclusions of the CIAP and NRC studies were similar, although there were differences in the estimated magnitudes of the environmental effects. Large-scale aircraft operations in the stratosphere were concluded to possibly lead to unacceptable reductions in stratospheric ozone. Most of the ozone reduction was estimated to be caused by nitrogen oxide emissions with a very small effect due to water vapor emissions. The climatic effects were considered to be potentially

significant but highly uncertain. The skin cancer incidence rate was estimated to increase about 2% for each 1% reduction in the ozone column.

In 1975 the High Altitude Pollution Program (HAPP) was initiated by the Federal Aviation Administration to extend the investigations carried out during CIAP so as to ensure that stratospheric aircraft emissions will not result in unacceptable environmental effects. Lawrence Livermore Laboratory (LLL) has been an active participant in both the CIAP and HAPP programs, having undertaken an extensive effort in numerical modeling of the atmospheric response to stratospheric perturbations. In addition to addressing the issue of engine emissions, the LLL numerical models have also been applied to other proposed threats to stratospheric ozone (e.g., chlorofluoromethanes (CFMs) and increased N_2O), thereby focusing on the overall problem of stratospheric chemistry and combined effects.

The purpose of this report is to review the major changes in the aircraft emission assessments since the end of CIAP and to provide a comprehensive discussion of the current modeling assessment. A general discussion of photochemical and transport modeling techniques is included along with a description of the LLL one-dimensional transport-kinetics model that was used in the assessment. Model simulations of the natural and perturbed stratosphere are included to compare theory with observations as a means of verification of model processes. Assessments are made of the potential effects of subsonic and supersonic aircraft fleets and of a proposed hydrogen-fueled hypersonic transport fleet. Studies are made of the effects on the results of uncertainties in chemical rate coefficients, vertical transport coefficients, speculative chemical reactions, temperature feedback, hydrostatic adjustment, and various model parameters. The potential effect on ozone of aircraft emissions is compared with potential changes due to other anthropogenic perturbations. The appendices contain more detailed technical discussions of some of the material contained in the main body of the report.

2. COUPLED TRANSPORT AND CHEMICAL KINETICS MODELS

Models of stratospheric chemistry have been primarily directed toward an understanding of the behavior of stratospheric ozone. Initially this interest reflected the diagnostic role of ozone in the understanding of atmospheric transport processes. More recently, interest in stratospheric ozone has arisen from concern that human activities might affect the amount of stratospheric ozone, thereby affecting the ultraviolet radiation reaching the earth's surface and perhaps also affecting the climate (Johnston, 1971; Crutzen, 1972; National Research Council, 1975a, 1975b, 1976a, 1976b; CIAP Monograph 5, 1975; Grobecker et al., 1974; Hudson, 1977), with various potentially severe consequences for human welfare. This concern has inspired a substantial effort to develop both diagnostic and prognostic models of stratospheric ozone.

The first quantitative model of stratospheric ozone was developed by Chapman (1930). Chapman's model calculated the ozone distribution on the basis of a pure oxygen atmosphere using a simple equilibrium model. During the 1930's and 1940's, pure oxygen models of the stratosphere were further developed (Mecke, 1931; Dutsch, 1946). However, as more information about the vertical and latitudinal distribution of ozone became available and the relevant reaction coefficients and photolysis cross sections for O_2 and O_3 were more accurately measured, it became clear that pure oxygen models failed to accurately predict the atmospheric behavior of ozone (Brewer and Wilson, 1968; Hunt, 1966a). In attempts to explain this disagreement with observations, the reactions of excited states of oxygen atoms and oxygen molecules were considered and rejected as inadequate to explain the discrepancy (Brewer and Wilson, 1968), and the reactions of ozone and oxygen atoms with hydrogen-containing compounds were considered (Bates and Nicolet, 1950; Hampson, 1964; Hunt, 1966b; Dutsch, 1968; Hestvedt, 1968; Leovy, 1969; Crutzen, 1969). When measurements of the rates of reaction of odd hydrogen species (H , OH , HO_2) with odd oxygen species (O , O_3) were made available in the late 1960's, it appeared that another loss process was needed. Crutzen (1970) and Johnston (1971, 1972) recognized the important role of the oxides of nitrogen (NO_x) in regulating stratospheric ozone, and Nicolet (1970) recognized the reaction of $O(^1D)$ with N_2O as a natural source of NO_x in the stratosphere. Stolarski and Cicerone (1974) first postulated the potential role of chlorine in influencing ozone, and

Rowland and Molina (1975) found that halogenated organic molecules (especially the chlorofluoromethanes) could act as sources of stratospheric chlorine. More recently, it has been suggested that bromine might also affect stratospheric ozone if a significant source were to exist (Wofsy et al., 1975).

2.1 CHEMISTRY OF THE STRATOSPHERE

Understanding of the chemical processes and cycles in the stratosphere has evolved rapidly over the past several years (Chang and Duewer, 1979). This section describes some of the chemical processes that are currently thought to be among the most important in determining or affecting stratospheric ozone concentrations. Chemical reactions in the following discussion will be referred to according to the numbering sequence in Table A-2 of Appendix A. The numbering sequence for photolysis reactions corresponds to Table A-4 of Appendix A.

The reaction

is the primary process in the production of odd-oxygen species in the stratosphere. The reactions

and

serve to interconvert the various odd-oxygen species ($O(^1D)$, O , O_3), and they help to limit the ozone (hence odd-oxygen) concentration. This set of reactions alone does not lead to the observed ozone concentrations, however. These reactions, first suggested by Chapman (1930), and some comparatively minor reactions involving excited oxygen species lead in a one-dimensional model to a stratospheric ozone column that is about twice the observed (see Table 1). Because

TABLE 1. Ozone columns calculated neglecting various families of chemical species. (Source: Chang and Duewer, 1979)

Families of Species Neglected*	Ozone Column (molecules/cm ²)	Altitude of O ₃ Maximum (km)
None (reference model)**	8.77×10^{18}	24
ClX family neglected	9.44×10^{18}	24
HO _x family neglected	8.26×10^{18}	24
NO _x family neglected	6.25×10^{18}	28
HO _x and ClX families neglected	8.31×10^{18}	24
NO _x and ClX families neglected	9.79×10^{18}	26
NO _x and HO _x families neglected	7.53×10^{18}	25
NO _x , HO _x and ClX families	16.06×10^{18}	23

*Families were neglected by setting the concentrations of species in the family and all their source species equal to zero.

**The reference model contains 18 ppb NO_x, 1 ppb HO_x, and 1.5 ppb ClX at 35 km. (NO_x = NO + NO₂ + HNO₃ + 2 x N₂O₅ + ClNO₃; HO_x = OH + HO₂ + 2 x H₂O₂; ClX = Cl + ClO + HCl). The model chemistry is that described in Luther (1978).

ozone destruction via the Chapman cycle is approximately proportional to the square of the ozone concentration, this set of reactions accounts for roughly only 25% of the actual ozone sink.* In order to account for the rest of the ozone loss, it is necessary to consider several other processes that can destroy odd-oxygen.

Odd-hydrogen species (HO_x, e.g. H, OH, and HO₂) can destroy odd-oxygen while being themselves regenerated (i.e., catalytically destroy odd-oxygen) via several reaction sequences. Examples of reaction sequences leading to net odd-oxygen loss include:

*Since ozone is the overwhelming component of odd-oxygen and it is always in chemical equilibrium with O(¹D) and O, for many discussions it is convenient to refer to ozone destruction rather than odd-oxygen destruction for the sake of brevity.

and

Each of these catalytic cycles involves only hydrogen-containing chemical species. The last sequence is of interest in that the first reaction generates odd-hydrogen radicals from water and the last reaction converts them back into water. Water is not normally treated as part of odd-hydrogen. For odd-hydrogens, reaction (17) is considered to be a major termination step that limits the abundance of reactive odd-hydrogen species in the stratosphere. This reaction, therefore, decreases the overall efficiency of the HO_x in destroying odd-oxygen. In doing so, the participation of reaction (17) in this particular chain nevertheless contributes to some net odd-oxygen destruction. Analysis of chemical interactions via catalytic cycles provides a basis for understanding the physical processes leading to the final observables such as the stratospheric column density of ozone, but it does not quantify the relative strength of particular reaction pathways.

The odd-nitrogen species (NO_x , e.g. N, NO, and NO_2) can catalytically destroy odd-oxygen by a number of reaction sequences such as:

and

Odd-chlorine species (ClX, e.g. Cl and ClO) can catalytically destroy odd-oxygen via reaction sequences such as:

The above catalytic cycles are neither exhaustive nor unique. Many others may be identified from the list of reactions in Tables A-2 and A-4.

In addition to these catalytic cycles resulting in net odd-oxygen loss, there are null cycles (do-nothing cycles). Reaction (3) $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ followed by (J4) $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$ instead of (4) will lead to no net change in odd-oxygen. Similarly, reaction (33) $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$ followed by (J12) $\text{ClO} + h\nu \rightarrow \text{Cl} + \text{O}$ instead of (35) will also lead to no net change in odd-oxygen. These null cycles compete with the catalytic destruction cycles, thereby diminishing the effectiveness of individual families of chemical species (NO_x , HO_x , and ClX) in destroying odd-oxygen. As it turns out, most of the NO_2 formed from reaction (3) or any other path returns via photolysis of NO_2 . Hence, the null cycle involving

reaction (J4) is very effective in controlling the efficiency of NO_x catalytic destruction of odd-oxygen. Null cycles involving ClO photolysis are not very effective since the reaction rate for (J12) is much smaller than that of (35). Consequently, ClX catalytic cycles are affected little by the presence of null cycles within the ClX family. The case for the HO_x family is similar.

The strength of catalytic destruction cycles can be reduced by removing the catalysts. This is accomplished through the formation of relatively inactive "reservoir" species from more active species. Examples of this include formation of nitric acid, chlorine nitrate, hydrochloric acid, water, hydrogen peroxide, and pernitric acid through reactions such as (18), (37), (45), (41), (19), (17), and (56). These more stable species can regenerate the active species slowly. In fact, these "reservoir" species are often the most abundant members within individual families of species. Transport out of the stratosphere serves as a major sink for these "reservoir" species and indirectly as a loss for the active species.

There are important coupling interactions among the chemical families that affect ozone. An analysis of models with computed ambient levels of HO_x , NO_x , or ClX separately (all roughly consistent with measured stratospheric concentrations) shows that any one of the three families of species could lead to an ozone column no more than 20% larger than the observed column, and no one family is of primary importance in determining the column (Table 1). In fact, computations with either ClX or NO_x alone (plus Chapman reactions) lead to an ozone column lower than that computed when all three families are considered (Table 1). To understand this result, one must go beyond the simple concept of catalytic cycles within individual families and consider the complex interactions between the various active species among the families.

The sequence of reactions (33) $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$, (36) $\text{ClO} + \text{NO} \rightarrow \text{NO}_2 + \text{Cl}$, and (J4) $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$ forms a null cycle involving two families of species that occurs at a fairly fast rate throughout the stratosphere. This null cycle not only provides an additional do-nothing path for the odd-nitrogens, but it is the only effective known null cycle for the odd-chlorine species. Consequently, it weakens the effectiveness of both ClX and NO_x in destroying odd-oxygen in the stratosphere. A similar null cycle involving HO_x and NO_x is (10) $\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$, (24) $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$, and (J4) $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$. This cycle is especially effective in the lower stratosphere. With these coupled null cycles competing with the catalytic cycles, it becomes clear how interference

mechanisms can lead to slightly more total ozone when all three families are present with apparently additive odd-oxygen destruction catalytic cycles.

Of course, this is an over-simplified qualitative picture. The actual quantification of all the possible paths is considerably more complicated. For example, reactions (24) and (36) are not only critical in providing the effective but otherwise absent null cycles for the ClX and HO_x families, but they also create additional net odd-oxygen destruction catalytic cycles if the NO₂ molecule so created returns to NO via (4) NO₂ + O → NO + O₂ instead of photolyzing. Another example of a mixed catalyst destruction sequence is the series of reactions: (60) HO₂ + ClO → HOCl + O₂; (J24) HOCl + hν → OH + Cl; (33) Cl + O₃ → ClO + O₂; and (10) OH + O₃ → HO₂ + O₂. This sequence has the net effect 2O₃ → 3O₂.

In addition, reactions that couple the various families can also catalyze the interconversion of active species and "reservoir" species. Reactions (56) HO₂ + NO₂ + M → HNO₄ + M and (58) HNO₄ + OH → H₂O + O₂ + NO₂; reactions (41) Cl + HO₂ → HCl + O₂ and (39) OH + HCl → H₂O + Cl; and reactions (60) ClO + HO₂ → HOCl + O₂ and (62) HOCl + OH → H₂O + ClO all have the net effect of the single reaction (17) OH + HO₂ → H₂O + O₂. These examples are but a fraction of the couplings of potential importance.

In summary, NO_x, HO_x, and ClX are all of comparable importance in catalyzing ozone destruction in the natural atmosphere, but the roles of the individual species are difficult to separate because the various reactive species are strongly coupled, not only via the formation or destruction of relatively inactive "reservoir" species, but also through positive and negative interference with the basic odd-oxygen destruction processes. Because of the complexity of these coupling mechanisms (and others not discussed) and the need to consider them all in estimating the interaction of various species, numerical models have become an essential tool in the interpretation of stratospheric measurements as well as in the prediction of the effects of potential perturbations.

2.2 MODELING PHOTOCHEMICAL AND TRANSPORT PROCESSES

As shown in Fig. 1, the local concentrations of trace species in an air parcel are determined by the chemical and photochemical processes and nonchemical

FIGURE 1. Processes affecting the concentration of species in an atmospheric volume.

sources and sinks occurring within the parcel, and by the transport and radiative fluxes into and out of the parcel. Mathematical models of the chemical processes in the stratosphere are governed by the chemical species conservation equation

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \underline{F}_i(c_i, \underline{x}, t) = P_i[c, J(\underline{x}, t, c), k(T(\underline{x}, t), \rho)] - L_i[c, J(\underline{x}, t, c), k(T(\underline{x}, t), \rho)] c_i + S_i(\underline{x}, t) \quad (1)$$

where $c_i = c_i(\underline{x}, t)$ is the concentration of the i^{th} chemical constituent; c is the general representation of all constituents; P_i and $L_i c_i$ are the production and loss of c_i caused by photochemical interactions; T is the ambient air temperature; ρ is the ambient air density; $\underline{F}_i$ is the transport flux of c_i ; S_i represents any other possible sinks or sources of c_i ; J represents photodissociation coefficients; k represents chemical reaction rate coefficients; and all of these variables are defined at a given spatial position $\underline{x} = \underline{x}(x, y, z)$ at time t . The explicit display of the major interdependent relations of these variables in Eq. (1) illustrates the nonlinearity and general complexity of this mathematical system. Equation (1)

is defined over a spatial domain D with appropriate boundary conditions. Formally, there is one conservation equation for each chemical species in the stratosphere. In practice, about three dozen individual chemical species are known to be of potential consequence in describing the chemical balances affecting the ozone budget in the stratosphere.

It should be noted that an approximation is introduced in the use of spatially and temporally averaged concentrations to calculate the nonlinear chemical terms in Eq. (1). Most of the reactions are bimolecular with rates of reaction of the form

$$k_{ij} c_i c_j$$

where k_{ij} is the rate constant for reaction of species i with species j . The approximation arises because one does not obtain the same average rate by (a) first averaging the concentrations and then multiplying, as one would find by (b) first multiplying then averaging. The latter method (b) gives the correct result, but for all practical purposes it is not computationally achievable. The former case (a) is a simplifying approximation that can be handled. The effect of this approximation can potentially be quite large, even for physically plausible atmospheric conditions (Hilst, 1972). Work is in progress to develop methods of estimating useful bounds for the errors that may be induced under various conditions.

Classification of Models

Depending on the nature and the extent of problems to be studied, any particular model may include different levels of detail in its representation of the spatial variation of trace species distributions. The difference in resolution serves as a useful and convenient basis for model classification.

Box models have spatial homogeneity as their fundamental assumption (complete uniform mixing of individual trace species). Consequently, these models are represented by a set of ordinary differential equations describing the time evolution of individual trace species as controlled by chemical interactions only, i.e., Eq. (1) averaged over all space under consideration. Such models have been very useful in the diagnosis of experiments in laboratory kinetics and in the analysis of global budgets of long-lived trace species.

One-dimensional models have been the most widely used diagnostic and prognostic tools in stratospheric research. These models are designed to simulate the vertical distribution of atmospheric trace species. They include a detailed description of chemical interactions and of atmospheric attenuation of solar radiation, but the effect of atmospheric transport is described in a simplified way. In one-dimensional models of the stratosphere, a longitudinal and latitudinal global average of the transport flux is assumed. The resulting net vertical transport flux F_{z_i} of any minor constituent c_i is represented through a diffusion approximation in which F_{z_i} is assumed to be proportional to the gradient of the mixing ratio of that trace species:

$$F_i = F_{z_i} = -K_z \rho \frac{\partial}{\partial z} (c_i / \rho) \quad , \quad (2)$$

where z is the altitude and K_z is the one-dimensional vertical diffusion coefficient. One of the major assumptions in applying Eq. (2) to a one-dimensional representation of the atmosphere is that the globally-averaged vertical transport can be represented as a diffusive process.

The models are considered to represent either global or midlatitude averages. One-dimensional models can describe the main features of atmospheric chemistry without excessive demands on computer time.

Two-dimensional models with spatial resolution in the vertical and meridional directions and improved representation of transport (mean motion and eddy mixing) are far more realistic than the one-dimensional models. The two-dimensional fluxes in Eq. (1) are now represented by the sum of two terms, $\underline{F}_i = c_i \underline{V} - \rho \underline{K} \nabla (c_i / \rho)$, where $\underline{V}$ is the mean meridional velocity and the 2×2 matrix $\underline{K}$ is the eddy diffusion coefficient tensor. These models can simulate both seasonal and meridional variations of trace species distributions. The price for this additional information is a considerable increase in computational cost and required input data. Unfortunately, even for these complex models, the transport representations must still be empirically derived from limited data. There is no feedback from changes in composition to the transport processes. This major coupling step can only be accomplished in a realistic sense in a three-dimensional model.

Three-dimensional models give, in principle, the closest simulation of the real atmosphere. The three-dimensional transport fluxes $\underline{F}_i = c_i \underline{V}$ are obtained

through the solution, in all three dimensions, of the appropriate equations of continuity for momentum, energy, and mass (species). These models can, in principle, include most, if not all, of the important feedback mechanisms in the real world. They are, however, very demanding of computer time and memory, and so far the chemistry has had to be simplified to such a degree that important details may have been lost.

One-dimensional models are generally the most detailed and complete in terms of the treatment of photochemical processes. The one-dimensional models used by the major modeling groups now include the Chapman reactions, the NO_x , HO_x and CIX catalytic cycles, and many of the transfer reactions among these basic cycles. In addition, essentially all one-dimensional models contain reactions for the species resulting from methane oxidation, and many have included bromine and sulfur chemistry in their calculations. Some even treat aerosol formation and loss.

The number of reactions included in present one-dimensional models range from approximately 60 to 400 chemical and photochemical reactions involving approximately 24 to 60 species whose concentrations are calculated. As an example, the LLL model presently contains 134 reactions to determine the distributions of 39 species.

The more extensive reaction sets used in some models include many minor reactions, but a comparison of representative models indicates that the chemical kinetics systems in current use are in essential agreement. However, reaction rate coefficients have been changed and additional reactions have been included over the last few years as a result of new laboratory measurements and as the understanding of the chemistry of the atmosphere continues to evolve.

Transport Representation

Globally-averaged vertical transport is represented in one-dimensional models using a vertical diffusion coefficient. The diffusion coefficients are derived from atmospheric data. Chemical tracers (CH_4 and N_2O) and radionuclides from past atmospheric nuclear tests (^{14}C , ^{90}Sr , ^{95}Zr , and ^{185}W) have been used as source data for deriving and testing the coefficients.

In the derivation of the coefficients, it is assumed that the value of K_z is a function of only the transporting motion field. An example of how

globally-averaged measurements of CH_4 may be used to derive a K_z profile is shown in Eq. (3):

$$\frac{\partial}{\partial z} \left\{ K_z \rho \left(\frac{\partial}{\partial z} \frac{[\text{CH}_4]}{\rho} \right) \right\} - k_{67} [\text{O}(^1\text{D})][\text{CH}_4] - k_{64} [\text{OH}][\text{CH}_4] - k_{68} [\text{Cl}][\text{CH}_4] = 0, \quad (3)$$

where $[\text{CH}_4]$, ρ , k_{67} , k_{64} and k_{68} are known from measurements and $[\text{O}(^1\text{D})]$, $[\text{OH}]$, and $[\text{Cl}]$ are measured or derived from model calculations. Because there are only a few CH_4 measurements available, there is significant uncertainty in the K_z profile. A similar problem exists for derivations using N_2O measurements, although the calculation is simplified somewhat since N_2O loss depends only on photolysis and reaction with $\text{O}(^1\text{D})$.

Vertical diffusion coefficient profiles that have been used by various modeling groups in the past have varied significantly, differing by as much as an order of magnitude in value in the middle stratosphere (National Research Council, 1976b). The K_z profiles currently in use tend to differ less than was the case several years ago. Two commonly used K_z profiles are shown in Fig. 2. In general the profiles are similar in their essential characteristics. They have a rather large value in the troposphere, a much lower value in the region near the tropopause, and a large value in the upper stratosphere.

The LLL K_z profile was derived using both CH_4 and N_2O measurement data. Figures 3 and 4 compare the model-derived species profiles with the measurements of CH_4 and N_2O . The small amount of data, particularly above 30 km, is apparent in these figures.

Current models reproduce the methane profile, but they do not accurately reproduce the N_2O , CFCl_3 and CF_2Cl_2 profiles using the same transport parameterization that yields agreement with CH_4 . Consequently, a compromise transport coefficient may be used that provides a reasonable fit to the data for the various species. The methane distribution is also affected by the OH content. Thus, changing the transport coefficient would require that some mechanism be found that reduces the OH concentration in the 20-30 km region, but such mechanisms are only speculative at present.

FIGURE 2 Vertical transport coefficients currently being used by two modeling groups.

Radiative Processes

Photodissociation processes in the atmosphere are often extremely important mechanisms for the production and destruction of chemical species. The photodissociation rate, J_i , for species i to give a product j is defined by

$$J_{i \rightarrow j} = \int_{\lambda} Q_{\lambda, i} \sigma_{\lambda, i} F_{\lambda}(z) d\lambda \quad , \quad (4)$$

FIGURE 3 Comparison of computed and observed CH₄ mixing ratio profiles. The parameter χ refers to solar zenith angle.

where $Q_{\lambda,i} = Q_{\lambda,i(i+j)}$ is the quantum yield for photodissociation of species i to result in production of species j ; $\sigma_{\lambda,i}$ is the photoabsorption cross section; and $F_{\lambda}(z)$ is the flux density. The flux density is affected by changes in the

FIGURE 4. Comparison of computed and observed N_2O mixing ratio profiles.

concentration profiles of absorptive species predicted by the model and by the overburden of absorptive and scattering species. Input parameters affecting the calculated photodissociation rate are the wavelength dependence of the quantum yield and absorption cross sections (which are based on laboratory measurements), the solar flux at the top of the atmosphere, the total column of absorptive species above the top of the model (which are based on atmospheric measurements), and the solar zenith angle (which varies by the season and time of day at a given latitude).

The importance of molecular multiple scattering and the surface albedo on determining atmospheric photodissociation rates is now well recognized (Luther and Gelinas, 1976; Callis et al., 1976; Kurzeja, 1976; Luther et al., 1978). Most one-dimensional models now include the effect of multiple scattering not only because of the effect it has on the photodissociation rates, but because of the impact it has on ambient species concentration profiles and on model sensitivity to perturbations (Luther et al., 1978). When multiple scattering is treated, the flux density in Eq. (4) includes contributions from both the direct and diffuse flux components.

Changes in stratospheric composition can affect the stratospheric temperature profile via the solar and longwave radiation balance. Changes in temperature affect chemical reaction rates, which in turn feed back on composition. This temperature feedback mechanism has been included in recent one-dimensional model calculations (McElroy et al., 1974; Luther et al., 1977; Tuck, 1977; Boughner, 1978). In these calculations the stratospheric temperature profile is calculated by using a radiative transfer model that includes solar absorption and longwave interaction by the radiatively important stratospheric species.

Physical Domain and Boundary Conditions

The choice of spatial domain depends on the chemical species of interest and the level of detail desired. For each individual species either boundary concentrations or fluxes must be prescribed. Because atmospheric measurements of many chemical species are inadequate, it is difficult to construct reliable boundary conditions for some species. In practice, an iteration between estimated boundary conditions, model simulation results, and appropriate comparisons with available atmospheric data must be carried out. The need for accurate boundary conditions

can be reduced by extending the physical domain beyond the minimum required by the problem at hand. Moving the boundary beyond a buffer zone serves to reduce the model sensitivity to uncertainties in boundary conditions. In the vertical direction, many models, especially one-dimensional models, cover the region from the earth's surface to above 50 km.

Averaging Processes

In the formulation of models, certain yet unspecified averaging processes must be applied so as to provide a link with physical reality and the means for interpretation of the solutions from such models. Formally $c_i(x,t)$ for Eq. (1) is assumed to be uniform over a unit volume in a unit time interval. But in a representation with reduced dimensionality and/or coarse spatial resolution, c_i must represent certain spatial and temporal averages. Without detailed data on spatial and temporal variations, it is not possible to devise a totally consistent averaging procedure for the nonlinear photochemical reaction rates. This is likely to be the case for many years to come. Nevertheless, the considerable computational difficulty created by diurnal variations in solar flux can be removed through diurnal averaging procedures. This allows the solution of time-dependent problems over long time durations using a diurnally-averaged model with a considerable savings of computer time.

Sources and Sinks

In addition to the sources and sinks caused by the interactive chemistry, the model must include the effect of sources and sinks caused by other processes. Net sources and sinks at the earth's surface for each species must be taken into account in determining necessary flux or concentration boundary conditions. Both wet and dry removal processes for trace atmospheric constituents must be parameterized. The effects of these removal processes are generally approximated using a first-order loss rate that varies with altitude and species. Cosmic ray production of nitric oxide is also included in the models in a parametric way.

Other Physical Data

Altitude distributions of major constituents such as N_2 and O_2 are generally fixed in the calculations with concentrations based on a reference such as the U.S. Standard Atmosphere (1976). Some trace species distributions may also be fixed based on atmospheric measurements. Species such as CO and H_2 have been treated this way in the past at LLL (these species are now calculated). Because of the difficulty in treating water vapor in the troposphere, many models fix the concentration of water vapor in the troposphere, while calculating its concentration in the stratosphere. Unless temperature feedback effects are included, the temperature profile is specified based on a standard reference such as the U.S. Standard Atmosphere (1976).

Time-Dependent and Steady-State Solutions

Once the mathematical model is fixed (i.e., all parameterizations of the relevant physical variables are determined), the system of differential equations are to be solved. For simplicity and computational economy, steady-state solutions of Eq. (1) are often useful and desirable. Such solutions add additional requirements for time-averaging procedures, since local incident solar fluxes vary both diurnally and seasonally and may vary on even longer time scales. In diagnostic applications, steady-state solutions used in a snapshot manner can yield useful information.

Fully time-dependent models are more useful both diagnostically and prognostically, although their solutions are considerably more complicated and computationally more expensive. For the analysis of atmospheric data on many short-lived species, time-dependent models, in particular diurnal models, must be used.

3. MODEL SIMULATIONS OF STRATOSPHERIC OBSERVATIONS

3.1 STRATOSPHERIC COMPOSITION

Comparison with observational data on trace species concentrations is an important aspect of validating the performance of numerical models of the stratosphere. Although comparisons with observations are a necessary part of model validation, these comparisons alone are not sufficient to validate the performance of the model because we know from past experience (Duewer et al., 1977) that models with significantly different chemistry and sensitivity can predict very similar ambient species profiles.

Two somewhat different sets of chemical reaction rate coefficients and photolysis cross sections were used in the calculations presented in this report. Most of the calculations were performed prior to the NASA Workshop at Harpers Ferry, West Virginia (June 1979), and utilized chemical rates based primarily on JPL (1979). After the NASA Workshop, we repeated several of the perturbation calculations using chemical rates based on the recommendations of the chemistry panel at the NASA Workshop. These two chemistries are described in Appendix A as 1979a and 1979b chemistries.

In this section, we compare the results of our current one-dimensional model using 1979b chemistry with measured trace species concentrations. Much of the measurement data used in the comparisons were derived from information communicated at the NASA Harpers Ferry Workshop. As such, some is preliminary in nature. The evaluation of measurements is strongly influenced by that of the NASA panels as reflected at the Workshop. We have also reported a band of model-predicted concentrations based on work presented at the NASA Workshop. Our model results using 1979a chemistry (see Appendix A) were within the band of model predictions indicated. Our discussion in this section closely parallels some of that in the NASA document, reflecting, in part, our participation in writing parts of that document.

O(³P)

There is good agreement between model-calculated distributions (Fig. 5) and the few available measurements. However, the O(³P) concentration is in a near photoequilibrium with O₃, and the ozone column used in the calculations is calculated for equinox conditions whereas the measurements are winter measurements. Because O₃ was not measured at the same time that O was, there is some danger that the apparent good agreement is fortuitous.

O₃

Ozone profiles vary significantly with latitude and season. Total column ozone ranges from about 200 m·atm·cm in the tropics to about 400 m·atm·cm near the

FIGURE 5. Comparison of computed and observed O(³P) volume mixing ratio. The model range applies to model calculations reported at the NASA Harpers Ferry Workshop, June 1979.

poles. The altitude of the peak concentration is lower near the poles than at the equator. The model-derived O_3 profile shown in Fig. 6 resembles observations of O_3 taken at middle latitudes. The range of rocket and balloon measurements shown in Fig. 6 is taken from the data for middle latitudes in the U.S. Standard Atmosphere (1976).

OH, HO₂

Within the plausible error in the measurements, there appears to be reasonable agreement between theoretical calculations and the few available measurements of OH and HO₂ in the stratosphere (see Figs. 7 and 8). Data are available only between 28 and 38 km for HO₂. The point-to-point variability of the measurements for both species exceeds measurement precision. This suggests that the different air masses measured may have significantly different histories. It would be desirable if, in the future, concurrent measurements of various species (OH, HO₂, O₃, H₂O, etc.) would be made. If such concurrent measurements

FIGURE 6. Comparison of computed and observed ozone concentration profiles. The rocket and balloon measurement data are taken from the U.S. Standard Atmosphere (1976).

FIGURE 7. Comparison of computed and observed OH mixing ratio profiles. The model range applies to model calculations reported at the NASA Harpers Ferry Workshop, June 1979.

become available, it may be possible to explain local variability, as well as to usefully examine ratios (e.g., HO_2/HO) in relation to those expected theoretically. Comparison of the total OH column calculated by current one-dimensional models with the observations of Burnett and Burnett (1979) does not indicate significant differences in average column content.

NO

The measurements shown in Fig. 9 are from midlatitudes and near-local-noon conditions. When compared to calculated noon profiles, the calculated profiles are

FIGURE 8. Comparison of computed and observed HO_2 mixing ratio profiles. The model range applies to model calculations reported at the NASA Harpers Ferry Workshop, June 1979.

significantly larger than the observations above 30 km. The maximum difference occurs in the upper stratosphere where NO is the dominant NO_x species. One contribution to the difference between models and observations is the overprediction of the total NO_x content by current models. The apparent NO maximum near 40 km lends some credibility to the hypothesis that the treatment of NO photolysis may underestimate the actual upper stratospheric NO sink.

Recent measurements of NO (discussed by H. Schiff and others at the N.A.T.O. Advanced Study Institute on Atmospheric Ozone held in Portugal in October 1979) find much higher concentrations in the upper stratosphere than previous measurements. These measurements agree well with model calculations. However, the reason for disagreement with previous observations (whether it is due to natural variability or measurement errors) must be resolved.

FIGURE 9. Comparison of computed and observed NO mixing ratio profiles. The model range applies to model calculations reported at the NASA Harpers Ferry Workshop, June 1979.

NO₂

Figure 10 compares the model-calculated range of distributions for NO₂ with that measured at sunset near the fall equinox at 40-50°N. The models approximate 30°N equinox conditions which leads to uncertainty regarding the differences found in the lower stratosphere.

FIGURE 10. Comparison of computed and observed NO_2 mixing ratio profiles. The model range applies to model calculations reported at the NASA Harpers Ferry Workshop, June 1979.

HNO_3

Current models predict more HNO_3 than is observed above about 25 km (Fig. 11). In part this may simply reflect the higher-than-observed NO_x concentrations currently calculated. However, this does not appear to be sufficient to explain the entire difference, nor is it likely that model overprediction of OH between 25 and 35 km is responsible for the difference, since model OH and observations are in good agreement between 28-35 km.

Total NO_y

Our theoretical model presently calculates approximately a factor of 2 more NO_y ($\text{NO} + \text{NO}_2 + \text{HNO}_3$) than has been measured (Figs. 9-12). However, it should be noted that in situ measurements of all three species are not available with readily comparable techniques to permit an unambiguous comparison between theory and measurements.

FIGURE 11. Comparison of computed and observed HNO₃ mixing ratio profiles. The model range applies to model calculations reported at the NASA Harpers Ferry Workshop, June 1979.

Part of the reason for the difference between model and observation may be that the model predicts too much N₂O in the upper stratosphere, since N₂O is the primary source for NO_x in the stratosphere by reaction with O(¹D). More measurements of N₂O in the upper stratosphere would be necessary to confirm this hypothesis. The N₂O content in one-dimensional models is sensitive to the choice of vertical transport coefficient used in the calculation.

Other possible factors that might cause the models to overpredict NO_y would include: (1) A lower rate coefficient for O(¹D) + N₂O → 2NO than is currently recommended. The data for this process are not in good agreement. However, if anything, they suggest a faster rate coefficient. (2) O(¹D) may be overestimated. This could happen if the quantum yield for O(¹D) production from O₃ photolysis has a stronger temperature dependence than is used in the models.

FIGURE 12. Comparison of computed total NO_y mixing ratio profiles. The model range applies to model calculations reported at the NASA Harpers Ferry Workshop, June 1979.

(3) The rate at which NO photolysis occurs may be underestimated in the models. Frederick and Hudson (1979) estimate their results to be uncertain by a factor of 3. Adoption of their treatment decreased the photolysis rate by a factor of ~ 3 from the previous value in the model which resulted in an increase of the model-calculated NO_x by about 40%.

HNO_3/NO_2

The ratio of HNO_3/NO_2 currently calculated by models (Fig. 13) is much higher than is observed by Evans et al. (1976) but is within the error bounds of other measurements. In none of these measurements were both species measured by similar techniques. Concurrent measurements taken at a given point with the same technique are needed to establish whether a discrepancy actually exists. Even then, because of the difference in chemical lifetimes, it would be difficult to determine the time history of both NO_2 and HNO_3 that led to the ratio observed. If a discrepancy does exist, one possible explanation would be that current estimates of OH in the lower stratosphere (below ~ 30 km) are too large. Another possibility would be that the sinks for HNO_3 are underestimated.

FIGURE 13. Comparison of computed and observed HNO_3/NO_2 concentration ratio profiles.

N₂O₅

We currently calculate a N₂O₅ concentration of ~ 2.5 ppb near sunrise. This can be compared to the value of 2 ppb deduced for N₂O₅ by Evans et al. (1978) based upon measurements of other species a few hours after sunrise. It should be noted that the measurement was not made at the latitude and season the model most nearly approximates. Until further measurements are made, the comparison is inconclusive.

Cl, ClO

In Fig. 14 we compare model predictions and observations of Cl and ClO. The model predictions shown apply to 32°N (where all reported measurements to date have been made) and mid-day solar zenith angles at equinox. The indicated range of calculated profiles encompasses the results of various groups and chemical models.

The single observed Cl profile (and one additional Cl observation at a single altitude) and calculated Cl profiles agree within the measurement uncertainty of +35%. However, the measurements suggest a larger vertical gradient in Cl mixing ratio than is predicted. More Cl measurements are needed to determine whether any seasonal or spatial variations exist and, if so, whether these are consistent with model predictions.

For ClO, at the mixing ratio maximum, with the exception of the 14 July 1977 measurement, the resonance fluorescence measurements are within a factor of about 2 of the predicted ClO abundances. The September through December ClO measurements show a significantly sharper than predicted gradient below the mixing ratio peak. Except for the summer of 1979, summer measurements give more ClO than the September through December measurements. The 14 July 1977 measurement gives six times more ClO than is predicted near the mixing ratio peak, and exceeds by about a factor of 3 the total chlorine mixing ratio believed to be present in the stratosphere. The laser heterodyne radiometer measurement also shows more than twice as much ClO as is predicted near the mixing ratio peak and a sharper than predicted decrease in ClO at lower altitudes. The millimeter-wavelength results imply slightly less ClO than the mid-range of model

FIGURE 14. Comparison of computed and measured mixing ratio profiles for Cl and ClO. The model range applies to model calculations reported at the NASA Harpers Ferry Workshop, June 1979. LLL model results using 1979a chemistry fell within the model range.

predictions and substantially less ClO than the July 1977 resonance fluorescence and the 20 September 1978 laser heterodyne results. A broader data base is needed to explain the difference in these results as well as the large (factor of 10) variation in the ClO profiles observed but not predicted by one-dimensional models.

Because the 14 July 1977 resonance fluorescence ClO measurement cannot be explained in light of our present understanding of stratospheric chemistry, Anderson et al. (1979) have given its analysis special attention. After careful examination, they have concluded that the large ClO values are not caused by instrument

malfunctions and, using simultaneous measurements of other species, have concluded it implies either:

1. ClO was injected into the observed region prior to the measurement in a time which is comparable with the chemical response time of odd oxygen; or
2. The reaction $\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$ is not rate limiting in the closure of the chlorine catalytic cycle; or
3. There exists an odd-oxygen production term proportional to ClX and competitive with direct O_2 photolysis in the middle and upper atmosphere.

At present it is uncertain which, if any, of these explanations is correct.

The differences between theoretical calculations and observations of the ClO gradient below 34 km also require attention. At present, speculations for explaining these differences range from the possibility of a missing chemical reaction or an incorrect rate constant in present theory to the possibility of it being an artifact of the transport parameterization used in current models, or an artifact of the measurement techniques.

Cl/ClO Ratio

Measurements and model calculations of the Cl/ClO ratio are shown in Fig. 15. The Cl/ClO ratios from the 28 July 1976 resonance fluorescence measurements (Anderson et al., 1979) agree to within measurement uncertainty with most calculations. It is difficult at present to make any conclusions regarding this comparison because of the experimental uncertainties, the limited amount of data, the apparent variability of ClO, and the poor agreement between models and observations for ClO.

HCl

Although there may be significant disagreement (as large as 30-40% when compared with the IR spectra data, much larger if compared to the filter or

FIGURE 15. Comparison of computed and measured Cl/ClO concentration ratio. The model range applies to model calculations reported at the NASA Harpers Ferry Workshop, June 1979. LLL model results using 1979a chemistry fell within the model range.

radiometer data) above 30 km (Fig. 16), the uncertainty in the observational data in this altitude range is such as to probably encompass the areas of disagreement.

ClONO_2

The only observational data for ClONO_2 are from one flight by Murcray (1979). As shown in Fig. 17, there is excellent agreement if the fast production

FIGURE 16. Comparison of computed and observed HCl mixing ratio profiles. The model range applies to model calculations reported at the NASA Harpers Ferry Workshop, June 1979. LLL model results using 1979a chemistry fell within the model range.

rate for ClONO_2 is used in the calculations, whereas there is a factor of 3 difference if the slower production rate is used (see Section 4 discussion regarding the rate of production of ClONO_2).

Until further data are available, it is difficult to make any conclusive statements regarding this species. However, the limited amount of data available does not indicate any gross discrepancies between theory and observations.

FIGURE 17. Comparison of computed and observed ClONO₂ mixing ratios. The model range applies to model calculations reported at the NASA Harpers Ferry Workshop, June 1979.

Total ClX

There now exists a limited number of measurements for Cl, ClO, HCl, and ClONO₂ in the stratosphere. Except for three measurements of ClO taken in summer (Anderson, 1979; Menzies, 1979), there does not appear to be any large discrepancy between the total amount of ClX predicted and that observed. However, the summer measurements of ClO are so large as to require much more total ClX than known sources are capable of producing. This implies the possibility of an unknown source for ClX in the atmosphere, an error in the observation, or some unusual episodic event.

3.2 MODEL SIMULATIONS OF PAST PERTURBATIONS

Possible Long-Term Solar Variations and the Effects on Temperature and Ozone*

In the study of potential anthropogenic influences on the stratospheric ozone budget it is necessary to first understand the natural variations of ozone. In order to achieve early detection of anthropogenic trends and to establish the magnitude of such effects, we must differentiate the natural stratospheric ozone variations from the man-made effects that are of comparable time scales. The suggested correlation between ozone and sunspot number is of primary interest. If this relation is real, then for the next few years the theoretically predicted effect of CFM's on ozone may not be directly detectable unless the effect of this ozone-solar cycle relation can be quantified and removed from the ozone data. At this time, the most plausible mechanism coupling the sunspot cycle and atmospheric ozone is the change in solar flux between 180 and 340 nm from solar maximum to solar minimum (Heath and Thekaekara, 1977; Callis and Nealy, 1978; Penner and Chang, 1978). Theoretically, a variation in solar flux between 180 and 340 nm of approximately 30% (maximum to minimum) can lead to local ozone changes as large as 10% near 35 km, and total ozone column changes of approximately 5% (Penner and Chang, 1978). This is comparable to the predicted CFM effect of ozone decreases of up to 5% around the year 1990. Consequently, the possible influence of periodic or aperiodic changes in solar UV flux intensities tends to obscure changes due to the present levels of CFM's, and this may continue for the next decade. The same is also true for the local ozone concentrations in the upper stratosphere.

The data that support a variation in solar UV fluxes during a solar cycle are limited (Heath and Thekaekara, 1977) and need to be confirmed with other independent measurements. Simon (1978) has pointed out the difficulty in the absolute calibration of the measuring instruments, especially those aboard a satellite.

*See Appendix D for a more detailed discussion.

Since the direct monitoring of solar UV fluxes and ozone are both of limited use in establishing the ozone-solar cycle relation, we are left with the monitoring of trace species other than ozone as a possible independent method for validating the effects of solar UV flux variations. We examined the possible variations of 31 trace species that result from hypothetical solar UV variations with the LLL time-dependent model of stratospheric chemistry, including self-consistently calculated stratospheric temperature and atmospheric adjustment to hydrostatic equilibrium (Penner and Chang, 1979). From this study we identified N_2O as a most likely candidate for monitoring to study coupling between variations in solar UV and atmospheric composition (see Appendix D). Furthermore, there remains the question of the effect of transport-related variability that can only be resolved with a set of upper stratospheric data.

The Atmospheric Nuclear Tests of the 1950's and 1960's*

Past atmospheric tests of nuclear devices larger than about one megaton (TNT) yield provide a potentially significant source of NO_x to the stratosphere. During the late 1950's and early 1960's, large numbers of such tests were carried out, and the NO_x released to the stratosphere in 1961 and 1962 should have been comparable to the amount that would be released by about 2.7 years operation of a large SST fleet (i.e., one emitting $\sim 10^8$ molecules $cm^{-2} sec^{-1}$). The paper by Chang, Duewer and Wuebbles (1979) gives an account of the predicted effects through early 1978. Figure 18 gives the computed ozone column change as a function of time. For computations made with 1979b chemistry (see Appendix A), the two curves give the ozone depletion calculated for injection altitudes based on a parameterization by Foley and Ruderman (1972) or on the lower altitude observations of Seitz et al. (1968). The two treatments are thought to bound the plausible range of injection altitudes.

Both treatments predict maximum ozone depletions of less than 2% for the largest annual-average change. The largest change is only about 1.25% if a 1-2-1 smoothing function is applied to annual perturbations. The computed changes are

*See Appendix F for a more detailed discussion.

FIGURE 18. The computed change in total ozone resulting from atmospheric nuclear testing during the 1950's and 1960's.

clearly within the observed variability in the ozone record as analyzed by Angell and Korshover (1978).

Figure 19 gives the computed changes at selected altitudes. The ozone concentration decreases at all altitudes above 25 km. However, at lower altitudes the concentration of ozone was computed to increase significantly, which accounts for the net increase in total ozone prior to 1962 shown in Fig. 18. Some of these computed changes are much larger than the change in the ozone column. However, the predicted ozone variations at specific altitudes are still only about the same magnitude as the variations in Umkehr-based ozone concentrations.

Thus, the model-predicted response to the atmospheric nuclear tests does not lead to conflict with the ozone record, but it also does not seem to explain much of

FIGURE 19. The computed change in local ozone concentration at various altitudes resulting from atmospheric nuclear testing during the 1950's and 1960's. Ozone concentrations in the lower stratosphere and upper troposphere (not shown) were computed to increase, which accounts for the net increases in total ozone prior to 1962 shown in Fig. 18.

the observed ozone variation. The predicted effect on ozone of the nuclear tests should be considered in any attempt to model ozone variations during the 1960's since the predicted changes in ozone at specific altitudes are comparable to both the observed variations and to the variations calculated for such phenomena as the hypothesized variation of ultraviolet light tied to the solar cycle, or the predicted change in ozone from CFM production through 1978.

Polar Cap Absorption Events

Crutzen et al. (1975) noted that large polar cap absorption (PCA) events should produce significant quantities of NO_x in the middle and upper stratosphere, especially at high latitudes. Indeed the PCA events of August 1972 were estimated to have produced several times as much NO_x as the ambient content of the atmosphere in the region above 40 km. In a comparison with Nimbus 4 ozone data, Heath et al. (1977) found that the agreement between predicted ozone change and observation was quite good north of 75° latitude and above 4 mb (the model under predicted the perturbation by roughly 30%). Since those calculations were made, several important changes in model chemistry have occurred. However, these changes have had only a modest effect on the sensitivity of the model to large injections of NO_x at high altitude and high latitude. There are two recent recalculations of the effect of the August 1972 PCA event in the literature. Fabian et al. (1979) found that their computed ozone change was in excellent agreement with observation if more recent estimates of the NO production per ion pair are used. However, the agreement between observation and computation at lower latitudes was less satisfactory, although still qualitatively encouraging. Borucki et al. (1978) report similar findings, and also find that their model substantially underpredicts the ozone perturbations at altitudes near 30 km.

The August 1972 PCA events seem to provide a useful test of the short-term (several days) response of stratospheric ozone to NO_x increases above about 40 km. Unfortunately, the test is not directly applicable to lower altitude, midlatitude NO_x perturbations occurring over long (several year) time periods. The nature of the NO_x injection and of the O_3 data do not permit resolution of questions about the adequacy of model simulations of transport phenomena or of the chemistry of the lower stratosphere. Thus, PCA events provide the only

phenomenon for which models forecast an observable and observed stratospheric ozone perturbation in response to an NO_x change, but the nature of the perturbation and the response differ from the problems associated with SST operations to an extent that precludes its direct use as a calibration point for SST predictions of column ozone changes. Nonetheless, the good agreement above 40 km is encouraging since it suggests at least that models are adequately representing the short-term response of ozone to NO_x injections at higher altitudes.

The Solar Eclipse on February 26, 1979*

In addition to ozone observations, measurements of other minor constituents during a solar eclipse could provide validation of the short time constant chemistry in atmospheric models. Consequently, experiments for upcoming solar eclipses, when properly supported by theoretical analysis, could contribute significantly to our understanding of atmospheric chemistry. In fact, given the proper data on trace species concentrations during an eclipse, such measurements could provide a direct demonstration that the currently proposed major reactions of NO_x , HO_x , and Cl_x species are indeed concurrently functioning in the stratosphere in the manner suggested by laboratory chemistry. However, the measurements yield little information about slower processes that can have large effects on model sensitivity.

We have examined theoretically (Wuebbles and Chang, 1979) the expected effect of a solar eclipse on stratospheric minor constituents. Primary emphasis was given to the total eclipse that occurred over North America on February 26, 1979. Variations similar to those computed for this particular case should be expected for other total eclipses. Totality was the longest (~ 3 minutes) at 50°N latitude for the February 1979 eclipse.

While ozone, tropospheric water vapor, and temperature were held fixed in the model for most of our eclipse calculations, the model was also run with calculated ozone to examine the expected response of ozone to an eclipse. Our analysis has shown that fixing the ozone distribution does not significantly affect the temporal variations calculated for other species during the eclipse. Solar flux variations during the eclipse were based on Hunt (1965).

*See Appendix E for a more detailed discussion.

Those species having chemical lifetimes less than a few hours are expected to vary significantly from normal diurnal behavior during a solar eclipse. Local concentrations of the species could be quite variable, and therefore we should focus on relative changes rather than absolute magnitudes.

The model-calculated response of ozone during an eclipse essentially agreed with Hunt (1965). A significant increase in O_3 is to be expected in the upper stratosphere and in the mesosphere as a result of the conversion of $O(^3P)$ to ozone through the reaction $O(^3P) + O_2 + M \rightarrow O_3 + M$ accompanied by decreased photolysis of O_2 and O_3 . The maximum increase in O_3 , found at the end of totality, was computed to be 15% and 45% at 50 and 55 km, respectively. Larger fractional changes are expected in the mesosphere. Since most of the atmospheric ozone is at lower altitudes in the stratosphere, an insignificant change in the total ozone column is expected. Significant changes were also predicted to occur in NO , NO_2 , Cl , ClO , OH and HO_2 concentrations.

The results of this study suggest that significant and detectable variations are expected for some of the important stratospheric minor constituents during a solar eclipse. Such observations, particularly simultaneous observations of trace species, would demonstrate clearly the simultaneous functioning of the various important photochemical catalytic cycles in the stratosphere.

The model calculations were completed prior to the eclipse. Measurements during the solar eclipse of February 26, 1979, were made with NASA's aircraft. This plane carried instruments to measure NO , O_3 , and temperature at 20 km (instrument of Starr, Craig, and others of NASA-Ames) and to measure the NO and NO_2 columns above 20 km (by David Murcray of University of Denver). Preliminary results by Starr and Craig show no change in O_3 at 20 km during the eclipse (as was predicted), and they show excellent agreement with the theoretically expected change in NO . A detailed comparison between this measurement and model calculations is being made. In any case, the results demonstrate that the reactions $NO + O_3$ and $NO_2 + h\nu$ occur in the stratosphere at rates similar to those computed theoretically.

4. POTENTIAL CHANGES IN OZONE CAUSED BY AIRCRAFT EMISSIONS

4.1 EMISSION INDEXES AND FLEET PROJECTIONS

In this report we consider the potential effects on atmospheric ozone of several different aircraft emissions scenarios. These emission scenarios were developed for three basically different applications: (1) the projected 1990 fleet, (2) a commercially viable fleet of supersonic transports, and (3) a commercially viable fleet of hypersonic transports. In all of the perturbation calculations discussed in Sections 4 and 5, the "ambient" or "unperturbed" atmospheric conditions refer to the model-calculated initial state rather than to atmospheric measurements.

1990 Fleets

We developed emission profiles for both high and low projected 1990 aircraft fleet sizes. In the case of the projected 1990 high fleet, we adopted the emissions factors and fleet projections used by Oliver et al. (1977) in their Table 2-33. The projection used by Oliver et al. (1977) was based on A. D. Little, Inc. (1976) with corrections to the mean flight altitude of the projected SST fleet of 142 Concorde and TU 144's and an emissions factor ~ 4 times larger than used by A. D. Little, Inc. (1976) for CF6 engines (which Oliver et al., 1977, treated as having the same emissions indexes as JT9D engines). The NO_x emission index for SST's was assumed to be 20 g NO_x /kg fuel.

In converting the projected emissions in Table 2.33 of Oliver et al. (1977) to a format compatible with the one-dimensional model, we treated the model as a Northern Hemisphere model, summed emissions over all latitudes between zero and 90°N at a given altitude, and converted kg/year at each altitude to molecules $\text{cm}^{-3} \text{ s}^{-1}$ over a 1-km-thick layer centered at even-kilometer altitudes. Table 2 gives the emission rates actually used in our calculation.

We also examined the effects of the projected subsonic fleet without the SST contribution using the emissions given in Table 2 for the subsonic fleet only. We generated a 1990 low estimate by multiplying the 1990 high estimate emissions by

TABLE 2. Projected 1990 aircraft emissions of NO_x (Oliver et al. (1977) high estimate). The low estimate of emission rates equals 0.633 times the high estimate.

Injection Altitude (km)	NO_x Injection Rate Total Fleet (molecules $\text{cm}^{-3}\text{s}^{-1}$)	NO_x Injection Rate Subsonic Only (molecules $\text{cm}^{-3}\text{s}^{-1}$)
6	90	90
7	179	179
8	265	265
9	665	665
10	1167	1167
11	1161	1161
12	520	520
13	75	75
14	18*	12
15	18	
16	33	
17	43	
18	29	
19	8	

*Emissions from the SST fleet are included at 14 km and above.

0.633, the ratio of the 1990 low estimate fuel usage to the 1990 high estimate fuel usage given in Table 2.25 of Oliver et al. (1977).

SST Fleets of Commercially Viable Size

In treating hypothetical SST fleets of commercially viable magnitude, we have considered a fleet emitting 1000 molecules of $\text{NO}_x \text{ cm}^{-3}\text{s}^{-1}$ and 1.77×10^5 molecules of $\text{H}_2\text{O cm}^{-3}\text{s}^{-1}$ over a 1-km-thick layer in the Northern Hemisphere, which is equivalent to 6.2×10^8 kg of NO_x (as NO_2) and 4.3×10^{10} kg of H_2O per year. These emission rates correspond to a fuel usage of 3.5×10^{10} kg yr^{-1} by SST's, assuming the emission indexes are 16 g NO_2/kg fuel and 1.25 kg $\text{H}_2\text{O}/\text{kg}$ fuel. The NO_x emissions index for currently realizable

SST engines has been estimated to be as high as 22 g NO₂/kg fuel or as low as 15.6 g NO₂/kg fuel. A still unresolved discrepancy exists between spectroscopic and probe sampling methods of determining NO_x emissions (Oliver et al., 1977). If the spectroscopic analyses are correct, the above-cited emission index should be increased by a factor of 2 to 3 for SST operations.

Future technologies may be capable of reducing the NO_x emission index by several fold. A three-fold reduction in the NO_x emission index is projected for some existing design concepts (Popoff et al., 1978). We consider NO_x emission indexes of 18 g NO₂/kg fuel for current technology and 6 g NO₂/kg fuel for future technology.

The number of SST's corresponding to a fuel usage of 3.5×10^{10} kg yr⁻¹ is difficult to determine on an absolute scale. The number of SST's corresponding to a given fuel usage is inversely proportional to the expected hours/day of flight and the fuel usage per hour. Estimates of the hours per day of flight at cruise altitude have varied from 4.4 to 7.5 hrs. Estimates of fuel usage have ranged from 16,800 to 19,100 kg/hr for the Concorde, from 52,000 to 60,000 kg/hr for the B2707, and as low as 44,000 kg/hr for a hypothetical advanced design similar to the B2707 (Popoff et al., 1978). Thus, more than a two-fold variation in engine emissions from a projected SST fleet is possible based on different estimates of aircraft operation and fuel consumption rate. A fuel usage of 3.5×10^{10} kg yr⁻¹, therefore, corresponds to about 750-1000 Concorde, or 180-660 advanced SST's. Thus, our standard emissions rates are compatible with a large fleet of SST's.

Hypersonic Transport Emissions

In addition to the effects of subsonic and supersonic fleets, we projected a range of emissions and environmental impacts of a possible hypersonic transport (HST) fleet. For this purpose, we adopted the emissions indexes given in CIAP Monograph 2 (1975), Chapter 6 for a fleet of research HST's of gross takeoff weight 2.27×10^5 kg operating at Mach 8 and cruise altitude of "36.68" km. According to data in CIAP Monograph 2, the hypothesized HST operations would consist of an initial acceleration to hypersonic speeds (and cruise altitude) using rocket engines, followed by about five minutes of SCRAMjet operation, followed by a cruise mode during which most emissions would consist of liquid hydrogen boil-off for cooling.

The SCRAMjet would use 670 kg/flight of liquid H_2 ; the rocket engines would use 2450 kg/flight of liquid H_2 , and 14,650 kg/flight of liquid oxygen (CIAP Monograph 2, p. 6-7); but it would only release a total of 1650 kg/flight of water vapor and 615 kg/flight of H_2 (CIAP Monograph 2, p. 6-8). Thus, the fuel use and emissions estimates given in CIAP Monograph 2 for rocket operations are incompatible, with not enough mass being emitted. This difficulty would be resolved by increasing the water vapor emissions by a factor of 10. Cooling at cruise altitude would consume an additional 309 kg of liquid hydrogen per flight.

The emissions consist of H_2O , H_2 , H, OH, NO, and O as given in Table 3. In analyzing the effects of HST emissions, only cooling and SCRAMjet emissions

TABLE 3. HST emissions on a per-flight basis. Data are from CIAP Monograph 2, Ch. 6, assuming a cruising speed of MACH 8, a cruise altitude of 36.68 km, and $H_2:O_2$ ratio of 1.

	Emissions per flight		Altitude (km)	Emissions rate for 1000 flights/day (molecules cm ⁻³ s ⁻¹)**
	(kg)	(moles)		
<u>SCRAMJet</u>				
H ₂ O	5705.	317,000	36.68	8504
H ₂	136.7	68,350	36.68	1820
H	13.1	13,100	36.68	350
OH	132.3	7,800	36.68	210
NO	137.4	4,500	36.68	123
O	34.4	2,150	36.68	58
<u>Rocket</u> (not included in calculation)				
H ₂ O*	16,500	917,000	0-36 mostly tropospheric	
H ₂	615	307,500	0-36	
<u>Cooling in Flight</u>				
H ₂	308.5	154,200	36	4130

* H_2O emissions from rockets have been increased by a factor of ten to permit mass balance.

**Emissions in a 1-km-thick layer.

were treated, and these were based on the data presented in Table 6-9 of CIAP Monograph 2. Rocket emissions were neglected since much of the rocket emissions would occur in the troposphere. In order to approximate a commercially viable fleet, we increased the emissions to correspond to an HST fleet with 1000 flights/day. Because even these emissions are relatively small, and the CIAP-Monograph-2-based emissions estimates may not apply to commercial-scale fleet operations (they are based on research flights), we also examined the effects of a 10-fold larger emission, perhaps interpretable as longer flights or flights of heavier aircraft. The emissions of H_2O , H_2 , NO , and OH were treated simply as a source of the molecules in question. Emissions of H-atoms (the code calculates H-atoms as an equilibrium species) were treated as emissions of an equivalent number of HO_2 molecules, while the small emissions of O atoms were ignored.

Because NO_x emissions are responsible for the major portion of the predicted change in total ozone, it might be attractive to use more than the stoichiometric amount of OH in the SCRAMjets in order to reduce NO_x emissions. According to CIAP Monograph 2, operating at a stoichiometric ratio of 1.5 instead of 1 would reduce NO_x emissions by more than a factor of three while increasing H_2O and H_2 emissions by factors of about 1.1 and 3, respectively. The net effect of these changes in emissions should be a smaller ozone perturbation.

We wish to emphasize that we performed no independent calculations of HST emissions indexes, and that the fleet projections are no more than crude parametric estimates of the approximate level of activity that might be associated with a mature, commercially successful fleet of HST's. If specific aircraft designs were to be proposed, the emissions should be independently projected.

4.2 CURRENT ASSESSMENT RESULTS

The LLL one-dimensional transport-kinetics model has been used to assess the potential chemical effects of aircraft engine emissions in the troposphere and the stratosphere. Calculations were made using projected fleet sizes for subsonic and supersonic aircraft as well as for a range of emission rates at particular injection altitudes. In order to determine the effect of uncertainties in various input

parameters on the assessment calculations, several sensitivity studies were also performed and are reported in the following section.

Subsonic and Supersonic Aircraft Fleets

The altitude of injection has a significant effect on the computed change in ozone because of the increase in residence time with altitude and because of the variation with altitude of the dominant chemical reactions and cycles. Table 4 shows the effect on total ozone at steady state of the same NO_x injection rate at different injection altitudes. An injection rate of $1000 \text{ molecules cm}^{-3} \text{ s}^{-1}$ over a 1-km-thick layer was used for NO_x , and there was no injection of H_2O .

Injections of NO_x over the altitude range of 7 to 20 km resulted in a net increase in total ozone in each case. The change in total ozone increased with increasing injection altitude for the troposphere and lower stratosphere. Throughout this region HO_x chemistry is the dominant chemical destruction process for ozone. When HO_x chemistry is more efficient than NO_x catalytic destruction of ozone, injections of NO_x lead to a net increase in odd oxygen production through the reaction sequences:

TABLE 4. The change in total ozone resulting from an NO_x injection of $1000 \text{ molecules cm}^{-3} \text{ s}^{-1}$ distributed over a 1-km-thick layer centered at the injection altitude. The calculations were made using 1979a chemistry (Appendix A).

Injection Altitude (km)	Change in Total Ozone (%)
7	0.25
9	0.40
11	0.64
13	0.84
17	1.34
20	1.31

and

The reaction sequence (5) acts to shift HO_x more toward OH, thereby increasing the loss rate of HO_x by the reaction $\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$. Reaction sequence (6) acts to reduce HO_x as OH and HO_2 are converted to H_2O and HNO_3 . Conversion to H_2O , and to a lesser extent HNO_3 , acts as a sink for HO_x , since the chemical lifetimes of these reservoir species is long compared to the time for transport into the troposphere. Injections of NO_x act to increase the rates of the above reactions. The net effect of reaction sequences (5) and (6) is a reduction of HO_x and an increase in odd oxygen production, both of which contribute to an increase in ozone. Of course, the odd-hydrogen species may have been generated through reaction of $\text{O}(^1\text{D})$ with H_2O . If this is the case, the odd oxygen produced via (5) or (6) only regenerates that used in the initiation of a catalytic cycle. It is important, nonetheless, because these sequences compete for HO_x with odd-oxygen destroying sequences.

Increases in NO_x concentration in the upper stratosphere lead to a reduction in ozone concentration in this region due to the greater importance of the NO_x catalyzed ozone destruction at these altitudes. The 20-km injection of NO_x resulted in a smaller net increase in total ozone than did the 17-km injection case, since more NO_x reached the upper stratosphere causing a greater reduction in ozone concentration at high altitudes relative to the increase at lower altitudes. This effect was found to be sensitive to the shape of the K_z profile used, however.

The standard model uses fixed-value boundary conditions for all species (except CCl_4) at the ground. Using flux boundary conditions for the species

N_2O , CH_4 , CH_3Cl , and HCl , resulted in slightly larger increases in total ozone ($< 0.1\%$ in absolute change) when compared to the fixed boundary condition case. Consequently, the choice of boundary condition has only a very small effect on the assessment results. Fixed-value boundary conditions are used in the model calculations unless otherwise noted.

The model was tested for interference effects by comparing the effect of simultaneous injections at the various injection altitudes given in Table 4 with the sum of the changes in ozone for individual injection altitudes. Table 5 shows that there is a destructive interference. That is, the simultaneous injections resulted in less change in total ozone than the sum of the changes caused by individual injections. This implies that summing the results of separate calculations for subsonic and supersonic fleets will not give the same answer as considering the effect of the two fleets simultaneously.

The effect of NO_x emissions by subsonic and supersonic fleets projected for 1990 are given in Table 6. Using the high estimate of the fleet sizes, the effect of subsonic and supersonic aircraft combined is estimated to be an increase in total ozone of 2.01%. This number represents the steady state change in ozone due to

TABLE 5. Synergism test using fixed boundary conditions and 1979a chemistry.

Case	$\Delta O_3(\%)$
Simultaneous injections	3.68
Sum of individual injections	4.78

TABLE 6. The computed change in total ozone at steady state using NO_x emission estimates for 1990 subsonic and supersonic fleets (1979b chemistry).

Case	Change in Total Ozone (%)	
	Subsonic and Supersonic	Subsonic Only
Oliver et al. (1977) high 1990 fleet estimate	2.01	1.86
Low 1990 fleet estimate	1.39	1.29

constant NO_x emission rates at the rates estimated for 1990. The subsonic fleet alone (injection altitudes up to 14 km) is estimated to cause an increase in total ozone of 1.86%. The small effect of the supersonic fleet is due primarily to the small fleet size projected for 1990. Using the lower estimate for fleet emissions, the corresponding numbers for ΔO_3 are 1.39% for the combined fleets and 1.29% for the subsonic fleet alone.

It should be noted that the effects of the existing 1979 subsonic fleet are of the order of 0.5% increase in total ozone. This effect is not negligible when compared to the estimated present-day effects of CFMs. Thus, an accurate assessment of the effects of subsonic aircraft will be important in interpreting ozone data for trends due to other anthropogenic influences.

The changes in ozone concentration for the high and low estimates of subsonic and supersonic fleet emissions are shown in percent in Fig. 20 and in absolute concentration in Fig. 21. The largest absolute increase in ozone concentration occurs near 12 km, and the region of increasing ozone extends up to about 26 km. Between 26 and 39 km there is a small decrease in ozone concentration.

FIGURE 20. The percent change in ozone concentration due to subsonic and supersonic aircraft computed for 1990 high and low fleet estimates (1979b chemistry).

FIGURE 21. Same as Fig. 20 except the change in ozone concentration is expressed as molecules cm^{-3} (1979b chemistry).

It should be recognized that the bulk of the ozone change calculated for the subsonic fleet occurs in the upper troposphere. As a result, it is sensitive to the treatment of such poorly understood phenomena as wet and dry removal processes and surface boundary conditions for rarely measured species. The tropospheric pressures differ from the pressure conditions used in most direct measurements of chemical rate coefficients (to a greater degree than stratosphere pressures). Heterogeneous reactions, which might have a significant effect on the calculations, are not included, and the one-dimensional treatment is not as good an approximation for the troposphere as it is for the stratosphere because of the strong latitudinal and longitudinal gradients in many trace species. Thus, the results for the 1990 fleet estimates are suggestive but are by no means definitive.

Assessments of potential changes in ozone due to future large fleets of supersonic transports have focused on injection altitudes of 17 and 20 km. In updating these assessments, we have assumed an emission index of 18 kg fuel for NO_x and 1250 kg fuel for H_2O . These emission indexes are based on current engine technology. It may be possible through future advances in technology that the NO_x emission index could be reduced to 6 kg (one-third of present value).

Calculations of O_3 given a constant fuel consumption rate at cruise altitude (3.5×10^{10} kg/yr in a hemispheric shell) are shown in Table 7 for different emission indexes. The NO_x emission rate of 1000 molecules $cm^{-3}s^{-1}$, which roughly estimates the emissions from a commercially viable fleet, was chosen as a reference case. The equivalent annual hemispheric injection rates of NO_x and H_2O are given in Table 8.

For each of the perturbations considered, there was an increase in total ozone. When the water vapor injection is included with the NO_x injection, there is less of an increase in total ozone because of the additional ozone destruction caused by HO_x which is produced from dissociation of H_2O . For the advanced

TABLE 7. The change in total ozone due to NO_x and H_2O emissions distributed over a 1-km-thick layer centered at the injection altitude.

Injection Altitude (km)	Injection Rate (molecules $cm^{-3}s^{-1}$)		Change in Total Ozone (%)	
	NO_x	H_2O	1979a Chemistry	1979b Chemistry
17	1000	0	1.34	1.25
17	1000	177,000	1.18	
17	333	177,000	0.32	
20	1000	0	1.31	1.14
20	1000	177,000	0.91	
20	333	177,000	0.07	

TABLE 8. Equivalent annual hemispheric injection rates for various NO_x and H_2O emissions.

Species	Injection Rate	
	(molecules $cm^{-3}s^{-1}$)	(kg/yr*)
NO_x	333	2.1×10^8
NO_x	1,000	6.2×10^8
H_2O	177,000	4.3×10^{10}

*Hemispheric injection assuming uniform injection over a 1-km-thick layer.

technology case (reduced NO_x emission), the increase in total ozone due to the NO_x injection is still greater than the reduction due to the H_2O injection, the net effect being a very small increase in total ozone.

In comparing the results from different models, a method that proved useful in the past was to compare the ratio $\Delta\text{NO}_y(\%)/\Delta\text{O}_3(\%)$ rather than just comparing ΔO_3 (Chang and Johnston, 1974; Chang, 1974). Although models differed in their computed values for ΔO_3 , they gave quite similar values for the ratio $\Delta\text{NO}_y/\Delta\text{O}_3$. At that time the models were predicting reductions in total ozone, and a typical value for the ratio was -5 or -6. Values of this ratio for the current model results are shown in Table 9. The ratio has a value of approximately 10 for a 17 km injection altitude with some dependence on the NO_x injection rate. ΔNO_y varies linearly with NO_x injection rate, but ΔO_3 is nonlinear, particularly for injection rates greater than 1000 molecules $\text{cm}^{-3}\text{s}^{-1}$. This is even more apparent for the 20-km injection altitude results where the ratio is 15.7 for an NO_x injection rate of 500 and increases to 24.6 for an injection rate of 2000. Because of the nonlinear characteristic of ΔO_3 for large injection rates, the ratio $\Delta\text{NO}_y/\Delta\text{O}_3$ is only useful for comparing model results for small injection rates.

TABLE 9. Changes in O_3 and NO_y column densities for various NO_x emission rates (1979a chemistry).

Injection Altitude (km)	NO_x Injection Rate (molecules $\text{cm}^{-3}\text{s}^{-1}$)	ΔO_3 (%)	ΔNO_y (%)	$\Delta\text{NO}_y/\Delta\text{O}_3$
17	500	0.72	7.0	9.7
17	1000	1.34	14.0	10.4
17	2000	2.37	28.0	11.8
20	500	0.75	11.8	15.7
20	1000	1.31	23.6	18.0
20	2000	1.91	47.0	24.6

Hypersonic Transport Fleet

The hypothesized hypersonic transport fleet making 1000 flights per day was calculated to cause a -0.218% change in column ozone. Emissions from a fleet ten times larger were calculated to cause a -2.06% change in column ozone. The NO_x emissions from the latter fleet by themselves caused an ozone change of -2.13%.

Figure 22 shows the local percentage changes in ozone vs. altitude for the 10,000 flight per day HST emissions and the NO_x emissions alone from 10,000

FIGURE 22. The change in ozone concentration caused by HST emissions for a fleet with 10,000 flights per day (1979b chemistry).

flights per day of HST's. (Because ΔO_3 is roughly linear in emissions rate over the range considered, large fleets were chosen to avoid comparing very small local changes that might contain significant numerical noise.) As is evident, the NO_x emissions dominate the ozone changes below ~ 40 km, while H_2O and H_2 emissions are responsible for most of the ozone change at higher altitudes. Because most of the ozone column is below 40 km, the integral column change is largely a result of the NO_x emissions.

4.3 SENSITIVITY STUDIES

Effect of Variations in K_z

Use of the vertical transport parameter K_z in the one-dimensional model enables atmospheric transport to be parameterized in a mathematically simple and convenient manner resembling diffusion. Various K_z profiles have been developed for use in one-dimensional models using N_2O and CH_4 measurement data. Because of variations in the data and because neither N_2O nor CH_4 are perfect tracers, there is no unambiguously correct K_z profile.

The K_z profile currently being used in the LLL one-dimensional model is shown in Fig. 23. The K_z values averaged over the stratosphere are considerably higher than was typical of K_z profiles used during the DOT's Climatic Impact Assessment Program (CIAP), which ended in 1975. Two profiles that were used for many of the assessments included in the CIAP Report of Findings (Grobeck et al., 1974) are also shown in Fig. 23. The Chang (1974) and Hunten (1975) K_z profiles result in slower transport between the middle stratosphere and the troposphere, so there is a larger build-up of emitted species in the stratosphere for constant injection rates.

Calculations of the change in total ozone as a result of an NO_x injection rate of $1000 \text{ molecules cm}^{-3} \text{ s}^{-1}$ are shown in Table 10 using the LLL, Chang (1974), and Hunten (1975) K_z profiles. The Chang (1974) and Hunten (1975) profiles are used to provide continuity with the earlier CIAP assessments; They are not representative of K_z profiles currently in use by any modeling group.

FIGURE 23. Vertical transport coefficient profiles used in the sensitivity study. The Chang (1974) and Hunten (1975) profiles are included for historical purposes.

The results in Table 10 show that changes in the K_z profile since 1975 have had a significant effect on the computed change in total ozone. Not only have changes in model chemistry caused a reduction (and reversal in sign) in the computed magnitude of ΔO_3 , but the changes in K_z have been significant as well. It is still true that the choice of K_z profile is a source of uncertainty in the one-dimensional calculations, but the range of results using currently popular profiles would not be as large as that in Table 10.

TABLE 10. The effect of the choice of K_z profile on the change in total ozone computed for an NO_x emission rate of 1000 molecules $\text{cm}^{-3}\text{s}^{-1}$ (1979a chemistry).

Injection Altitude (km)	Change in Total Ozone (%)		
	LLL K_z	Chang (1974) K_z	Hunten (1975) K_z
17	1.34	1.91	2.65
20	1.31	2.49	2.07

Effect of Variations in Background ClX

The effect of aircraft engine emissions on stratospheric composition is coupled with other stratospheric perturbations. As chlorofluoromethanes (CFM's) continue to be released to the atmosphere, there will be a gradual increase in the background concentration of ClX ($\text{Cl} + \text{ClO} + \text{HCl}$). Model calculations indicate a present day stratospheric ClX concentration of more than 1 ppbv. Assuming CFM releases at the 1976 release rate indefinitely into the future, the background ClX concentration is projected to increase to 2 ppbv around 1990 and to 4 ppbv around 2020. To assess the effect of changes in background ClX concentration on the model sensitivity, several NO_x perturbation calculations were repeated using a range of ClX concentrations. The results are shown in Table 11. In each case the ClX concentration was held constant. So the change in total ozone is the steady state value for a constant injection rate (i.e., the ΔO_3 value does not pertain

TABLE 11. The effect of variations in background ClX on the computed change in total ozone (1979a chemistry).

Injection Altitude (km)	NO_x Injection Rate (molecules $\text{cm}^{-3}\text{s}^{-1}$)	Change in Total Ozone (%)		
		1.14 ppb ClX	1.83 ppb ClX	3.76 ppb ClX
17	500	0.65	0.72	0.89
17	1000	1.22	1.34	1.69
17	2000	2.14	2.37	3.03
20	500	0.61	0.75	1.12
20	1000	1.04	1.31	2.03
20	2000	1.42	1.91	3.28

to any particular year) relative to a natural atmosphere with the same ClX concentration.

Table 11 shows that the change (increase) in total ozone resulting from an NO_x injection increases as the ClX concentration increases. The reason for the increase in ΔO_3 is related to the mechanism by which an NO_x injection leads to an increase in total ozone. The increase in total ozone comes about because for these magnitudes of NO_x injections, NO_x interferes with the more efficient ozone destruction by HO_x and ClX. Increasing the background ClX concentration means that there is more ozone destruction by ClX in the ambient case, so there is more that can be interfered with by the injected NO_x .

The change in total ozone versus NO_x injection rate is shown in Figs. 24 and 25 for ClX concentrations of 1.14, 1.83 and 3.76 ppbv. The change in total ozone is approximately linear with NO_x injection rate for injection rates up to 500 molecules $\text{cm}^{-3}\text{s}^{-1}$ (over a 1-km-thick layer). The nonlinear relationship between ΔO_3 and NO_x injection rate begins to show up for injection rates between 500 and 1000 molecules $\text{cm}^{-3}\text{s}^{-1}$, becoming more noticeable at larger injection rates. Linearity becomes a poor approximation at a lower injection rate for a 20-km injection than for a 17-km injection.

The ClX concentration, in addition to affecting the magnitude of ΔO_3 , also affects the relative magnitudes of the 17- and 20-km perturbations. For 1.83 ppbv ClX, the change in total ozone is nearly the same for both 17- and 20-km injection altitudes for injection rates up to 800 molecules $\text{cm}^{-3}\text{s}^{-1}$. For larger injection rates, ΔO_3 is larger for the 17-km injection than for the 20-km injection. On the other hand, when ClX is 3.76 ppbv ΔO_3 is larger for the 20-km injection than for the 17-km injection.

Effects of Speculative Reactions and Mechanisms

There are several reactions that have been suggested to be of possible importance in the stratosphere but have not been measured yet. Also, there are a few reactions for which anomalous pressure/temperature dependencies have been suggested but not demonstrated. We have examined the sensitivity of model predictions to a subset of such hypothetical reactions. The subset selected was based on the following criteria: (1) the hypothesized reaction or mechanism has at

FIGURE 24. The change in total ozone as a function of NO_x injection rate at 17 km for various background ClX concentrations (1979a chemistry).

least some support from laboratory work, and (2) the hypothesized reaction appears to have the potential for causing a major change^{*} in predicted effects of SST's or

^{*}In this context a major change would consist of a change in the computed steady-state effect of chlorofluoromethanes at 1975 levels by at least 50% or a change in sign or 2-fold increase in computed SST effects. Not all of the cases studied actually have such large effects and some mechanisms not studied might have larger effects.

FIGURE 25. The change in total ozone as a function of NO_x injection rate at 20 km for various background ClX concentrations (1979a chemistry).

CFM's. The reasons for selecting these two criteria were to reduce the number of possible cases to be considered and to focus attention on mechanisms that appear to have a maximum potential for altering model predictions. It must be stressed that most of the mechanisms considered here have no more than a weak basis in actual measurement. The purpose of this section is to suggest experiments that might deserve some priority. It is not to suggest that the hypothesized mechanisms or their computed effects are particularly likely to be true.

In this section we will discuss the major effects on the computed ambient atmosphere and model sensitivity of the various mechanisms considered. Although the changes to the ambient species concentration profiles may tend to either improve or worsen the agreement with observations for various species, we have not established a criterion for agreement (or disagreement) upon which to evaluate the likelihood that the mechanism actually occurs or to eliminate it from consideration. By combining the description of the effects on the ambient profiles discussed in this section with the comparison with observations discussed in Section 2, the reader can form his own opinion on this matter.

1. Chlorine Nitrate Formation

In terms of published evaluations of mechanistic data, perhaps the most plausible speculation is that roughly 75% of the reaction between ClO and NO_2 forms a relatively short-lived species isomeric with chlorine nitrate, and the effective rate of chlorine nitrate formation is only about one-fourth of the observed rate of reaction between ClO and NO_2 . In JPL (1979) (and NASA, 1979) no firm choice is made between the assumption that all of the reactions between ClO and NO_2 lead to chlorine nitrate and the assumption that only about 25% do, although most modelers have adopted the first assumption. The choice of treatment for this reaction is one of the major differences between the 1979a and 1979b chemistries. As can be seen from Table 12, if the slower rate of chlorine nitrate formation is assumed, the calculated effects of an SST fleet become more positive than in the base case, while the computed effects of CFM's become more negative. In each case, the fractional change is of the order of a factor of 1.3. Clearly, the correct treatment of chlorine nitrate formation is of substantial importance. It is also worth noting that if the isomeric products have greater photolytic stability than ClONO_2 , or if, as impurities, they account for some of the observed absorption spectrum of ClONO_2 , the effect of chlorine nitrate isomers on predictions might actually be reversed. This could happen if the mean rate of loss of some ClONO_3 products were to be slower than that presently assumed for ClONO_2 so that larger concentrations of ClONO_3 species would be generated.

When the low rate is assumed for chlorine nitrate formation, a significant ($>10\%$)* change in the ambient state is computed for Cl , ClO , HCl , HOCl , and

*All percent changes reported in this section refer to fractional changes in the quantity relative to the standard (1979b model) ambient conditions or model sensitivity.

TABLE 12. Results of sensitivity calculations for speculative chemical reactions and mechanisms.

Model Content	Ambient Ozone Column (Dobson units)	Change in Total Ozone (%)		
		17-km NO _x Injection*	20-km NO _x Injection*	CFM** Production
Baseline Model (1979b) - NASA Harpers Ferry Workshop, ~2 ppb ClX	322	1.25	1.14	-14.6
Slower rate of ClONO ₂ formation	312	1.42	1.54	-19.3
Photolysis of XONO ₂ to XO + NO ₂ products	324	1.35	1.20	-12.2
Pressure and temperature dependent HO _x disproportionation reactions	339	0.47	-0.40	-8.9
HCl production from ClO + OH, ClO + HO ₂	334	0.74	0.02	-4.4
ClO ₃ production, K _{equilibrium} as for ClO ₂ from NASA 1010, no other reaction of ClO ₃	322	1.24	1.11	-14.0
OCIO ₂ production K _{equilibrium} as for ClO ₂ from NASA 1010, subsequent chemistry described in text	337	1.51	1.40	-6.91
OCIO ₂ production K _{equilibrium} as for ClO ₂ from JPL (1979) subsequent chemistry described in text	323	1.27	1.16	-14.0
OCIO ₂ production K _{equilibrium} as for ClO ₂ from NASA 1010, subsequent chemistry described in text and P,T dependent HO _x disproportionation reactions	353	0.49	-0.51	0.73

*Rate of emission is 1000 molecules (NO) cm⁻³s⁻¹ over a 1-km-thick layer.

**Constant release rate at 1976 levels.

ClNO_2 , all of which increase by nearly a factor of 2 at 25-30 km, while ClNO_3 is reduced by a factor of 3 to 4 at almost all altitudes. Thus, this hypothesis exacerbates the apparent disagreement between observation and calculation for the shape of the ClO vertical profile and destroys the apparent agreement between calculation and the preliminary chlorine nitrate measurement reported by Murcray (1979).

2. Photolysis of XONO_2 Species

Almost equally uncertain are the products of the photolysis of species of the form XONO_2 , where $\text{X} = \text{OH}, \text{Cl}, \text{NO}_2$. In the base case it has been assumed that all of these reactions lead to $\text{X} + \text{NO}_3$. This assumption is largely based on the experimental results of Chang et al. (1979) for chlorine nitrate.

Other products are possible, perhaps the most distinct (in terms of model predictions) would be $\text{XO} + \text{NO}_2$ (or for N_2O_5 , $2\text{NO}_2 + \text{O}$). In a computation in which all of these photolyses were assumed to yield $\text{XO} + \text{HO}_2$ products (except N_2O_5 which was assumed to yield $2\text{NO}_2 + \text{O}$), the computed effects of SST emissions became more positive by 5-10% (of the change computed for the base case) while the effects of CFM's became less negative by about 17%. Thus, resolving the question of photolysis products of XOCIO species is of modest importance to perturbation calculations.

In terms of species concentrations, only NO_3 and N_2O_5 displayed large changes (both were reduced by a factor of two to three at the region of their largest mixing ratios, and by up to 90% at some (lower) altitudes). Several other species displayed changes on the order of 10-15% at some altitudes.

3. Pressure-Dependent Rates for HO_x Disproportionation Reactions

A significant pressure, inverse temperature and water vapor dependence has been reported for the reaction $\text{HO}_2 + \text{HO}_2 \xrightarrow{\text{M}, \text{H}_2\text{O}} \text{H}_2\text{O}_2 + \text{O}_2$ (Cox, 1978; Hamilton and Lii, 1977; Cox and Burrows, 1979). Furthermore, while the measurements of the reaction $\text{HO}_2 + \text{OH}$ at low pressures seem only mildly inconsistent with each other, the indirect values inferred at higher pressures (Hochanadel et al., 1972; DeMore and Tschuikov-Roux, 1974; DeMore, 1979) are substantially (2 to 4 fold) faster than the values measured at low pressures. In this context, the poorly understood pressure, temperature, and water vapor dependence of $\text{HO}_2 + \text{HO}_2$ suggests the possibility that $\text{HO}_2 + \text{OH}$ may also be affected by

similar phenomena. As can be seen in Table 12, when we assumed that the expression given by Cox (1978) for $k_{\text{HO}_2+\text{HO}_2}$,

$$k_{\text{HO}_2+\text{HO}_2} = \frac{(3.25 \times 10^8 + 4 \times 10^{-10} [\text{M}] / (1 + 3.5 \times 10^{-16} [\text{M}] e^{-2060/T}))}{8 [\text{M}] + 4.08 \times 10^{20}}, \quad (7)$$

and an expression for $k_{\text{OH}+\text{HO}_2}$ designed to yield a low-pressure value compatible with Chang and Kaufman (1978), and a high pressure value compatible with the larger rate constants reported at high pressure, i.e.,

$$k_{\text{HO}_2+\text{OH}} = (5 \times 10^{-30} \times \text{M} + 3 \times 10^{-11}) (300/T)^3, \quad (8)$$

there were major changes in model predictions for both SST's and CFM's. Here it should be emphasized that the expression used for the rate constant for reaction of HO_2 with OH is completely arbitrary. It was designed to approximately fit high- and low-pressure data. Had a Lindeman-Hinshelwood expression been fit to the same data, or had a constant ratio to the $\text{HO}_2 + \text{HO}_2$ rate been assumed, the effects would have been different (probably larger) but equally plausible. The form chosen reflects the postulation of a pressure independent abstraction mechanism coupled with a pressure dependent enhancement reflecting complex formation (with a limiting value well above 1×10^{-10} at room temperature).

Elucidation of the pressure and temperature dependencies of the HO_x radical disproportionation reactions should be of high priority to those concerned with SST effects and of considerable importance to those concerned with CFM production effects. The assumed change in the $\text{HO}_2 + \text{OH}$ reaction is substantially more important than the change in the $\text{HO}_2 + \text{HO}_2$ reaction within the stratosphere. However, the $\text{HO}_2 + \text{HO}_2$ reaction is of significant importance in the troposphere, and the effects of subsonic aircraft operations are expected to be sensitive to it, as would be the effects of CH_3CCl_3 emissions.

When the above assumptions were made about the HO_x disproportionation reactions, many species changed by roughly a factor of two between ~ 10 and 20 km. Roughly two-fold reductions (between ~ 10 and 20 km) occurred for OH, HO_2 , Cl, ClO, and CH_2O while H_2O_2 was reduced by roughly the square of the fractional reduction in HO_2 . Computed NO and NO_2 displayed two-fold increases over the same altitude range. Species that were only slightly changed included HNO_3 (<10% changes) and CH_4 ($\sim 10\%$ increase at high altitudes).

Thus, changes in the HO_x disproportionation rates akin to those considered here would cause substantial changes in computed profiles of short lived species in the region from 10 to 20 km. Some of these changes tend to improve agreement with observation, others tend to reduce it. Although CH_4 increases at higher altitudes, the increase is not large enough to demand a major revision in K_2 even if future experiments should suggest the pressure-dependent disproportionation rates used here to be fair approximations of reality. For CH_4 to increase substantially at higher altitudes, it would be necessary for an increase in $k_{\text{OH}+\text{HO}_2}$ to extend to substantially lower air densities.

All of the above speculations have at least some direct basis in laboratory measurements. The speculations that follow are even more tenuous than the above.

4. HCl Formation from $\text{HO}_x + \text{ClO}$

The reaction between OH and ClO could yield $\text{HO}_2 + \text{Cl}$ or $\text{HCl} + \text{O}_2$ at low pressures, or at higher pressures it might yield a moderately stable species of the form HOOCCl (a peroxide) or HOClO (an acid). Either of these last species might be expected to be unstable with respect to disproportionation in a condensed phase, but gas phase stability seems possible. In any case, the production of $\text{HCl} + \text{O}_2$ from $\text{HO} + \text{ClO}$ would seem likely to have the most drastic effect on model predictions. The overall reaction has a rate constant of 9.2×10^{-11} at room temperature, and the products $\text{HO}_2 + \text{Cl}$ account for at least 65% of the products (Leu and Lin, 1979). These products have little effect on model sensitivity.

An investigation of the effect of this reaction producing HCl assuming a rate constant of $2 \times 10^{-12} \text{ cm}^3/\text{sec}$ suggested that model sensitivity to a CFM perturbation could be reduced by $\sim 40\%$; at $1 \times 10^{-12} \text{ cm}^3/\text{sec}$ the sensitivity would be reduced by roughly 20%.

A similar argument could be applied to the reaction:

The only evidence suggesting a plausible role for reaction (10) is that at temperatures below room temperature, the rate of the overall reaction increases substantially as the temperature is reduced (C. Howard et al., NOAA Aeronomy Laboratory, Boulder, private communication, 1979). This suggests the possibility

that a five-centered complex might be formed and $\text{HCl} + \text{O}_3$ eliminated. If the rate of HCl formation via this reaction were to be as large as $1 \times 10^{-12} \text{ cm}^3/\text{sec}$, then the effect of CFM's would be reduced by $\sim 50\%$, and, if the rate were to be even larger, increases might be computed from CFM releases.

Table 12 gives the sensitivities obtained when both $\text{HO} + \text{ClO} \rightarrow \text{HCl} + \text{O}_2$ and $\text{HO}_2 + \text{ClO} \rightarrow \text{HCl} + \text{O}_3$ were assumed to have rate constants of $1 \times 10^{-12} \text{ cm}^3/\text{sec}$. As is evident, these reactions might have a major impact on both CFM and SST effects, and they might have a smaller but significant effect on computed CFM effects at rates as low as $\sim 1 \times 10^{-13} \text{ cm}^3/\text{sec}$.

The effect on the model sensitivity to an NO_x perturbation is largely a result of there being a lessened rate of ClX and HO_x catalytic destruction of ozone with which NO_x can interfere. Also, null cycle sequences involving ClX and HO_x are not as effective in competing with ozone-destroying sequences for NO . The reduced sensitivity to CFM perturbations results from both an increase in the rate at which HCl is formed and a transfer of ClO and HO_x radicals into null cycle sequences from odd-oxygen destroying sequences.

There is the possibility that the reaction $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_3$ might occur to some extent. An analysis of available data (H. Johnston, University of California at Berkeley, private communication, 1979) suggests an upper limit of about 5% of the total rate for this reaction. If the similar reaction $\text{HO}_2 + \text{ClO} \rightarrow \text{HCl} + \text{O}_3$ had a branching ratio of less than 0.05, it would have no more than a modest effect on model sensitivity (based on calculations made in 1978, the reaction $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_3$ would need to have a branching ratio of nearly 0.1 to be of even marginal significance in stratospheric perturbation studies).

The model-calculated ambient atmosphere with rates for both $\text{OH} + \text{ClO} \rightarrow \text{HCl} + \text{O}_2$ and $\text{HO}_2 + \text{ClO} \rightarrow \text{HCl} + \text{O}_3$ set to $10^{-12} \text{ cm}^3/\text{sec}$ contained about half as much Cl , ClO , ClONO_2 , ClNO_2 and HOCl as did the normal ambient, whereas HCl increases of about a factor of two were calculated near 30 km. No other measured species were significantly ($> 10\%$) affected, although H_2O_2 and CH_3OOH were reduced by about 30% between 25 and 35 km.

Although model predictions are indeed sensitive to these reactions, the likelihood that they occur is probably not very great. Thus, while an effort should be made to measure them, an upper limit less than $\sim 10^{-13} \text{ cm}^3/\text{sec}$ would resolve most of the issues they raise.

5. ClO_3 Chemistry

A final mechanism that was studied was the possibility that O_2 and ClO add to form a molecule with a binding strength comparable to that of ClOO , the complex formed from Cl and O_2 . There is evidence for some such phenomenon from the effect of added O_2 on the quantum yield for ozone loss in systems containing Cl_2 , O_3 and O_2 (Wongdontri-Stuper et al., 1978; J. Birks, University of Colorado, private communication, 1979).

If it is assumed that the formation and decomposition rate constants for the process $\text{ClO} + \text{O}_2 \rightarrow \text{ClO}_3$ are those given in NASA 1010 (1977) for $\text{Cl} + \text{O}_2 \rightarrow \text{ClO}_2$ and no subsequent chemistry occurs (only the formation and thermal decomposition of the complex occur), then model sensitivities are virtually unaffected. Approximately 2 to 5% of the inorganic chlorine in the lower stratosphere is in the form of ClO_3 , and all computed changes in ambient concentrations are small. Even though the coupling between ClO and ClO_3 is very rapid, and ClO_3 is computed to be larger than ClO between ~6 and 22 km, most of the ClO_3 apparently comes from the much more abundant HCl and ClONO_2 . However, if the structure of the ClO_3 complex were OClO_2 , then it is possible that the following reactions would occur:

and

Because ClO and OClO have comparable heats of formation, the endoergicity of the photolysis would approximate 60 kcal plus the binding energy of the complex. This suggests an endoergicity for reaction (11) comparable to that for NO_2 photolysis. Thus, at least in principle, reaction (11) might have an effective J value as large as about 10^{-3} sec^{-1} . The reaction $\text{OClO} + \text{NO} \rightarrow \text{NO}_2 + \text{ClO}$ has a rate constant of about $3 \times 10^{-13} \text{ cm}^3/\text{sec}$ at room temperature (JPL, 1979). Given the similarities in the reactions, a similar sort of rate constant might be estimated for $\text{OClO}_2 + \text{NO}$. If one assumes that the J value for OClO_2 photolysis is 10^{-4} sec^{-1} , that the rate of reaction with NO is $1 \times 10^{-12} \text{ cm}^3/\text{sec}$, and that the formation and decomposition rates are those given for ClO_2 in NASA 1010 (1977), then one estimates a moderate (20%) increase in the (small) ozone increase computed from SST operations and more than a 50%

reduction in the effect of CFMs. If on the other hand one assumes the same subsequent chemistry but a lower stability for the complex, say that given for ClO_2 in JPL (1979), then no significant effect on model sensitivity is predicted.

Thus, for the formation of a complex between O_2 and ClO to significantly affect model sensitivity, the complex must have a binding energy approaching 6 kcal, and either photolysis or reaction with NO must be reasonably fast. However, if the complex were to be stable (bound by more than 8 kcal) and the subsequent chemistry were reasonably fast, one might even compute a decrease in ozone for NO_x injections and an increase in column ozone from CFM increases. Similarly, if the HO_x reactions were pressure dependent and OClO_2 were to have the chemistry discussed above, one would calculate a decrease in column ozone for the 20-km NO_x injection and an increase in column ozone from the CFM scenario (see Table 12). There is, of course, a lengthy chain of speculative assumptions required to achieve such results.

Even though the OClO_2 chemistry discussed above is completely speculative, its potential for large effects may justify the attempt to study it by those chiefly interested in CFM effects.

Finally, it should be noted that the simplest (but probably not the most likely) route back to computed effects of SST operations (like those obtained in CIAP Monograph 3 (1975) and NRC (1975a) would be for the HO_x disproportionation reactions to have fast rates (either via the pressure/temperature effects hypothesized above, or through an error in the post 1976 measurements) and for the reaction of $\text{HO}_2 + \text{NO}$ to be slower than is now thought to be the case. Although it seems unlikely that the growing body of experimental results involving HO_2 chemistry would all be wrong (at least at low pressures where many of the measurements have been direct and the data analysis reasonably straightforward), it cannot be denied that the new measurements have produced a startling number of unexpected negative temperature dependencies for apparently bimolecular reactions involving HO_2 (and ClO as well). While theories of reaction rates can no doubt be created to fit such data, the pre-existing theories do not easily lead to the observed rate constants. Although it seems very likely that the resolution of such problems will indeed come via a modification of theory, additional confirmatory measurements of some of the anomalous temperature dependences using independent, if perhaps less direct, techniques would still be welcomed.

Effects of Uncertainties in Chemical Rate Coefficients

Probably the best method for assessing the sensitivity of model predictions to errors in the inputs that describe fairly well understood quantities (e.g., rate constants for which experimental precision is the dominant source of error) is a Monte Carlo calculation (e.g., Stolarski et al., 1978). As yet, no such calculation has been carried out for a perturbation resulting from aircraft operations. In part this reflects the hypothesis that prediction error is dominated by error in poorly known reactions with unquantifiable error.

Even a full sensitivity analysis (like that of Butler, 1979) has not yet been performed. The most recent sensitivity study on the NO_x system was a partial sensitivity analysis carried out in 1975 by Duewer et al. (1975, 1977). The major conclusions of that study were that large prediction errors were possible, and that a few reactions dominated the error. Subsequent events have shown the first conclusion to be valid. The large changes in model sensitivity to NO_x injection that have occurred have been dominated by changes in the rate coefficients for the five reactions that were identified as plausible sources of error in the 1975 and 1977 reports. In the intervening years, many rate coefficients have been determined or redetermined with substantially improved accuracy. For the majority of the reactions in the model, experimental precision is probably a reasonably good estimate (as well as a lower bound) to the actual error in the measured rate, and model predictions are only weakly sensitive to modest errors in most rate coefficients. Nonetheless, the composite error in prediction caused by such errors could be significant, although, since it is unlikely that random errors will reinforce each other, this is not too likely to be realized.

Several reactions that still seem plausible candidates for serious errors and that seem to have the potential to change the qualitative conclusions that might be drawn from model predictions are discussed in the preceeding section. Here we will explore a historical method of assessing overall model uncertainty. Table 13 gives the change in O_3 calculated for several perturbations using the structure of our current model but using the rate coefficients recommended in NBS 866 (1975) and NBS 513 (1978) as well as the current results. In calculating the response for 1975 and 1977 chemistries, we excluded species (such as HOCl or HNO_4) that the LLL model contemporary with the rate compendium in question did not include. In

TABLE 13. The effect of the choice of rate coefficients on model sensitivity using the structure of the current LLL model.

Chemistry	1950 Ambient O ₃ (DU)	Change in Total Ozone (%)				
		1990 High Subsonic	17 km SST*	20 km SST*	CFM 1978	CFM Steady-State
1975 (NBS 866)	288	-0.31	-3.94	-9.12	-0.76	-7.5
1977 (NBS 513)	366	1.43	1.20	-0.52	-0.98	-12.7
1979a** (JPL, 1979)	324	2.01	2.57	2.18	-1.92	-19.4
1979b (NASA, 1979)	327	1.86	2.00	1.08	-1.30	-14.6

*NO_x injection rate of 2000 molecules cm⁻³s⁻¹ over a 1-km-thick layer. The contribution to CIX due to CFMs is not included in these calculations.

**The rate of OH + ClO → HCl + O₂ is set to zero.

addition, we include the results of calculations made using the 1979a chemistry with the rate coefficient for the reaction OH + ClO → HCl + O₂ set to zero.

The conclusion to be drawn from Table 13 is that over the last five years, changes in evaluated recommendations for chemical rate coefficients have resulted in substantial changes in the model predicted response to perturbation, and that even recent recommendations appearing a few months apart carry a significant amount of uncertainty. (However, the differences between model predictions are not such as to change any qualitative conclusions if one restricts ones self to post-1976 models with consistent physics.)

A comparison of the results in Table 13 with the results of LLL calculations in earlier years given in Table 14 for some of the perturbations demonstrates that other changes in model structure have had quantitatively significant effects, but would have had little effect on the qualitative conclusions drawn from model predictions of aircraft effects.

The uncertainty limits for reactions in the various evaluations (NBS 513 (1975), NBS 866 (1978), NASA 1010 (1977), JPL (1979), NASA Harpers Ferry) have generally become smaller when individual reactions are considered. However, over the same

TABLE 14 Ozone perturbation calculations for an NO_x injection rate of 2000 molecules $\text{cm}^{-3}\text{s}^{-1}$ reported in previous LLL annual reports.*

Report Date	Change in Total Ozone - %	
	17 km Injection	20 km Injection
2/73	—	-33.
7/74	-4.80	-10.15
5/75	-5.30	-11.23
6/76 early work	-5.30	-11.23
6/76 late work	-1.75	-5.21
9/77 early work	-1.31	-4.79
9/77 late work	1.96	0.55
9/78	3.21	3.59
9/79	2.00	1.06

*1979 results do not include the contribution to chlorine from CFMs. 1976-1978 results include varying levels of chlorine.

period, new and often highly uncertain reactions have been recognized, and it is far from obvious that the error that might be associated with rate coefficients actually included in models has gotten smaller over the last decade. Moreover, "new" reactions have been introduced to the modeling community at a fluctuating but not obviously decreasing rate.

Effect of Temperature Feedback and Hydrostatic Adjustment

In the calculations up to this point, the U. S. Standard Atmosphere (1976) temperature profile was used, and temperature was not allowed to change. Changes in the concentrations of species that are radiatively important (either solar or longwave) will affect the temperature profile by changing radiative fluxes and heating or cooling rates. At a given pressure level, as the temperature changes, the air density will also change as defined by the equation of state. Since chemical reaction rates are affected by changes in temperature and air density, it is important to assess the magnitude of these effects on the assessment calculation.

Air density can be computed in a one-dimensional model by assuming hydrostatic equilibrium (i.e., the pressure at any height is determined by the weight of the column of air above that point, and the air density is determined by the equation of state given the temperature). Expressed mathematically,

$$dP = -\rho g dz \quad (13)$$

and

$$P = \rho RT \quad (14)$$

where P is pressure, ρ is density, g is the acceleration of gravity, z is altitude, R is the gas constant and T is temperature. The temperature is computed using a radiative transfer model assuming radiative equilibrium in the stratosphere (see Appendix A). In our calculations, the temperature profile is computed above 13 km, and is specified below this altitude. Changes in surface temperature may be imposed, but they are not calculated in this version of the model. The model includes solar absorption and longwave exchange by O_3 , H_2O and CO_2 along with solar absorption by NO_2 (Luther et al., 1977).

We assume that the change in surface temperature is negligible. Ozone reductions of up to 30% due to NO_x injections were computed to cause less than a 0.1 K change in surface temperature by Ramanathan et al. (1976). An increase in the stratospheric water vapor mixing ratio of 2 ppmv is estimated to cause an increase in surface temperature of < 0.2 K (Grobecker et al., 1974, p. F125). Increasing the surface temperature in our model by 0.2 K causes a change in total ozone of -0.06%. Neglecting changes in surface temperature of this magnitude has no significant effect on the results.

In studying the effect of temperature feedback and hydrostatic adjustment on model sensitivity, we considered four calculation alternatives: (1) temperature feedback with hydrostatic adjustment, (2) temperature feedback without hydrostatic adjustment, (3) constant temperature using the ambient computed temperature and pressure profiles,* and (4) constant temperature using the U.S. Standard Atmosphere temperature and pressure profiles. The results are presented in Table 15.

*The temperatures and pressures were computed at equilibrium using temperature feedback and hydrostatic adjustment, then they were kept fixed for the perturbation calculation.

The constant temperature calculation using the ambient computed temperature profile (consistent with hydrostatic adjustment) is the reference case with which to compare the effects of temperature feedback and hydrostatic adjustment. Table 15 shows that inclusion of temperature feedback leads to a larger increase in total ozone compared to the constant temperature calculation (ambient profile). When hydrostatic adjustment is included, the increase in total ozone is even larger. To understand these effects, we need to look at the change in temperature versus height.

For analysis purposes, we consider the results for an NO_x injection rate of $1000 \text{ molecules cm}^{-3}\text{s}^{-1}$ and an H_2O injection rate of $177,000 \text{ molecules cm}^{-3}\text{s}^{-1}$ at 20 km. The change in local ozone concentration is shown in Fig. 26 and the change in the temperature profile is shown in Fig. 27. The temperature increases below 20 km causing an increase in the chemical destruction rate of ozone. Thus, there is less of an increase in ozone concentration in this region when temperature feedback is included. Conversely, above 20 km the temperature decreases, thereby slowing the rates of reaction and leading to less ozone reduction in this region.

The change in absolute ozone concentration is shown in Fig. 28. Most of the difference between the three calculations occurs in the 20-40 km region. The reactions that are most important in terms of ozone destruction are more strongly dependent upon temperature in the 20-40 km region than at other altitudes.

In the case with hydrostatic adjustment, the air in the 14-20 km region expands due to the rise in temperature. As the air expands it lifts the atmosphere above so that a given pressure level is raised in altitude relative to the ambient profile. Conversely, where the temperature decreases, there is contraction. The combination of expansion below and contraction above results in a raising of the altitude of the pressure levels at altitudes below 43 km. At this altitude the combined effects of expansion and contraction cancel each other, and the pressure remains unchanged at this altitude. Thus, the pressure is increased at altitudes between 14 and 43 km.

Since density is determined by the equation of state [Eq. (14)], the change in density at any altitude can be expressed in terms of the fractional changes in temperature and pressure at this altitude

$$\frac{\Delta \rho}{\rho} = \frac{\Delta P}{P} - \frac{\Delta T}{T} \quad (15)$$

TABLE 15. The effect of temperature feedback and hydrostatic adjustment on model sensitivity (1979a chemistry).

Injection Altitude (km)	Injection Rate (molecules cm ⁻³ s ⁻¹)		Change in Total Ozone (%)			
	NO _x	H ₂ O	Temperature Feedback with Hydrostatic Adjustment	Temperature Feedback without Hydrostatic Adjustment	Constant* Ambient Temperature	U.S. Standard Atmosphere Temperature
17	1000	0	1.45	1.30	1.20	1.34
17	1000	177,000	1.37	1.24	1.04	1.18
17	333	177,000	0.43	0.40	0.26	0.32
20	1000	0	1.36	1.17	1.10	1.31
20	1000	177,000	1.29	1.03	0.70	0.91
20	333	177,000	0.33	0.27	-0.02	0.07

*See footnote on page 74.

FIGURE 26. The change in ozone concentration caused by an NO_x injection of $1000 \text{ molecules cm}^{-3}\text{s}^{-1}$ and an H_2O injection of $177,000 \text{ molecules cm}^{-3}\text{s}^{-1}$ at 20 km (1979a chemistry).

ΔP and ΔT have the same sign in the region 14-20 km, and they have opposite signs between 20 and 43 km. Consequently, the effects of ΔP and ΔT on $\Delta \rho$ are additive above 20 km, and they tend to cancel each other below 20 km. The combined effect is a small decrease in density between 14 and 18 km and an increase in density at all higher altitudes. The largest fractional increase (0.74%) in ρ occurred at 22 km. An increase in air density tends to increase ozone by increasing the rate of reaction of

FIGURE 27. The change in temperature versus altitude for the 20 km injection perturbation described in Fig. 26 (1979a chemistry).

$O + O_2 + M \rightarrow O_3 + M$ and other three-body reactions. Most three-body reactions tend to convert more-active species into less-active species.

The results with temperature feedback and hydrostatic adjustment represent the most complete model calculations in terms of physical processes and feedback mechanisms. The changes in ozone concentration computed with these processes included are shown in Figs. 29 and 30 for various injection rates of NO_x and H_2O at an injection altitude of 17 km. The results for an NO_x injection rate of

FIGURE 28. Same as Fig. 26 except the change in ozone concentration is expressed in molecules cm^{-3} (1979a chemistry).

1000 molecules $\text{cm}^{-3}\text{s}^{-1}$ with and without a simultaneous H_2O injection are nearly identical below 26 km. The injection of H_2O only leads to noticeable differences in the computed change in ozone concentration above 26 km.

Given the same H_2O injection rate, the results for NO_x injection rates of 1000 or 333 molecules $\text{cm}^{-3}\text{s}^{-1}$ are quite different. The lower NO_x injection rate causes much less change in ozone concentration in the middle and lower stratosphere; the relative magnitudes of the change in ozone concentration being roughly proportional to the NO_x injection rate. This result indicates that the

FIGURE 29. The change in ozone concentration due to various NO_x and H_2O injection rates at 17 km. The injection rates have units of molecules $\text{cm}^{-3}\text{s}^{-1}$ over a 1-km thick layer. The calculations include temperature feedback and hydrostatic adjustment (1979a chemistry).

NO_x injection rate is a much more important (and sensitive) parameter than the H_2O injection rate in estimating the effects of projected aircraft fleets.

Another important conclusion from Table 15 is that the choice of temperature profile in a constant temperature calculation can have a significant effect on model sensitivity. The difference between the ΔO_3 values using the ambient or the U.S. Standard Atmosphere temperature profile is the same magnitude as the difference between including and not including temperature feedback.

FIGURE 30. Same as Fig. 29 except the change in ozone concentration is expressed in molecules cm^{-3} (1979a chemistry).

4.4 COMPARISON WITH OTHER RESULTS

In terms of model predicted effects of a given perturbation, there are two types of comparisons that might be made: (1) a comparison with earlier results and (2) an intercomparison of the predictions of various models at a given time. Comparison with earlier results offers a guide to the stability of the values of

widely accepted inputs (e.g., chemical rate coefficients and solar flux calculations) and the effects of changes in "state-of-the-art" treatments of various physical parameters. A comparison with contemporary results offers a guide to the effects of differing values for input parameters that do not have widely accepted values (e.g., rainout parameterizations and thermal feedback effects).

There have been several previous assessments of the effects of high altitude aviation on the environment. The CIAP reports (CIAP Monographs, 1975; Report of Findings, 1974) summarize the results of many investigators who worked on the problem during the early 1970's. The Report of Findings (Grobeck et al., 1974) stresses the effects of fleets expected before 1990. The National Academy of Sciences report (NRC, 1975a) presents another summary of almost the same body of work with an emphasis on the larger fleets to be expected at some future time if supersonic transports were to be a commercial success.

The COMESA (1975) and COVOS (1976) reports cover English and French studies made at about the same time. These reports stress effects from moderate numbers of Concorde. Many of these results as well as the results of some later studies by Crutzen and ourselves are summarized by Oliver et al. (1977).

More recent assessment results were reported by Luther (1978) and Popoff et al. (1978). Oliver et al. (1978) reviewed the assessments made between December 1976 and June 1978.

Figure 31 provides a summary of previous LLL assessments of the effects of SST operations based on an injection of 2000 molecules (NO) $\text{cm}^{-3}\text{s}^{-1}$ distributed over a 1-km-thick layer centered at 17 or 20 km. This injection rate was a standard for assessment and comparison purposes and did not pertain to any particular fleet estimate. The results in Fig. 31 demonstrate the combined effects of the evolution of our understanding of stratospheric chemistry and evolution of the treatment of physical phenomena such as multiple scattering of light, the averaging of reaction rates over diurnal cycles, the treatment of boundary conditions, and the transport parameterization. Although many different factors have contributed to the variation described in Fig. 31, the evolution of model chemistry has been the most important single factor.

Figure 32 demonstrates the influence of changes in the evaluations of various rate coefficients. The results were obtained using our 1979 model, but the rate coefficients used in the model were modified to agree with those recommended in NBS 866 (1975), NBS 513 (1978), and JPL (1979). This provides three assessments at

FIGURE 31. The historical evolution of LLL model calculations of the change in total ozone due to an NO_x injection of 2,000 molecules cm⁻³s⁻¹ over a 1-km thick layer centered at either 17 km (open circles) or 200 km (solid circles). The values for 1978 are approximate because they are extrapolated from model calculations in 1978 that used half this NO_x injection rate.

two-year intervals and a fourth (current) value six months more recent than the last. The chemistries so generated do not correspond precisely to any in previous use at LLL. Moreover, only the O₃, NO and NO₃ photolysis rates were adjusted to reflect earlier treatments of photolysis. All other photolysis rates were left at 1979 values. The 1975 chemistry corresponds more nearly to that used in our 1976 calculations than our 1975 calculations.

Figures 31 and 32 demonstrate that the model predicted response to NO_x injections has varied substantially over the past eight years, and that much of that variation has come via differences in the recommended values for rate constants (combined with newly recognized chemical reactions). While it is encouraging to

FIGURE 32. The change in total ozone due to an NO_x injection of $2,000 \text{ molecules cm}^{-3}\text{s}^{-1}$ computed using the structure of the current one-dimensional model with variations in model chemistry corresponding to various sets of photochemical rate recommendations. The reaction $\text{OH} + \text{ClO} \rightarrow \text{HCl} + \text{O}_2$ was not included in this 1979a calculation.

note that the post-1977 assessments have not varied as widely as the earlier assessments did, it is discouraging to note that the most pronounced variations came several years apart (in 1972 and 1976-1977) and that during the intervening years (1973-1975) the assessments were nearly as stable as those of the last three years.

In the CIAP era, intercomparison of different models revealed that for those using similar chemistries a very considerable range of predicted perturbations could be explained on the basis of differences in the fractional change in NO_x caused largely by differences in the parameterizations of vertical transport (Chang and Johnston, 1974).

Partly because the range of one-dimensional transport parameterizations in current use is much smaller than it was before 1975, there is much more of a consensus among modelers than there was in 1975. At the NASA sponsored Harpers Ferry workshop (June 1979) nine different modeling groups computed the effects of an injection of $10^8 \text{ molecules NO cm}^{-2}\text{sec}^{-1}$ distributed over roughly 1-km altitude centered at roughly 17 or 20 km. For a 17-km injection the range of values for the change in total ozone was +1.3 to +3.4% (only one was greater than 2.6%), and for the 20-km injection the range was +1.1 to +4.6% (only one was greater than

3%). In both cases, the LLL predictions were slightly smaller than the majority of the other models, although in neither case were the LLL predictions the extreme predictions. Because the models were independently formulated, the small range of predicted effects suggests that none of the predictions is seriously affected by errors in coding or through unique treatments of some processes. Much of the present difference in model predictions still appears to be explainable on the basis of differences in the vertical transport coefficients used.

A final comparison would be between models of differing dimensionality. Unfortunately, only a few direct comparisons can be made since the chemistries used in multidimensional models have usually been simpler than those used in one-dimensional models. Recent two-dimensional results (Hidalgo, 1978; R. C. Whitten, private communication, 1979) have been at least qualitatively similar to one-dimensional results with similar chemistry. That is, recent two-dimensional calculations, like recent one-dimensional calculations, predict that a large supersonic transport fleet would cause small (1-3%) ozone column increases over most of the globe with an increase in the lower stratosphere (and upper troposphere) and a decrease at higher altitudes. Published three-dimensional calculations have not included a complete model chemistry (Cunnold et al., 1977) but have been qualitatively similar to those obtained with models of lower dimensionality in the past.

In summary, independent one-dimensional model predictions of the effects of NO_x injections are presently in good agreement with each other. They also seem to be in semiquantitative agreement with models of higher dimensionality and similar chemistry. However, model predictions have changed substantially over the last eight years, and there is little that suggests similar changes in model sensitivity might not occur in the future.

5. POTENTIAL CHANGES IN OZONE RESULTING FROM OTHER PERTURBATIONS

Many potentially significant perturbations to stratospheric ozone have been proposed. In order to put the effects of aircraft engine emissions presented in Section 4 in perspective, we present assessments for other anthropogenic perturbations. Just as the effects of aircraft emissions were shown to depend on the effects of other perturbing influences, such as the concentration of ClX and the atmospheric temperature structure, the changes in O_3 resulting from the other perturbations considered here also depend on the interference effects of multiple perturbations.

Our effort has been primarily directed toward the assessment of predicted changes for individual perturbations since future perturbation scenarios are often quite uncertain. Of the perturbation scenarios considered here, only the increases in the concentrations of chlorofluoromethanes and CO_2 are well established. Changes in stratospheric H_2O , increases in N_2O and increases in stratospheric CH_3CCl_3 are predicted on uncertain knowledge of budgets and, in the case of CH_3CCl_3 , uncertain tropospheric chemistry. Where possible, we include comparisons to observations as well as a review of previous assessments with a history of the effects of various model changes and improvements in chemistry.

5.1 CHLOROFLUOROMETHANES

It has been firmly established that the chlorofluoromethanes, CFCl_3 and CF_2Cl_2 , have been increasing in the troposphere and stratosphere, and the observed increase is consistent with model estimates based on the historical production rates. The CFM's are photolyzed in the stratosphere to yield free chlorine which may catalytically destroy ozone.

Computed concentration profiles of CFCl_3 and CF_2Cl_2 are compared with measurements in Figs. 33 and 34, respectively. Tropospheric concentrations of CFCl_3 and CF_2Cl_2 computed in our model are about 10% and 14% smaller, respectively, than those measured by R. Rasmussen (private communication, 1979). The differences could be caused by too-fast model transport into the upper

FIGURE 33. Comparison of computed and observed CFC_{13} mixing ratio profiles.

stratosphere since transport parameters are derived by model fitting to upper atmospheric CH_4 and N_2O .

Quantitative estimates of the depletion of ozone have changed as models, physics, and chemistry have improved. In 1976 the predicted change in total O_3 due to steady-state production of CFM's at 1973 rates was estimated to be -7.5% (National Research Council, 1976b). In 1977 a major change in the model chemistry occurred when the rate for

was measured to be almost 40 times faster than previously thought (Howard and Evenson, 1977). In addition, some models at that time included diurnally averaged reaction rates and multiple scattering effects. The depletion estimates in 1977 ranged from -10.8 to -16.5% for the various modeling groups (Hudson, 1977); the LLL estimate was -15.0%. With our current model, we predict a change of -14.2%

FIGURE 34. Comparison of computed and observed CF₂Cl₂ mixing ratio profiles.

in total O₃ at steady-state assuming constant CFM production at the 1976 rates. (The 1976 production rates are 3.2% smaller for CFCl₃ and 2.9% larger for CF₂Cl₂ than those for 1973.) In order to evaluate the effect on model sensitivity of changes to the model, we have calculated the change in ozone at steady state for 1976 CFM release rates using a number of different chemistries. The results labeled: 1976 Chang et al. (1979) and: 1977 Chang et al. (1979) given in Table 17 and Fig. 35 were obtained by changing only the two- and three-body chemical reaction rates in our current model to the values used in 1976 and 1977

TABLE 16. Recent LLL one-dimensional model calculations of the effect of continued release of CFM's at the 1976 rate.

Model Chemistry	Unperturbed Total O ₃ c. 1950 (molecules cm ⁻²)	ΔO ₃ (%)	
		In 1978	At Steady State
1975 NBS 866 with 1979 model	7.73x10 ¹⁸	-0.8	-7.5
1976 Chang et al. (1979) (Appendix F)	7.49	-0.4	-4.2
1976 Old NO Photolysis	7.67	-0.6	-5.8
1976 Non-Diurnal	8.50	-0.0	-1.3
1977 NBS 513 with 1979 model	9.80	-1.0	-12.7
1977 Chang et al. (1979) (Appendix F)	9.18	-1.1	-11.2
1977 Non-Diurnal	10.1	-0.5	-4.7
1979a chemistry	8.81	-1.5	-14.0
1979a less OH + ClO	8.68	-2.0	-19.4
1979b chemistry	8.81	-1.3	-14.2

(see list of reactions and rates in Appendix F). Rates for the CH₄ oxidation reactions were left at their current values, although in 1976 and 1977 the full CH₄ oxidation scheme was not in our model. We also studied the effect of not including diurnal averaging for these two chemistries, and we studied the effect of using the old NO photolysis parameterization (which results in ~ 50% less NO_x in the ambient stratosphere) for the 1976 chemistry.

For the model calculations labeled 1975 NBS 866 and 1977 NBS 513, the reaction rates and photolysis rates were made consistent with those publications. The O₃ quantum yield for O(¹D) was set to zero at wavelengths higher than 310 nm, and the old NO photolysis parameterization (based on Cieslik and Nicolet, 1973) was used.

Using our standard model (with diurnal averaging and the NO photolysis rates of Frederick and Hudson (1979)), we calculate changes in total ozone of -4.2%, -11.2%, -14.0%, and -14.2% for the 1976, 1977, 1979a and 1979b chemistry models, respectively. Ambient column ozone increased from 7.49 x 10¹⁸ cm⁻² for the 1976 chemistry to 9.18 x 10¹⁸ cm⁻² for the 1977 chemistry. This is primarily a

FIGURE 35. The change in ozone concentration at steady state resulting from CFM's released at the 1976 rate. Various photochemical rate data were used in the calculations.

result of the rate change for reaction $\text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2$. With the faster rate the efficiency of the NO_x and HO_x catalytic ozone destruction cycles are reduced, resulting in higher ambient ozone levels. Cl_x then plays a relatively larger role in regulating the ozone concentration. These changes result in a larger ozone reduction for a given CFM perturbation ($\Delta\text{O}_3 = -11.2\%$ for the 1977 chemistry for constant CFM production at the 1976 rates compared to only -4.2% for the 1976 chemistry).

Many changes to chemical rate constants on the order of 30% or more occurred between our 1977 chemistry and our 1979b chemistry. One major change affecting the CFM perturbation calculation was the inclusion of HOCl. HOCl is formed by the reaction,

and is destroyed by photolysis,

Destruction of O_3 is more efficient at lower altitudes if HOCl is included in the model (compare current chemistry with that for 1977 and 1976 in Fig. 35). When HOCl is included, ClX shifts to more Cl and less ClO. Also, a new catalytic ozone destruction cycle is created that does not depend on the limited amount of O atom,

The major differences between O_3 sensitivity to CFM perturbation with the 1979a rates and the 1979b rates occur at high altitude (see Fig. 35). Differences in the rate of $\text{OH} + \text{HO}_2$ and of NO photolysis account for most of the difference in sensitivity at higher altitude. Results for the two chemistries are similar at lower altitudes because of a cancellation of effects. Differences and similarities in model sensitivity to the CFM perturbations as a function of altitude are mainly the result of changes in the relative roles of HCl and ClONO₂ as inactive chlorine reservoirs in the two chemistries.

In our 1979b model chemistry, ClONO₂ is relatively more important since the three-body rate of formation is almost four times faster than that used with the 1979a chemistry. In our 1979a chemistry, HCl is a more important chlorine reservoir since it is efficiently produced by the reaction

[Reaction (20) is not included in the 1979b chemistry.]

Figure 36 shows a number of calculated time histories for ozone under various assumptions regarding the future release rates for CFM's. For curve A it was assumed that CFM production continued at the 1976 rate until 1982, then it was lowered by 25%. In 1987, it was lowered again by 25%. The eventual steady-state ozone depletion for this case was 7.5%. For curve B, the 1976 production rate continued until 1982 and was then cut by 25%. The ozone depletion at steady state was 10.8% for this case. For curve C the 1976 production rate was used for the entire time, and the steady-state ozone depletion was 14.0%. For curve D the 1976 production rate was assumed to continue through 1980, then the CFM production was increased by 7%/year up to the year 2000. The steady-state depletion for this

FIGURE 36. The change in total ozone as a function of time for various CFM release rate scenarios. Curve A: 1976 CFM release rate until 1982, then it is reduced by 25% and in 1987 it is reduced again by 25%. Curve B: 1976 release rate until 1982, then it is reduced by 25%. Curve C: 1976 release rate constant throughout the period. Curve D: 1976 release rate through 1980, then the release rate increased 7%/yr up to the year 2000, constant thereafter. Curve E: same as D except the increase in release rate begins in 1978. All calculations were with 1979a chemical rates.

case is 37.9%. Case E is almost the same as case D except that the increased CFM production begins in 1978. The rate of increase is such that the production rate doubles by 1990 and doubles again by 2000. The steady-state ozone depletion is 38.6%. (The 1979a chemical rates were used in all of these model calculations.)

An enlargement of the period from 1980 to 2000 is shown in Fig. 37. Also shown is a model using 1979b chemistry with CH_3CCl_3 added to the model for the case of constant 1976 production rates (case C'). For all scenarios the predicted additional reduction in total O_3 over the next 10 years is less than 2.5%. This is less than the estimated level of detectability (NASA Stratospheric Panel on Long-Term Trends, 1979).

The predicted time histories for the ozone concentration at 40 km are shown in Fig. 38. For the largest perturbation case, the ozone concentration is predicted to be reduced by an additional 4.5% by the year 1990, which is smaller than the detection limits estimated by the NASA panel for observation by balloon, rocket, or Umkehr. A trend in ozone concentration might be observed by satellite at the 1 level, but the result would be below the 95% confidence limit. Thus, a relatively long time period (>10 years) may be needed in order to confirm or refute the model predictions of CFM effects by comparison with observed ozone changes.

5.2 CHANGE IN STRATOSPHERIC H_2O

Changes in stratospheric water vapor may be caused by a variety of mechanisms. Changes due to direct injection of water vapor by aircraft and the resulting effects on the atmosphere are discussed in Section 4. Perturbations to the atmospheric composition (e.g., CO_2 or NO_2) may also cause changes in stratospheric H_2O indirectly by changing the temperature of the tropical tropopause. A temperature increase of 4 K at the tropical tropopause would increase the saturation vapor pressure by a factor of 2 (Liu et al., 1976). H_2O may also increase as a result of increases in CH_4 which is oxidized to yield H_2O in the stratosphere. Stratospheric H_2O apparently increased by approximately 30% during the period from 1964 to 1973 (Mastenbrook, 1971, 1974), but it is not obvious that these changes apply to the upper stratosphere or even that the water vapor measurements are reliable.

FIGURE 37. An enlargement of the period from 1980 to 2000 for the calculations presented in Fig. 36. Curve C' is the same scenario as Curve C except the 1979b model chemistry is used and CH_3CCl_3 is added.

We consider here changes in our calculated O_3 and temperature due to changes in H_2O alone. In general, these changes must be considered along with perturbations in other atmospheric species, the coupled perturbations possibly having a nonlinear effect on ozone. Our separate calculations for increases in H_2O , however, provide a background for understanding coupled perturbations.

FIGURE 38. The change in ozone concentration at 40 km as a function of time for scenarios described in Fig. 36. Curve C' is the same scenario as curve C except the 1979b model chemistry is used and CH_3CCl_3 is included.

Changes in stratospheric H_2O affect ozone directly by increasing HO_x and indirectly by changing the temperature. In our model, H_2O is computed throughout the stratosphere given a boundary value at 13 km. Figure 39 shows the calculated change in temperature due to increasing H_2O by a factor of 2 at 13 km. The full line shows the case when hydrostatic equilibrium is included; the dashed line the case when it is not. Also shown is the percentage change in stratospheric H_2O as a function of altitude. The change in H_2O was the same for both cases. In both the hydrostatic and non-hydrostatic cases, the temperature is decreased because of increased cooling by H_2O and due to decreased solar

FIGURE 39. The change in temperature and the change in H_2O concentration in the stratosphere resulting from a doubling of the H_2O concentration at 13 km (below which H_2O is fixed). The change in H_2O concentrations was the same for calculations with or without hydrostatic adjustment (1979a chemistry).

absorption by O_3 . Near the tropopause our calculated temperature decreases by almost 2 K, thus providing a negative feedback to any supposed increase in H_2O as a result of increases in the tropopause temperature.* The detailed changes in

*In these calculations the temperature structure below 14 km was held constant at its observed value. If the tropospheric temperature is perturbed by 2 K when H_2O is doubled, the calculated change in ozone concentration changes from -11% to -4% at 40 km, due to increases in the background ozone concentration at high altitude resulting from hydrostatic adjustment. Increasing the surface temperature 2 K caused the total ozone column to decrease by 0.6%.

temperature with altitude are related to changes in H_2O , O_3 and, in the case of hydrostatic adjustment, changes in density. As shown in Fig. 40, O_3 is decreased at most altitudes (except near 30-35 km) providing decreased solar absorption. The change in total ozone was -3.45% without temperature feedback. When temperature feedback was included, the change in total ozone was -2.15% without hydrostatic adjustment and -3.03% with hydrostatic adjustment.

FIGURE 40. The change in ozone concentration versus altitude resulting from doubling the H_2O concentration at 13 km (1979a chemistry).

Changes in O_3 result from several competing mechanisms. Increases in H_2O cause increased HO_x which in general causes increased destruction of O_3 . In the 30-35 km region, however, the increased OH causes NO_x ($NO + NO_2$) to decrease since a larger fraction is tied up in the reservoir species HNO_3 . Thus, C_3 is actually increased between 30 and 35 km for both the case of temperature feedback without hydrostatic adjustment and the case of no temperature feedback (Fig. 40).

Comparing the case of temperature feedback without hydrostatic adjustment to the case with no temperature feedback (Fig. 40), temperature feedback acts to lessen the ozone perturbation in the atmosphere. Figure 39 shows that temperature decreases at all altitudes in the stratosphere. A decrease in temperature increases k_1 and decreases k_2 for the reactions

and

The reduction in temperature, therefore, tends to increase the ozone production rate and decrease the odd-oxygen destruction rate.

When hydrostatic adjustment is included along with temperature feedback, the reduction in ozone concentration is larger at altitudes above 27 km and smaller at lower altitudes. Hydrostatic adjustment affects the quantities $[O_2]$ and $[M]$ in reaction (21). A general decrease in temperature, as occurs in this case, causes the atmosphere to contract, thereby lowering the altitude of a given pressure level. In the upper stratosphere, $[M]$ and $[O_2]$ decrease as the atmosphere contracts. $[M]$ may either increase or decrease at lower altitudes depending upon the combined effect of the change in temperature and the change in scale height, H , where $H = kT/mg$. Expression (23) relates $[M]$ to temperature and scale height

$$[M] T = [M]_0 T_0 e^{\left[- \int_{z_0}^z \frac{1}{H} dz \right]} \quad (23)$$

where the subscript 0 refers to values at $z_0 = 0$. Changes in temperature dominate at low altitudes, resulting in an increase in $[M]$ when T decreases. At higher altitudes changes in the exponential expression dominate and $[M]$ decreases.

Since $[O_2] = 0.21[M]$, changes in $[M]$ significantly affect the ozone production rate via reaction (24).

The equilibrium ozone concentration is given approximately by the expression

$$[O_3]^2 = \frac{k_1 J_1 [O_2]^2 [M]}{k_2 J_2 (1 + A)}, \quad (24)$$

where J_2 refers to the photolysis rate for O_3 , J_1 is the photolysis rate for O_2 , and A is a term associated with destruction of odd oxygen by ClX , HO_x and NO_x (Nicolet, 1975). For any given altitude level, J_1 and J_2 also may change as a result of changes in the overburden of O_3 . In the case shown, the combination of changes in O_2 , M , J_1 and J_2 lead to larger O_3 depletion above about 27 km with hydrostatic adjustment when H_2O is doubled than when hydrostatic adjustment is not included. The details in the profile of $O_3(z)$ near 45 km for the case with temperature feedback and hydrostatic adjustment are due to changes in the relative roles of cycles for catalytic destruction of ozone together with changes in the temperature dependent rates, k_1/k_2 .

5.3 INCREASE IN N_2O

Concern that human perturbations to the nitrogen cycle might lead to enhanced concentrations for atmospheric N_2O has stimulated interest in the budget for this gas. Tropospheric N_2O is the major source for stratospheric NO_x so perturbations in N_2O are expected to alter stratospheric chemistry.

The fertilizer source of fixed nitrogen is currently estimated to be about 4.2×10^7 tN/yr, which converts to a source of 1.5×10^6 tN/yr as N_2O (estimate of Logan et al., 1978). Combustion provides about 1.5×10^6 tN/yr as N_2O directly (Weiss and Craig, 1976; Pierotti and Rasmussen, 1976). These anthropogenic sources are thus currently significant relative to the natural sources and could grow in the future and lead to a doubling of N_2O perhaps by the early part of the next century (Logan et al., 1978). This doubling time is very uncertain due to the lack of detailed understanding of the cycle for N_2O .

The level of atmospheric N_2O determines the atmospheric response to chlorine changes, and vice versa, mainly because of the coupling of chemistry by

ClONO_2 . Figure 41 illustrates how the percentage change in total O_3 with increased N_2O depends on the level of background ClX and on the chemical rate constants in the model. The dashed curves were produced using chemical rate constants that were used in 1978 (see Luther, 1978). The solid line refers to results using the 1979a rate constants. The major differences between the 1978 and 1979 chemistries as they affect this perturbation are: (1) the NO photolysis rate is slower in the 1979 chemistries so that the background level of NO_x is $\sim 50\%$ higher, and (2) the ClONO_2 formation rate via $\text{ClO} + \text{NO}_2 \xrightarrow{M} \text{ClONO}_2$ is almost four

FIGURE 41. The change in total ozone resulting from an increase in N_2O expressed in multiples of the present ground level concentration, which is 325 ppbv. The results produced using the 1979a chemistry are indicated by the solid line. The results using chemical rate data that were used in 1978 (Luther, 1978) are shown by the dashed curves. The dash-dot line refers to results using the fast ClONO_2 formation rate (see text).

times slower in the 1979a chemistry. Both changes tend to diminish the predicted O_3 increase as N_2O is increased. Even for 1.95 ppbv ClX, ozone decreases for all N_2O perturbations with the 1979a chemistry. This remains true even for the fast rate of $ClONO_2$ formation as indicated by the dot-dash line in Fig. 41, so most of the qualitative change in results is due to the change in NO photolysis.

Figure 42 shows the percent change in O_3 as a function of altitude for the 1979a chemistry for 2 perturbations of N_2O : 1.5 times and 3.0 times the present ground level concentration which is 325 ppbv. The predicted change in total O_3 depends on the net effect of increases in O_3 below about 23 km and decreases above that level. Changes in chemistry can shift the balance of these two regions and cause effects of different magnitude and sign for various N_2O perturbations.

FIGURE 42. The change in ozone concentration versus altitude resulting from N_2O increases of 1.5 and 3.0 times the present ground level concentration (1979a chemistry).

Thus, the assessment of the effects of future perturbations in N_2O depends on both uncertain chemistry and uncertain knowledge of the N_2O budget.

5.4 DOUBLING OF CO_2

Systematic measurements of CO_2 since 1958 (Keeling et al., 1976a and b) have shown a rise in atmospheric CO_2 concentrations that has been attributed primarily to the use of fossil fuels. The CO_2 levels were 315 ppm in 1958, 320 ppm in 1965, and 334 ppm in 1978. By the year 2000 atmospheric CO_2 is expected to be between 365 and 400 ppm. Detailed prediction of the doubling time depends on uncertain knowledge of the budget for CO_2 . Assuming that fossil fuel usage continues to increase at 4.3%/yr and that about half of the CO_2 released resides in the atmosphere, the atmospheric CO_2 concentration would double by about 2030, but estimates using other assumptions vary from 2015 to 2070. It is possible that the concentration could be limited to less than 500 ppm by shifting away from fossil fuels and relying more on solar and nuclear energy.

An increase in CO_2 is expected to lead to changes in the thermal structure of the atmosphere. In particular, a doubling of CO_2 has been estimated to increase the global mean surface temperature by 1.5 to 3 K due to the greenhouse effect (Schneider, 1975; Augustsson and Ramanathan, 1977). The temperature should decrease in the stratosphere, where the infrared opacity is smaller than in the troposphere.

The calculated change in temperature as a function of altitude for doubled CO_2 (320 to 640 ppm) is shown in Fig. 43. These calculations assumed normal summer temperatures in the troposphere (U.S. Standard Atmosphere, 1976). We tested the effect of tropospheric temperature changes by increasing the specified temperature below 14 km by 2 K when CO_2 was doubled (Fig. 44). The calculated ozone profile for this case was nearly the same as for the case when the tropospheric temperature remained unchanged and CO_2 was doubled (local ozone concentrations were within 2.6% at all altitudes). The calculated temperatures above 14 km were also similar, differing by less than 0.7 K. In this test the background atmosphere remained fixed (no hydrostatic adjustment). When hydrostatic adjustment was included, the local ozone increase near 40 km was about 15%, which was larger than the perturbation for no tropospheric temperature change

FIGURE 43. The change in stratospheric temperature for a doubling of the CO₂ concentration (320 to 640 ppm). Changes in the ozone concentration also affect the change in temperature in this calculation (1979a chemistry).

but smaller than the calculated change when hydrostatic adjustment was neglected entirely. The detailed structure of the temperature change for the cases with and without hydrostatic adjustment may be understood by examining the calculated changes in ozone shown in Fig. 44. Without hydrostatic adjustment, the stratospheric temperature decrease leads to an increase in O₃ at all altitudes. The O₃ increase tends to offset the calculated temperature decrease due to CO₂ above 40 km by increasing solar absorption by O₃. The calculated temperature decrease is a maximum near 42 km.

FIGURE 44. The change in ozone concentration resulting from a doubling of the CO_2 concentration (1979a chemistry).

With hydrostatic adjustment, however, ozone decreased above 45 km even though the temperature decreased. This is due to the decrease in background air density in agreement with expressions (23) and (24). As a result of the ozone decrease, the temperature (Fig. 43) decreased further above 45 km.

The change in total O_3 for a doubling of CO_2 was +5.06% with hydrostatic adjustment and +4.74% without. The larger change for the hydrostatic case reflects the behavior of O_3 near 25 km, as shown in Fig. 45. At this level, the photolysis

FIGURE 45. Same as Fig. 44 except the change in ozone concentration is expressed in molecules cm^{-3} .

rates for O_2 and O_3 both decreased for doubled CO_2 as a result of the larger optical depth (more O_3 above 25 km). The change in optical depth is larger for the case without hydrostatic adjustment, so J_1 , particularly, decreases more for this case, causing a smaller increase in O_3 . When the surface temperature was increased 2 K, the change in total ozone was 4.17% without hydrostatic adjustment.

5.5 INCREASE IN CH_3CCl_3

The use and release of methylchloroform, CH_3CCl_3 , which is used as a cleaning agent, has been increasing at a steady rate. Its presence in the atmosphere has been observed since 1974 (Cox et al., 1976), and it has been suggested that its

continued use will lead to a reduction of ozone (McConnell and Schiff, 1978). The sinks for CH_3CCl_3 are photolysis and reaction with OH in the stratosphere,

Stratospheric destruction of CH_3CCl_3 leads to release of Cl atoms which are able to destroy ozone. Reaction (26) is also effective in the troposphere, so the growth of stratospheric CH_3CCl_3 is limited. The effectiveness of reaction (26) for removing tropospheric CH_3CCl_3 , however, is fairly uncertain. The major uncertainties result from inadequate knowledge of the tropospheric OH distribution and the rate of reaction. The rate for reaction (26) is uncertain since there are several conflicting measurements of its rate at room temperature and of its temperature dependence (JPL, 1979). Comparison of the budget for CH_3CCl_3 with available measurements leads to an estimate for the tropospheric lifetime of between 9 and 11 years (Chang and Penner, 1978). Model calculated lifetimes are considerably shorter, implying larger tropospheric destruction rates, on average, than conform to the measurements. For example, using the historical release rate data from Neely and Plonka (1978) in our one-dimensional model, we calculate an average abundance near the surface for January 1978 of 47.3 pptv using the 1979a chemistry. The rate coefficient for reaction (26) was $2.5 \times 10^{-12} \exp(-1450/T)$ (see JPL, 1979). We calculate 66.1 pptv using the 1979b chemistry and a rate coefficient of $5.4 \times 10^{-12} \exp(-1820/T)$ for (26). These rates differ by about a factor of 2 at temperatures characteristic of the upper troposphere and by about 50% near the surface. Measurements taken by R. Rasmussen (private communication, 1979) give an average concentration of 101 pptv for CH_3CCl_3 . Our values would be higher if we had included solar absorption by clouds in the troposphere which decreases the photon flux density affecting $\text{O}(^1\text{D})$ production via $\text{O}_3 \xrightarrow{h\nu} \text{O}_2 + \text{O}(^1\text{D})$. $\text{O}(^1\text{D})$ production is the main source for OH in the troposphere since $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$. Absorption by clouds is expected to decrease $\text{O}(^1\text{D})$ in the lower troposphere, on average, by perhaps as much as a factor of 2. Our calculated surface OH concentration should then decrease between 30 and 50%, and some of the current discrepancy in CH_3CCl_3 concentration would be removed. The OH concentration, however, needs considerable clarification

since model calculations are less than in situ observations (Philen et al., 1978). Thus, our calculated ozone depletion estimates by CH_3CCl_3 must be considered preliminary.

With CH_3CCl_3 , CFCl_3 , and CF_2Cl_2 releases included in our model, the calculated reduction in total ozone in 1978 was 1.7% (relative to 1950) using 1979b chemistry, whereas without CH_3CCl_3 , O_3 decreased by 1.3%. The total stratospheric chlorine burden increased by 7%. Figs. 37 and 38 show the time history for O_3 depletion at constant 1976 production rates for CFCl_3 , CF_2Cl_2 . The CH_3CCl_3 release rate at the earth's surface is constant at 1.23×10^7 molecules $\text{cm}^{-2} \text{s}^{-1}$ beyond 1978. At steady state ozone decreased 15.2%, whereas without CH_3CCl_3 it decreased 14.2%. Of course, the effects of CH_3CCl_3 could be much greater if its use were to continue to increase.

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APPENDIX A. DESCRIPTION OF THE LLL ONE-DIMENSIONAL TRANSPORT-KINETICS MODEL

In Section 2, we gave a general description of the theoretical models used to study the stratosphere with particular emphasis placed on one-dimensional transport-kinetics models. In this appendix, we will describe particular aspects of the LLL one-dimensional transport-kinetics model in relation to the previous discussion.

PHYSICAL DOMAIN

The LLL one-dimensional model extends from the ground to 56.25 km. The model currently calculates the vertical concentration distributions of 39 (2 of which are used only in sensitivity studies) atmospheric trace constituents. The model contains 134 (14 of which are used only in sensitivity studies) chemical or photochemical reactions. Table A-1 lists the species solved for in the model. Of these species, $O(^1D)$, H, and N are assumed to be in instantaneous equilibrium. The vertical grid structure is variable, but for the calculations reported here, we have a 0.5-km-thick layer at the surface, 1-km thick layers extending from 0.5 to 34.5 km, a 1.75-km thick layer between 34.5 and 36.25 km and 2.5-km thick layers extending to 56.25 km.

TRANSPORT REPRESENTATION

As discussed previously, the vertical transport in the one-dimensional model is parameterized through a diffusion coefficient, K_z . The K_z profile used primarily in the calculations for this report was originally based on an analysis of N_2O and CH_4 measurements (NAS, 1976) with considerations also given to measurements of radionuclide debris transport in the lower stratosphere.

TABLE A-1. Species calculated in the LLL one-dimensional model.

$O(^3P)$	Cl	CH_4
O_3	ClO	HCO
NO	$ClONO_2$	CH_2O
NO_2	$ClNO_2$	CH_3
N_2O	HCl	CH_3OOH
HNO_3	$OCIO^*$	CH_3O
OH	HOCl	CH_3O_2
HO_2	CH_3Cl	CO
H_2O_2	CF_2Cl_2	H_2
NO_3	$CFCI_3$	$O(^1D)$
N_2O_5	CH_3CCl_3	N
H_2O	ClO_3	H
HONO	CCl_4	
HNO_4		

*Used only in sensitivity studies.

The LLL one-dimensional model has been designed such that profiles of K_z utilized by other groups (or at previous times) can be easily incorporated. Such profiles have been utilized to test the sensitivity of the results to transport parameterization uncertainties (see Section 4).

CHEMISTRY

We have used two 1979 versions of model chemistry in this report (see Tables A-2 through A-4). 1979a chemistry was based primarily on the rate recommendations in JPL (1979). However, several reactions discussed in JPL (1979) are omitted in the model, and several reactions not discussed in JPL (1979) are included. This chemistry was used for many sensitivity calculations carried out in the spring of 1979. 1979b chemistry was based almost exclusively on the draft chapter on chemical reaction rates prepared at the NASA Harpers Ferry Workshop

TABLE A-2. Chemical reactions and rate coefficients where $k = A e^{B/T}$ used in the 1979 model chemistry.

Reaction	A*	B	Note
1. $O + O_2 \xrightarrow{M} O_3$	See Table A-3		3
2. $O + O_3 \rightarrow 2O_2$	1.5×10^{-11}	-2218	1
3. $O_3 + NO \rightarrow NO_2 + O_2$	2.3×10^{-12}	-1450	1
4. $O + NO_2 \rightarrow NO + O_2$	9.3×10^{-12}	0	1
5. $N_2O + O(^1D) \rightarrow N_2 + O_2$	4.8×10^{-11}	0	1
	5.1×10^{-11}	0	2
6. $N_2O + O(^1D) \rightarrow 2NO$	6.2×10^{-11}	0	1
	5.9×10^{-11}	0	2
7. $N + O_2 \rightarrow NO + O$	4.4×10^{-12}	-3220	1
8. $N + NO \rightarrow N_2 + O$	3.4×10^{-11}	0	1
9. $O(^1D) + H_2O \rightarrow 2OH$	2.3×10^{-10}	0	1
10. $O_3 + OH \rightarrow HO_2 + O_2$	1.6×10^{-12}	-940	1
11. $O + OH \rightarrow O_2 + H$	4.0×10^{-11}	0	1
12. $O_3 + HO_2 \rightarrow OH + 2O_2$	1.1×10^{-14}	-580	1
13. $O + HO_2 \rightarrow OH + O_2$	3.5×10^{-11}	0	1
14. $H + O_2 \xrightarrow{M} HO_2$	See Table A-3		3
15. $O_3 + H \rightarrow OH + O_2$	1.4×10^{-10}	-470	1
16. $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	2.5×10^{-12}	0	1
17. $HO_2 + OH \rightarrow H_2O + O_2$	4.0×10^{-11}	0	1
18. $OH + NO_2 \xrightarrow{M} HNO_3$	See Table A-3		1
19. $OH + HNO_3 \rightarrow H_2O + NO_3$	8.5×10^{-14}	0	1,10
20. $H_2O_2 + OH \rightarrow H_2O + HO_2$	1.0×10^{-11}	-750	1
21. $N_2 + O(^1D) \xrightarrow{M} N_2O$	See Table A-3		3

*When two entries are given, the lower one corresponds to 1979a chemistry and the upper one corresponds to 1979b chemistry.

TABLE A-2. (Continued)

Reaction	A*	B	Note
22. $\text{N} + \text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{O}$	2.1×10^{-11}	-800	1
23. $\text{NO} + \text{O} \rightleftharpoons \text{NO}_2$	See Table A-3		3
24. $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$	4.3×10^{-12} 3.4×10^{-12}	200 250	1 2
25. $\text{H}_2 + \text{O}(^1\text{D}) \rightarrow \text{OH} + \text{H}$	9.9×10^{-11}	0	1
26. $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$	1.0×10^{-11}	-500	1
27. $\text{N} + \text{O}_3 \rightarrow \text{NO} + \text{O}_2$	2.0×10^{-11}	-3000	4
28. $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	1.2×10^{-13}	-2450	1
29. $\text{OH} + \text{OH} \rightleftharpoons \text{H}_2\text{O}_2$	See Table A-3		3
30. $\text{H}_2\text{O}_2 + \text{O} \rightarrow \text{OH} + \text{HO}_2$	2.8×10^{-12}	-2125	1
31. $\text{CO} + \text{OH} \rightleftharpoons \text{H} + \text{CO}_2$	See Table 3		3
32. $\text{O}(^1\text{D}) + \text{M} \rightarrow \text{O} + \text{M}$	2.2×10^{-11}	99	5
33. $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	2.8×10^{-11}	-257	1
34. $\text{Cl} + \text{NO}_2 \rightleftharpoons \text{ClONO}_2$	See Table A-3		3
35. $\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$	7.7×10^{-11}	-130	1
36. $\text{NO} + \text{ClO} \rightarrow \text{NO}_2 + \text{Cl}$	7.8×10^{-12}	250	1
37. $\text{ClO} + \text{NO}_2 \rightleftharpoons \text{ClONO}_2$	See Table A-3		3
38. $\text{HCl} + \text{O}(^1\text{D}) \rightarrow \text{Cl} + \text{OH}$	1.4×10^{-10}	0	1
39. $\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$	2.8×10^{-12}	-425	1
40. $\text{O} + \text{HCl} \rightarrow \text{OH} + \text{Cl}$	1.14×10^{-11}	-3370	1
41. $\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2$	4.5×10^{-11}	0	1
42. $\text{CFCl}_3 + \text{O}(^1\text{D}) \rightarrow 3\text{Cl}$	2.2×10^{-10}	0	1,6
43. $\text{CF}_2\text{Cl}_2 + \text{O}(^1\text{D}) \rightarrow 2\text{Cl}$	1.4×10^{-10}	0	1,6
44. $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$	3.5×10^{-11}	-2290	1

TABLE A-2. (Continued)

Reaction	A ^a	B	Note
45. $\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{HCl} + \text{HO}_2$	8.9×10^{-12} 1.7×10^{-12}	-925 -384	11 2
46. $\text{ClONO}_2 + \text{O} \rightarrow \text{ClO} + \text{NO}_3$	3.0×10^{-12}	-808	1,10
47. $\text{CH}_3\text{Cl} + \text{OH} \rightarrow \text{Cl} + \text{H}_2\text{O} + \text{HO}_2$	2.2×10^{-12}	-1142	1
48. $\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2$	2.0×10^{-11} 8.7×10^{-12}	0 0	1 3
49. $\text{NO}_2 + \text{O} \rightarrow \text{NO}_3$	See Table A-3		3
50. $\text{NO}_2 + \text{NO}_3 \rightarrow \text{N}_2\text{O}_5$	See Table A-3		3
51. $\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$	See Table A-3		3
52. $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$	1.0×10^{-20}	0	7
53. $\text{O}(^1\text{D}) + \text{O}_3 \rightarrow 2\text{O}_2$	1.2×10^{-10}	0	1
54. $\text{HO}_2 + \text{HO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{H}_2\text{O}$	See Table A-3		3
55. $\text{O} + \text{NO}_3 \rightarrow \text{O}_2 + \text{NO}_2$	1.0×10^{-11}	0	1
56. $\text{HO}_2 + \text{NO}_2 \rightarrow \text{HNO}_4$	See Table A-3		3
57. $\text{HNO}_4 \rightarrow \text{HO}_2 + \text{NO}_2$	See Table A-3		3
58. $\text{OH} + \text{HNO}_4 \rightarrow \text{H}_2\text{O} + \text{NO}_2 + \text{O}_2$	6.0×10^{-12}	-750	1,8
59. $\text{Cl} + \text{HNO}_4 \rightarrow \text{HCl} + \text{NO}_2 + \text{O}_2$	3.0×10^{-12}	-300	8
60. $\text{HO}_2 + \text{ClO} \rightarrow \text{O}_2 + \text{HOCl}$	7.0×10^{-13}	500	1
61. $\text{Cl} + \text{HOCl} \rightarrow \text{HCl} + \text{ClO}$	3.0×10^{-12}	-300	8
62. $\text{OH} + \text{HOCl} \rightarrow \text{H}_2\text{O} + \text{ClO}$	3.0×10^{-12}	-800	1
63. $\text{O} + \text{HOCl} \rightarrow \text{OH} + \text{ClO}$	1.0×10^{-11}	-2200	1
64. $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	2.4×10^{-12}	-1710	1
65. $\text{O} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{OH}$	3.5×10^{-11}	-4550	1
66. $\text{O}(^1\text{D}) + \text{CH}_4 \rightarrow \text{CH}_2\text{O} + \text{H}_2$	1.0×10^{-11}	0	1
67. $\text{O}(^1\text{D}) + \text{CH}_4 \rightarrow \text{CH}_3 + \text{OH}$	1.3×10^{-10}	0	1

TABLE A-2. (Continued)

Reaction	A*	B	Note
68. $\text{CH}_4 + \text{Cl} \rightarrow \text{HCl} + \text{CH}_3$	9.9×10^{-12}	-1359	1
69. $\text{Cl} + \text{CH}_3\text{Cl} \rightarrow \text{HO}_2 + \text{CO} + 2\text{HCl}$	3.4×10^{-11}	-1256	1,6
70. $\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{CH}_3\text{O}$	7.0×10^{-12}	0	1
	8.0×10^{-12}	0	2
71. $\text{Cl} + \text{CH}_2\text{O} \rightarrow \text{HCl} + \text{HCO}$	9.2×10^{-11}	-68	1
72. $\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2$	6.0×10^{-12}	0	1
	1.0×10^{-12}	0	2
73. $\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$	5.0×10^{-13}	-2000	1
74. $\text{OH} + \text{CH}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{HCO}$	1.0×10^{-11}	0	1
	1.7×10^{-11}	-100	2
75. $\text{O} + \text{CH}_2\text{O} \rightarrow \text{HCO} + \text{OH}$	3.2×10^{-11}	-1550	1,10
	2.8×10^{-11}	-1540	2
76. $\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$	5.0×10^{-12}	0	1
77. $\text{OH} + \text{CH}_3\text{OOH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$	5.0×10^{-12}	-750	1,10
	6.2×10^{-12}	-750	2
78. $\text{CH}_3 + \text{O} \rightarrow \text{CH}_2\text{O} + \text{H}$	1.0×10^{-10}	0	1
79. $\text{CH}_3\text{O}_2 + \text{O}_3 \rightarrow \text{CH}_3\text{O} + 2\text{O}_2$	1.0×10^{-14}	-600	9
80. $\text{CH}_3\text{O}_2 + \text{O} \rightarrow \text{CH}_3\text{O} + \text{O}_2$	3.0×10^{-11}	0	9
81. $\text{ClO} + \text{OH} \rightarrow \text{HO}_2 + \text{Cl}$	9.2×10^{-12}	0	1
	2.0×10^{-11}	0	12
82. $\text{CH}_3 + \text{O}_2 \xrightarrow{M} \text{CH}_3\text{O}_2$	See Table A-3		3
83. $\text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2$	Not Used ($\sim 10^{-22}$)		
	2.0×10^{-12}		12
84. $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$	1.2×10^{-11}	-2200	1
	Not Used		
85. $\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2$	4.2×10^{-11}	-350	1
	Not Used		
86. $\text{OH} + \text{CH}_3\text{OOH} \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} + \text{OH}$	5.0×10^{-12}	-750	1,10
	Not Used		

TABLE A-2. (Continued)

Reaction	A*	B	Note
87. $O + HNO_4 \rightarrow OH + NO_2 + O_2$	1.0×10^{12} Not Used	-2200	1,10
88. $OH + ClONO_2 \rightarrow HOCl + NO_3$	1.2×10^{-12} Not Used	-333	1,10
89. $Cl + ClONO_2 \rightarrow 2Cl + NO_3$	1.7×10^{-12} Not Used	-607	1,10
90. $HONO + OH \rightarrow H_2O + NO_2$	6.6×10^{-12} Not Used	0	1
91. $OH + NO \xrightarrow{M} HONO$	See Table A-3 Not Used		3
92-97. (Not used. Reactions used only in sensitivity studies)			
98. $O + OClO \rightarrow ClO + O_2$	2.5×10^{-11}	-1166	1
99. $NO + OClO \rightarrow NO_2 + ClO$	2.5×10^{-12}	-600	1

NOTES TO TABLE A-2

1. Draft report of NASA Harpers Ferry Workshop.
2. JPL (1979). Where only one entry is given for the rate coefficient 1979a and 1979b are the same. Usually this means references 1 and 2 give the same recommendation.
3. The reaction is pressure dependent. See Table A-3 for discussion.
4. Estimate designed to be compatible with upper limit given in reference 1, and low enough to have no significant effect on model performance. Reaction is retained only to facilitate reintroduction if the evaluated upper limit should prove to be in error.
5. Weighted average of the rates of $O(^1D) + N_2$ and $O(^1D) + O_2$ from references 1 and 2.
6. Product chemistry has been simplified.
7. Estimated reaction rate. This estimate is designed to include a possible heterogeneous contribution to the overall reaction. Important only in the lower troposphere.

NOTES TO TABLE A-2 (Continued)

8. Estimated reaction rate. This rate is estimated based on the assumption that HNO_4 and HOCl resemble H_2O_2 (as treated in JPL, 1979) in reactions with Cl and OH .
9. Estimated reaction rate. Rate is estimated based on the assumption that CH_3O_2 closely resembles HO_2 in reaction with O or O_3 .
10. Products are not given in references 1 or 2. The assumed products are based on the products that seem most plausible based on chemical considerations.
11. Rate based on a draft of reference 1 that trivially differs from the final draft.
12. 1979a chemistry treated the reactions of HO and ClO based on privately communicated qualitative preliminary results. The treatment is nearly an upper limit to the plausible rate coefficients based on the recent results of Leu and Lin (1979).

(June, 1979). It has a few comparatively minor differences from the final draft of that report, and it includes a few reactions not assessed at the NASA Workshop.

Two reactions treated in the 1979a chemistry are controversial and are of some importance to our sensitivity studies. These are

and

In the 1979a chemistry, we used the slower of the two JPL-recommended rate constants for chlorine nitrate formation, and we adopted an expression for HCl formation from $\text{OH} + \text{ClO}$ that is about half the upper limit for that reaction path. In the 1979b chemistry, we used the faster of the two recommendations for the chlorine nitrate formation rate coefficient. Three considerations inspired this choice: (1) the majority of the chemistry panel seemed to favor the faster expression, (2) even if the bulk of the reaction between ClO and NO_2 leads to other products (as suggested by those favoring the slower rate coefficient), the other products might easily have an effect on stratospheric chemistry similar to that of ClONO_2 , and (3) it improved the comparison between calculation and observation for both ClO and ClONO_2 .

TABLE A-3. Rate coefficients used for pressure-dependent reactions.

Expression 1

$$k = \frac{A_0[M](300/T)^{n_0}}{1 + A_0[M](300/T)^{n_0}/A_1(300/T)^{n_1}} \cdot 0.6 \left\{ 1 + \left[\log_{10} \left(\frac{A_0[M](300/T)^{n_0}}{A_1(300/T)^{n_1}} \right) \right]^2 \right\}^{-1}$$

Reaction	A_0^*	n_0	A_1	n_1	Note
$\text{HO}_2 + \text{NO}_2 \xrightarrow{M} \text{HNO}_4$	2.1×10^{-31}	5.0	6.5×10^{-12}	5.0	1
$\text{OH} + \text{NO}_2 \xrightarrow{M} \text{HNO}_3$	2.6×10^{-30}	2.9	2.4×10^{-11}	1.3	1
$\text{ClO} + \text{NO}_2 \xrightarrow{M} \text{ClONO}_2$	1.6×10^{-31}	3.4	1.5×10^{-11}	1.9	1,2
	3.5×10^{-32}	3.8	1.5×10^{-11}	1.9	1,2
$\text{O} + \text{O}_2 \xrightarrow{M} \text{O}_3$	6.2×10^{-34}	2.1		0	1
$\text{CH}_3 + \text{O}_2 \xrightarrow{M} \text{CH}_3\text{O}_2$	2.2×10^{-31}	2.2	2.0×10^{-12}	1.7	1
$\text{O}(^1\text{D}) + \text{N}_2 \xrightarrow{M} \text{N}_2\text{O}$	3.5×10^{-37}	0.45		0	1
$\text{Cl} + \text{NO}_2 \xrightarrow{M} \text{ClNO}_2$	1.6×10^{-30}	1.9	3.0×10^{-11}	1.0	1
$\text{H} + \text{O}_2 \xrightarrow{M} \text{HO}_2$	5.5×10^{-32}	1.4		0	1
$\text{OH} + \text{NO} \xrightarrow{M} \text{HNO}_2$	6.7×10^{-31}	3.3	3.0×10^{-11}	1.0	1
$\text{OH} + \text{OH} \xrightarrow{M} \text{H}_2\text{O}_2$	2.5×10^{-31}	0.8	3.0×10^{-11}	1.0	1
$\text{NO}_2 + \text{NO}_3 \xrightarrow{M} \text{N}_2\text{O}_5$	1.4×10^{-30}	2.8	9.0×10^{-13}	-0.7	1
	$1.8 \times 10^{-32} e^{+1316/T}$	0	$9.5 \times 10^{-13} e^{+58/T}$	0	3

*When two entries are given, the lower one corresponds to 1979a chemistry and the upper one corresponds to 1979b chemistry.

TABLE A-3. Continued

Reaction	A_0^*	n_0	A_1	n_1	Notes
$O + NO \xrightarrow{M} NO_2$	1.2×10^{-31}	1.8	3.0×10^{-11}	-0.3	1
	$1.6 \times 10^{-32} e^{+584/T}$	0			4
$O + NO_2 \xrightarrow{M} NO_3$	9.0×10^{-32}	2.0	2.2×10^{-11}	0	1
	1.0×10^{-31}	0		0	4
$N_2O_5 \xrightarrow{M} NO_2 + NO_3$	$1.16 \times 10^{-3} e^{-11180/T}$	2.8	$7.52 \times 10^{+14} e^{-11180/T}$	-0.7	5
	$1.6 \times 10^{-5} e^{-9864/T}$	0	$7.94 \times 10^{+14} e^{-11122}$	0	4
<hr/>					
$HNO_4 \xrightarrow{M} HO_2 + NO_2$		$k = \frac{5.2 \times 10^{-6} e^{-10015/T}}{1 + 4.86 \times 10^{-12} M^{0.61}}$			7
$OH + CO \xrightarrow{M} H + CO_2$		$k = 1.35 \times 10^{-13} \left(1 + \frac{M}{2.46 \times 10^{+19}} \right)$			1
$HO_2 + HO_2 + H_2O \rightarrow H_2O_2 + H_2O + O_2$		$k = \frac{1.1 \times 10^{-34} e^{+3730/T}}{1 + M * 3.5 \times 10^{-16} e^{-2060/T}}$			6

NOTES TO TABLE A-3

1. Expression given in NASA (1979). 1979a chemistry differed from 1979b chemistry in that the parameter 0.6 in expression 1 was set equal to 0.8 in the expression used for 1979a chemistry
 2. Both expressions are recommended with no clear preference. The lower value is used in the 1979a chemistry and the upper one is used in the 1979b chemistry.
 3. Private communication, D. Golden, SRI International, Inc. (1979).
 4. Based on data in NBS 513 (1978).
 5. Based on data in reference 1 and the equilibrium constant from NBS 513 (1978).
 6. Based on Cox (1978).
 7. Based on Graham et al. (1978).
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In our 1979b chemistry we omitted the reaction forming HCl from $\text{OH} + \text{ClO}$. The decision to include this reaction in the 1979a chemistry was based on privately communicated preliminary results that seemed to suggest that the reaction probably occurred, but they have since been interpreted as providing only an upper limit. Both of these controversial choices of rate coefficient have a significant impact on model sensitivities (especially for ClX) but they oppose each other. As a result, 1979a and 1979b chemistries yield qualitatively similar perturbational sensitivities for both NO_x and ClX perturbations. The 1979b chemistry is less controversial than the 1979a chemistry and is to be preferred for purposes of comparison with other workers. All primary assessments have been repeated using 1979b chemistry. However, several sensitivity studies were not repeated, since it seemed unlikely that the qualitative results of those sensitivity studies would differ if they were repeated, and because the 1979a chemistry is well within the limits of reasonable uncertainty in our present knowledge of the atmosphere. The two chemistries are also useful in emphasizing the existence of processes for which no clear recommendation is available.

Our treatment of photolysis reactions has also been modified. There is evidence for a moderate temperature dependence in many photoabsorption cross sections. With the exception of ozone, NO, and O_2 photolysis, we have not treated this temperature dependence explicitly, but have used cross sections

TABLE A-4. Photolysis reactions. Alternative products of reaction are shown in parentheses, but they were not used in either the 1979a or 1979b chemistry.

Reaction	Note
1. $O_2 \rightarrow 2O$	1,2
2. $O_3 \rightarrow O + O_2$	1,3
3. $O_3 \rightarrow O(^1D) + O_2$	1,3
4. $NO_2 \rightarrow NO + O$	1,4
5. $N_2O \rightarrow N_2 + O(^1D)$	4
6. $NO \rightarrow N + O$	5
7. $HNO_3 \rightarrow OH + NO_2$	4
8. $H_2O_2 \rightarrow 2OH$	4
9. $HO_2 \rightarrow OH + O$	4
10. $ClONO_2 \rightarrow Cl + NO_3$ ($ClO + NO_2$)	4,6
11. $HCl \rightarrow H + Cl$	4
12. $ClO \rightarrow Cl + O$	7
13. $ClO \rightarrow Cl + O(^1D)$	Not used
14. $ClNO_2 \rightarrow Cl + NO_2$	4
15. $OCIO \rightarrow ClO + O$	7
16. $CF_2Cl_2 \rightarrow 2Cl$	4,8
17. $CFCI_3 \rightarrow 3Cl$	4,8
18. $CCl_4 \rightarrow 4Cl$	4,8
19. $N_2O_5 \rightarrow NO_3 + NO_2$ ($2NO_2 + O$)	4,6
20. $NO_3 \rightarrow NO + O_2$	4
21. $NO_3 \rightarrow NO_2 + O$	4
22. $H_2O \rightarrow H + OH$	9
23. $HNO_4 \rightarrow HO + NO_3$ ($HO_2 + NO_2$)	10,6
24. $HOCl \rightarrow OH + Cl$	4
25. $CH_3OOH \rightarrow CH_3O + OH$	4
26. $CH_2O \rightarrow HCO + H$	11
27. $CH_2O \rightarrow CO + H_2$	11
28. $CH_3Cl \rightarrow CH_3 + Cl$	4
29. $HONO \rightarrow OH + NO$	4

NOTES FOR TABLE A-4.

1. Contributes to the optical depth of the model atmosphere.
 2. The Schumann-Runge bands are given a special treatment based on Hudson and Mahle (1972).
 3. The quantum yields of reactions 2 and 3 are given a special treatment based on the temperature dependent treatment of JPL (1979).
 4. Based on the data of JPL (1979). Where data for several temperatures is given, we have used the data at ~ 230 K.
 5. Nitric oxide photolysis is based on the treatment of Frederick and Hudson (1979). We have used the photolysis rates averaged over the sunlit hemisphere for day time photolysis rates. 1979a chemistry used the treatment of Cieslik and Nicolet (1973).
 6. The products used for XNO_3 ($X = Cl, OH, NO_2$) changed between our 1979a and 1979b chemistries. For 1979a they were based on the path of lowest endoergicity (except for N_2O_5 which was based on a recommendation of Johnston). For 1979b they are all based on analogy with $ClONO_2$ data of Chang et al. (1979). This treatment is highly uncertain.
 7. Based on data in Watson (1974).
 8. Product chemistry has been simplified.
 9. Treatment based on Thompson et al. (1963).
 10. Treatment based on Graham et al. (1978).
 11. Treatment based on quantum yields of Moortgat and Warneck (1979) and cross sections of McQuigg and Calvert (1969).
-

measured at roughly 230 K for all temperatures. As a result our calculated trace species photodissociation rates should be more accurate for the stratosphere than for the lower troposphere.

For ozone photolysis we use quantum yields based on the recommendations of NASA (1979). Our treatment of O_2 photolysis is based on Hudson and Mahle (1972) while our treatment of NO photolysis is based on Frederick and Hudson (1979).

BOUNDARY CONDITIONS

The model now allows for either fixed concentrations or a flux condition at the surface as a lower boundary condition. For most of the calculations in this study, six species were assumed to have fixed concentrations (See Table A-5), while a surface flux was assigned to the other species. Zero flux was assumed except for those species shown in Table A-5. When those species with fixed boundary conditions in Table A-5 were given flux boundaries, a flux was determined to give an ambient concentration the same as those in Table A-5.

Zero flux was assumed for all species except NO and NO₂ at the upper boundary. NO and NO₂ are assumed to have a very small flux from the mesosphere into the stratosphere.

Water vapor concentrations are fixed in the troposphere and calculated in the stratosphere. All runs are made with fixed boundary conditions unless otherwise noted.

TABLE A-5. Boundary conditions.

<u>Fixed Concentrations (molecules cm⁻³)</u>	
N ₂ O	8.25 x 10 ¹²
CH ₄	4.03 x 10 ¹³
H ₂	1.42 x 10 ¹³
CH ₃ Cl	1.56 x 10 ¹⁰
H ₂ O	4.30 x 10 ¹⁷
CO	3.04 x 10 ¹²
<u>Surface Flux (molecules cm⁻² s⁻¹)</u>	
NO	3.41 x 10 ⁹
NO ₂	6.59 x 10 ⁹
HNO ₃	1.67 x 10 ⁹
HCl	3.67 x 10 ¹⁰
CCl ₄	1.40 x 10 ⁶
CF ₂ Cl ₂	function of time
CFCl ₃	and scenario
CH ₃ CCl ₃	(see Section 5)

SOURCES AND SINKS

In addition to sources and sinks from the chemistry and boundary conditions described above, there are additional sinks due to dry and/or wet removal for many species in the model. A source for nitric oxide from cosmic ray dissociation of N_2 is also included based on the results of Nicolet (1974).

Wet removal processes are parameterized by a first-order loss rate. The wet removal of the trace species HNO_3 , H_2O_2 , HCl , ClO , $ClONO_2$, $ClNO_2$, HNO_4 , $HOCl$, CH_2O and CH_3OOH is assumed to vary with altitude as shown in Table A-6. NO_2 is assumed to have a loss rate half the above rate.

Dry deposition rates at the surface are also parameterized by a first-order loss rate as shown in Table A-7.

TABLE A-6. Wet removal parameterization

Altitude, km	Loss Rate, sec^{-1}
0	3.86×10^{-6}
1	3.86×10^{-6}
2	3.86×10^{-6}
3	3.86×10^{-6}
4	3.86×10^{-6}
5	3.86×10^{-6}
6	1.93×10^{-6}
7	1.93×10^{-7}
8	9.58×10^{-7}
9	4.78×10^{-7}
10	0

TABLE A-7. Deposition rates in the lowest layer ($z = 0$).

Species	Loss Rate (sec^{-1})	Species	Loss Rate (sec^{-1})
$\text{O}(^3\text{P})$	2.0×10^{-5}	NO_3	2.0×10^{-5}
O_3	1.0×10^{-5}	N_2O_5	2.0×10^{-5}
NO	1.0×10^{-6}	H_2O	0
NO_2	3.0×10^{-6}	HNO_4	2.0×10^{-5}
N_2O	0	HOCl	2.0×10^{-5}
HNO_3	2.0×10^{-5}	HCO	2.0×10^{-5}
OH	2.0×10^{-5}	CH_2O	1.0×10^{-5}
HO_2	2.0×10^{-5}	CH_3	2.0×10^{-5}
H_2O_2	2.0×10^{-5}	CH_3OOH	2.0×10^{-5}
Cl	2.0×10^{-5}	CH_3O	2.0×10^{-5}
ClONO_2	2.0×10^{-5}	CH_3O_2	2.0×10^{-5}
ClO	2.0×10^{-5}	CO	5.0×10^{-7}
CH_4	0	ClO_3	2.0×10^{-5}
H_2	1.0×10^{-7}	OCIO	2.0×10^{-5}
CH_3Cl	0	HONO	2.0×10^{-5}
ClNO_2	2.0×10^{-5}	CFCl_3	0
HCl	2.0×10^{-5}	CF_2Cl_2	0
CCl_4	0	CH_3CCl_3	0

MULTIPLE SCATTERING

In order to accurately compute photodissociation rates, it is important to describe radiative processes, such as multiple scattering, in addition to attenuation by gases such as O_2 , O_3 and NO_2 . The importance of molecular scattering varies significantly with wavelength over the spectral range 200–750 nm. At shorter wavelengths gaseous absorption dominates and very little solar flux reaches the lower atmosphere. The region 250–330 nm is a transition region where molecular scattering is very important, especially at the longer wavelengths in this interval.

Beyond 330 nm, surface reflection is very important since the atmosphere is nearly transparent in this spectral region.

Multiple scattering is included in the model using a simplified method that is computationally fast so that it can be used for diurnal calculations. The method is similar to that of Isaksen et al. (1977) in terms of the numerical method but quite different in terms of the physical assumptions. The atmosphere is divided into optically thin layers and each layer can absorb and scatter radiation. The layer is assumed to scatter radiation isotropically with half of the scattered flux going upward and the other half downward at an average zenith angle of $\pm\bar{\theta}$. The earth's surface is also assumed to scatter isotropically, and a surface albedo of 0.25 is used to approximate the effect of clouds on the upward scattered radiation. Using a high surface albedo and no clouds gives results that are nearly identical to those from dividing the atmosphere into clear and cloudy regimes and averaging the results (the exception being the region below the cloud layer, which is not important for the model applications considered here). For each atmospheric layer there is a contribution to the solar flux density from the direct flux and by the diffuse fluxes incident on the layer from above and from below. The flux density due to the various fluxes together can be much greater (depending on the wavelength and altitude) than the flux density computed considering only gaseous absorption (Luther and Gelinas, 1976; Luther and Wuebbles, 1976).

TEMPERATURE FEEDBACK

The temperature profile above 13 km is calculated using a stratospheric radiative transfer model, and the temperature profile is specified at lower altitudes. The model includes solar absorption and long-wave interaction by O_3 , H_2O , and CO_2 , along with solar absorption by NO_2 . The techniques adopted for treating long-wave radiative transfer are the same as those described by Ramanathan (1974). This formulation was chosen because it is computationally efficient, and its accuracy has been demonstrated (Ramanathan, 1974, 1976) by comparison with much more complex models. The effects of and justification for the simplifying assumptions used in the model are discussed by Ramanathan (1976).

A band absorptance formulation is used to treat the 9.6- μm band of O_3 and the fundamental and several hot and isotopic bands of CO_2 in the 15- μm region. An emissivity formulation is used to treat long-wave radiative transfer by H_2O . Solar absorption by O_3 is treated by using the empirical formulation given by Lindzen and Will (1973). The band absorptance formulation by Houghton (1963) is adopted for solar absorption by H_2O , and the band absorptance formulation by Ramanathan and Cess (1974) is adopted for solar absorption by CO_2 . The empirical formulation of Luther (1976) is used for solar absorption by NO_2 . Solar absorption by O_3 and NO_2 are treated independently because absorption by these species is weak in the region where their absorption bands overlap. Solar radiation scattered from the troposphere is included by assuming an albedo of 0.3. Doppler broadening effects are included for CO_2 and O_3 as described in Appendix B of Ramanathan (1976). The temperature dependences of the band absorptance and band intensity are included in the longwave calculations of CO_2 and O_3 .

A single cloud layer is included at 6.5 km with 42% cloud cover as was suggested by Cess (1974). The lapse rate within the troposphere is assumed to be -6.5 K/km, and the temperature at the earth's surface is specified to be 288 K.

NUMERICAL METHOD

Each of the 39 species in the model has its concentration calculated at each of 44 vertical levels extending from the surface to 55 km. The numerical technique used to solve the set of over 2000 differential equations (resulting from a continuity equation for each species at each grid level) is the method described by Chang et al. (1974). The main advantage of this method, which is a variable order, multistep, implicit method, is its ability to solve sets of mathematically stiff differential equations for almost any set of input parameters, initial and boundary conditions, in particular those resulting from the chemical kinetics system described in Table A-2.

THE DIURNAL AND DIURNAL-AVERAGED MODELS

We have developed a fully diurnal-averaged model that is consistent with our diurnal model. The diurnal model is used to generate species profiles for comparison with measurements and for perturbation studies involving short time integrations (e.g., solar eclipse effects). The diurnal-averaged model is used for perturbation and sensitivity studies involving longer time integrations.

The procedure that is used in developing the fully diurnal-averaged model is also applicable to two-dimensional models. If the continuity equation is averaged over a time period (24 hours in our case) that is very small compared to the time scale of the problem of interest, then one obtains averaged terms of the form $\overline{k_{ij} c_i c_j}$ and $\overline{J_i c_i}$ where c_i is the concentration of species i at time t and altitude z , k_{ij} is the two-body chemical rate coefficient, and J_i is the photodissociation rate coefficient for species i .

We define the diurnal weighting factors $\alpha_{ij}(z)$ and $\beta_i(z)$ by

$$\overline{k_{ij} c_i c_j} = \alpha_{ij} \overline{k_{ij}} \overline{c_i c_j}$$

and

$$\overline{J_i c_i} = \beta_i \overline{J_i} \overline{c_i} .$$

Since k_{ij} is defined and is independent of time, we have

$$\alpha_{ij} = \overline{c_i c_j} / \overline{c_i} \overline{c_j}$$

and

$$\beta_i = \overline{J_i c_i} / \overline{J_i} \overline{c_i} .$$

The computation of photodissociation rates can be an expensive part of stratospheric model calculations, hence evaluation of $\overline{J_i}$'s in the diurnal-averaged model can be expensive. If we define β_i by

$$\beta_i = \overline{J_i c_i} / (J_i^{\text{noon}} \overline{c_i}) ,$$

then the computation in the diurnal-averaged model is greatly simplified. The diurnal model is used to determine $\overline{c_i c_j}$, $\overline{J_i c_i}$, $\overline{c_i}$, $\overline{c_j}$, and J_i^{noon} so that α_{ij} and β_i can be obtained for every chemical and photochemical reaction in the model.

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APPENDIX B. EFFECT OF CHANGES IN OZONE ON UV DOSE AND SKIN CANCER INCIDENCE

Because reductions in total ozone would permit greater amounts of UV radiation to reach the surface of the earth (Cutchis, 1974, 1978; Halpern et al., 1974), a number of studies have been performed with the goal of assessing biological sensitivity to ozone-induced changes in UV radiation (National Research Council, 1973). One approach has been to correlate skin cancer incidence data directly with ozone layer thickness. The possible influence of such factors as duration of sunlight, clothing and exposure habits, and optical path length have been considered (McDonald, 1971; van der Leun and Daniels, 1975). Another approach has been to explicitly consider the dose of UV radiation received as a function of ozone amount and other climatic variables (Green and Mo, 1975). The radiation dose is then related to cancer incidence after weighting by a wavelength-dependent function accounting for variation in radiation efficacy. Both of these approaches are discussed in this section.

OZONE REDUCTIONS AND UV DOSE*

Green and coworkers developed a semi-empirical model for calculating UV radiation at the surface of the earth in the spectral region 280-340 nm (Green et al., 1974a,b; Mo and Green, 1974). They have calculated erythema (sunburn) dose as a function of total ozone, solar zenith angle, latitude, season, and cloud amount. Their model was also used in the Climatic Impact Assessment Program's analysis of ozone depletion (Green et al., 1975).

One feature of this model, and UV dosimetry in general, is that the receiver is assumed to be horizontal. The geometry of humans, however, is such that the majority of exposed skin would normally be in a nonhorizontal position. In fact, the horizontal projection of an upright person amounts to only a few percent of total surface area (Fanger, 1970).

*See Burt and Luther (1979).

The report of the National Research Council (1976a) summarizes the specific sites of origin of primary melanoma skin cancer. The data show the predominant localization of sites of origin to areas of the skin that are constantly exposed, such as the trunk and legs of males. These are, in general non-horizontal surfaces, which suggests that receiver orientation should be considered in the study of UV dose. We have extended earlier studies of erythema dose to include the effect of receiver orientation (Burt and Luther, 1979).

Using a modification of the Green model, we calculated the instantaneous erythema dose for different times of day, date, latitude, ozone amount and receiver position. In analyzing the effects of receiver orientation, we numerically integrated over wavelength and time to produce daily erythema doses for Northern Hemisphere latitudes assuming the receiver is stationary. Integrations were performed for the 15th day of each month using a time step of approximately 20 minutes. The total ozone was specified as a function of latitude based on data from the Nimbus III satellite reported by Lovill (1972).

The azimuth of the receiver was specified in two ways. First, to obtain a measure of the upper bound on erythema dose at middle latitudes in the Northern Hemisphere, the receiver was held fixed in a south-facing position. Second, to estimate the average dose for a population where there is random orientation (i.e., no preferred orientation), calculations were made while averaging over azimuth angle (a rotated receiver). Doses were computed at 20° intervals in the azimuth angle, and the average of these was used for integration. The inclination angle was held fixed at values of 0, 45, and 90 degrees. α is the angle of the receiver relative to horizontal. For a horizontal receiver, $\alpha = 0$.

Figure B-1 shows the daily erythema dose averaged over a year for a south-facing surface assuming cloudless conditions. In middle latitudes the daily average erythema dose on a surface with $\alpha = 45^\circ$ ranges from 90 to 96% of the dose on a horizontal surface. The dose is significantly less for inclination angles greater than 45° .

Figure B-2 shows the daily erythema dose averaged over a year for a rotated surface. In this case the daily average erythema dose in middle latitudes on a surface with $\alpha = 45^\circ$ is approximately 83% of the dose on a horizontal surface. At higher latitudes the dose on the rotated surface is significantly less than that on the south-facing surface.

FIGURE B-1. Daily erythema dose averaged over a year for a southfacing surface.

A semilog scale is used in Figs. B-1 and B-2 to demonstrate the effect of inclination angle on the doubling distance for erythema dose. In middle latitudes the computed erythema dose on a horizontal surface doubles over 16° of latitude moving toward the equator. The angle of inclination has very little effect on the doubling distance as evidenced by the similar slopes of the curves in Figs. B-1 and B-2.

The computed doubling distance is consistent with measurements of annual-average erythema dose (Urbach and Davies, 1975), but it differs from the doubling distance for the incidence of skin cancer. Data on the incidences of skin

FIGURE B-2. Daily erythema dose averaged over a year for a rotated surface.

cancer in middle latitudes show a doubling over 8 to 12° of latitude (National Research Council, 1976b). Consequently, predicting the effect of a reduction in total ozone on the skin cancer incidence rate is more complex than just assessing the change in erythema dose and scaling proportionately.

The effect of a reduction in total ozone of 10% on the annual-average daily erythema dose for a rotated surface is shown in Fig. B-3. The results were almost identical for the south-facing surface. The amplification factor on erythema dose ($\Delta \text{dose} / \Delta \text{O}_3$) varies from 1.3 to 1.4 at low latitudes, from 1.6 to 2.0 at middle latitudes, and is approximately 3 at high latitudes. It is a property of atmospheric

FIGURE B-3. The percent change in daily erythema dose for a rotated surface averaged over a year as a result of a 10% reduction in ozone.

transmission that a 10% reduction in the ozone column causes the greatest percent change in transmission for the largest optical depth. Because the ozone column and solar zenith angle both increase with latitude, the amplification factor is largest at high latitudes. While the percent increase in daily erythema dose at high latitudes is much greater, the total amount of radiation is very small compared to lower latitudes. Since the majority of the world's population lives south of 55°N , amplification factors in the range 1.3 to 2.0 are most realistic.

Reducing the ozone column increases both the direct and diffuse flux components, but by different factors. Since the relative contribution of the direct

and diffuse flux components to erythema dose depends upon α , the amplification factor also depends upon α . This dependence is lessened at high latitudes where the flux is almost entirely diffuse.

Figure B-4 shows the distance moved south that is equivalent to a 10% reduction in ozone based on the annual average data for a rotated surface shown in Fig. B-2. The shaded area indicates the range of values as α is varied from 0 to 90°. In middle latitudes the increase in daily average erythema dose due to a 10% ozone reduction is roughly equivalent to moving south a distance of 350 to 450 km with no ozone perturbation. The equivalent distance is much greater at latitudes

FIGURE B-4. The distance moved south equivalent to a 10% ozone reduction computed for a rotated surface. The shaded area indicates the range of values as the inclination angle is varied from 0 to 90°.

toward the equator from 30°N . There is no equivalent distance for latitudes less than 15°N because the erythema dose at these latitudes with a 10% ozone reduction is greater than the unperturbed erythema dose at the equator.

UV RADIATION AND SKIN CANCER

A comprehensive study of the linkage between UV radiation and skin cancer was recently completed by Cutchis (1978). Skin cancer incidence data in countries having a predominantly white population were compared with respect to geographic, time, age, and anatomic site variations. The hypothesis that an increase in UV radiation dose is associated with an increase in the incidence of squamous cell carcinoma, basal cell carcinoma, and malignant melanoma was tested by investigating recent epidemiological data over a wide latitude band. Squamous cell and basal cell carcinomas are the most common forms of skin cancer, and they are rarely fatal. Malignant melanoma, although less common, is often fatal. Some of the principal findings of Cutchis' investigation are:

- "1. The hypothesis that solar ultraviolet radiation is a dominant factor in the introduction of squamous and basal cell carcinomas in predominantly white populations is strongly supported by an examination of available worldwide incidence data.
- "2. A very large number of inexplicable anomalies of various kinds are found in the worldwide incidence data which are inconsistent with the hypothesis that solar ultraviolet radiation is a significant factor in the induction of malignant melanoma, leading to the conclusion that the primary cause(s) for this class of tumors must be sought elsewhere.
- "3. There is clear evidence of a latitude gradient for squamous cell and basal cell carcinoma (hereafter referred to as "other skin cancer") incidence on a worldwide basis; there is no similarly clear evidence of a latitude gradient for the incidence of malignant melanoma.
- "4. The ratio of the incidence of other skin cancer for males to that for females exceeds unity for all countries, and has a strong latitude gradient, increasing toward the equator; for malignant melanoma incidence this sex ratio may be slightly greater or smaller than unity with an average value of about 0.9, and has no apparent latitude gradient. For most geographic regions, the malignant melanoma sex ratio is less than unity, a finding which is inconsistent with the solar ultraviolet radiation hypothesis for malignant melanoma.

- "5. The incidence of malignant melanoma for males in Norway is 20 times higher than in Zaragoza, Spain. Since Norway is much farther from the equator than Spain, this finding contradicts the lifetime solar UV dose hypothesis. There is no evidence in the literature that such a large discrepancy (greater than 20) can be rationally attributed to ethnic differences in Caucasian populations. Neither Norway nor Zaragoza are singularities. Residents in all Mediterranean countries of Europe enjoy very low malignant melanoma mortality rates, while residents of all Scandinavian countries and Finland suffer high mortality rates.
- "6. Age-specific incidence curves for malignant melanoma differ fundamentally from those for other skin cancer. In recent years the risk for other skin cancer increases almost exponentially with age, while for malignant melanoma the risk is essentially the same for adults between approximately 40 and 65 years of age. The recent age-specific incidence curves for Connecticut and New Mexico are almost identical. From these data it can be deduced that malignant melanoma incidence is not a significant function of lifetime dose or, in all likelihood, the number of acute UV doses received.
- "7. There has been a worldwide increase in the incidence of both other skin cancer and malignant melanoma in almost all countries with a predominantly white population. However, exceptions can be found. Squamous cell carcinoma incidence decreased in Finland from approximately 6 per 100,000 in 1960 to 3.5 in 1973, whereas malignant melanoma during this same period increased from 2 to 3.5. In Australia, mortality from malignant melanoma doubled from 1950 to 1964 but mortality from other skin cancer decreased by 50 percent during the same period. These and other similar cases in which the time variations of incidence over a long period of time run in opposite directions constitute anomalies for the solar radiation hypothesis linking solar radiation to malignant melanoma.
- "8. Malignant melanoma mortality exceeds other skin cancer mortality for both males and females and has increased with time, whereas other skin cancer mortality has decreased with time. There is evidence in some countries of a latitude gradient for malignant melanoma mortality. Since malignant melanoma also occurs in younger age groups, it poses a far more serious problem to public health. Its causative factors are clearly in urgent need of being established.
- "9. Other skin cancer favors the most exposed anatomic sites (head and neck, and hands), whereas malignant melanoma favors the relatively unexposed anatomic sites (trunk and lower limb). The lower limb is more favored in the legs of females, however, and this finding is consistent with the solar radiation hypothesis.
- "10. Anatomic site frequency distribution changes with latitude for squamous cell carcinoma, but anomalously appears to be independent of latitude for malignant melanoma, e.g., malignant

melanoma cases for the head and neck constitute approximately 18 percent of all melanoma cases in Finland, southern Texas, and Australia.

- "11. Two dichotomies exist in anatomic site behavior for malignant melanoma which suggest the existence of two carcinogenic agents, neither of which is solar ultraviolet radiation. These are:
 - "A. The age-specific incidence rates for malignant melanoma in the face and foot were similar to those for other skin cancer, i.e., almost exponential with age, whereas those for the trunk and lower limb were approximately independent of age for adults older than 35 years.
 - "B. The incidence of malignant melanoma in the face and foot was invariant with time, whereas in the trunk and lower limb the incidence has been rising very rapidly with time. The beginning of the latter increase can be traced back to the 1880's.
- "The dating back of the increase in the postulated carcinogen associated with the trunk and lower limb to the 1880's rules out the frequently expressed hypothesis that the changes in clothing and life styles since World War II and the resulting increased UV doses received were responsible for the increase in malignant melanoma in those sites. Malignant melanoma incidence in the face was independent of sex which rules out identification of the other postulated carcinogen as solar radiation.
- "12. Malignant melanomas were typically found in members of the professional and managerial classes, whereas other skin cancers were typically found in semi-skilled and skilled workers. This particular finding is inconsistent with the hypothesis that lifetime UV dose is associated with malignant melanoma but may be consistent with an acute UV dose hypothesis.
- "13. Many carcinogenic agents other than solar radiation have been identified or suspected in the etiology of squamous and basal cell carcinomas. However, the great majority of cases appear to be sun-related, particularly for squamous cell carcinomas.
- "14. Analysis of the data indicates that urbanization is an important factor in the etiology of basal cell carcinoma. It appears to be about as significant a factor as solar radiation in northern U.S. cities.
- "15. There is recent evidence in Finland, Norway, Denmark, and Warsaw that urbanization is a factor in the etiology of malignant melanoma.
- "16. The three categories of malignant melanoma, i.e., lentigo-maligna, superficial spreading, and nodular, appear to have characteristics (anatomic site distribution, tumor development time, median age) which can be made compatible with a two- or three-carcinogen theory for the etiology of malignant melanoma.

- "17. The etiology of malignant melanoma is in a chaotic state. Recently published articles suggest the possibility that virus-like particles and diet (polyunsaturated foods) may be implicated in the etiology of malignant melanoma.
- "18. The data for malignant melanoma incidence in Geneva, Switzerland and Zaragoza, Spain should be further examined for possible etiological clues: Geneva has had an anomalously high male/female sex ratio (2.2) and Zaragoza has had extremely low incidence values for both males and females.
- "19. The biological amplification factor for other skin cancer is equal to or greater than unity but it is unlikely that it exceeds a value of 2. Determination of this factor is a complex multi-dimensional problem and the development of a dose-response model free of uncertainty and controversy is an almost hopeless proposition at the present time."

Another recent study by Martell and Poet (1979) suggests that ultraviolet radiation contributes to restitution rather than to induction of single breaks in the chromosomes of the cells of higher organisms. This argument is contrary to the view that ultraviolet radiation causes chromosome aberrations characteristics of malignancy. They claim that tumors which have been induced in mice and rats by repeated, large doses of UV radiation are unlike human skin tumors in type and tissue site, making the results of questionable applicability to man.

Martell and Poet (1979) suggest that alpha radiation may be a primary agent of human skin cancer. Alpha radiation is an effective mutagenic agent capable of producing a wide variety of structural changes observed in human tumors. Radon daughters that concentrate on exposed skin merit special consideration as agents of skin cancer. They conclude that if structural changes in chromosomes prove to be essential to malignancy, then the case for ultraviolet radiation as an etiological agent will be difficult to defend.

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APPENDIX C. POTENTIAL CLIMATIC EFFECTS OF STRATOSPHERIC PERTURBATIONS*

Perhaps the most widely discussed effect of a reduction in ozone is the biological effect due to increased uv radiation at the earth's surface. A change in the total amount or redistribution of radiatively important atmospheric species might also be significant in terms of the climatic effects. Calculations of the change in global mean surface temperature caused by stratospheric perturbations generally show changes of much less than 1 K, but there could be much larger changes regionally, especially at high latitudes. Calculations with two- and three-dimensional models suggest that an increase in surface temperature would increase the intensity of the hydrologic cycle, thus increasing global mean precipitation. Uncertainties regarding cloud feedback processes and how climatic changes will affect cloudiness make it difficult at this time to accurately quantify such climatic changes. The sections that follow are intended to provide only rough estimates of the potential climatic effects of large SST fleets. Any effects that appear to be significant would, therefore, be candidates for more detailed study in the future.

COMPARISON OF CHANGES IN SOLAR ABSORPTION BY O_3 AND NO_2

In the case of a stratosphere perturbed by an NO_x injection, Luther (1976) showed that the increase in solar absorption by NO_2 at steady state was a significant fraction (35 to 50%) of the decrease in solar absorption by O_3 . Since that time, the sensitivity of O_3 to an NO_x injection has decreased in the transport-kinetics models. Consequently, the change in solar absorption by NO_2 is now expected to be a much larger fraction of the change in solar absorption by O_3 .

Solar absorption by O_3 is shown in Fig. C-1 as a function of O_3 column density. The absorption rate given is the instantaneous value for a solar zenith angle of 60° . The radiative transfer model used to compute the solar absorption rate includes Rayleigh scattering and assumes a cloudless, plane-parallel atmosphere

*See Luther (1978).

FIGURE C-1. Solar absorption by ozone for a solar zenith angle of 60° . A_s is the surface albedo.

above an isotropically scattered ground (Luther, 1978). The solar absorption by NO_2 is shown in Fig. C-2 also for a solar zenith angle of 60° .

Ambient and perturbed species concentration profiles were computed using the LLL one-dimensional transport-kinetics model. Two perturbation cases were considered: injections at 17 or 20 km of NO_x and H_2O . The injection rate for NO_x was $1000 \text{ molecules cm}^{-3}\text{s}^{-1}$, and the injection rate for H_2O was $177,000 \text{ molecules cm}^{-3}\text{s}^{-1}$ uniformly distributed over a 1-km-thick layer.

FIGURE C-2. Solar absorption by NO₂ for a solar zenith angle of 60°.

Temperature feedback and hydrostatic adjustment were included in these calculations. Changes in the O₃ and NO₂ column densities and solar absorption rates for a solar zenith angle of 60° and a surface albedo of 0.25 are summarized in Table C-1. The unperturbed column densities are 8.196×10^{18} molecules/cm² (0.305 atm.cm) for O₃ and 4.702×10^{15} molecules/cm² for NO₂.

In both cases, the injection of NO_x resulted in a small increase in total O₃. Although the changes in the O₃ column density are small, the changes in the O₃ column density are small, the change in the local O₃ concentration may

TABLE C-1. Increases in total atmospheric solar absorption by O_3 and NO_2 due to NO_x injections at the rate of $1000 \text{ cm}^{-3}\text{s}^{-1}$ and H_2O injections at the rate of $177,000 \text{ cm}^{-3}\text{s}^{-1}$. Calculations are for a solar zenith angle of 60° and a surface albedo of 0.25.

Quantity	Injection Altitude	
	17 km	20 km
ΔO_3	1.37%	1.29%
ΔNO_2	5.04%	10.51%
$\Delta \text{Abs}(O_3)$	0.20 W/m^2	0.19 W/m^2
$\Delta \text{Abs}(NO_2)$	0.06 W/m^2	0.12 W/m^2

be several percent. The change in column density reflects the net difference between regions of O_3 increase (below 26 km) and O_3 decrease (above 26 km). Consequently, although the change in the net heating may be small, the redistribution in altitude of where this heating occurs may be significant. The change in the local concentration of NO_2 is shown in Fig. C-3.

Changes in O_3 and NO_2 concentrations due to an NO_x injection lead to increases in the total solar absorption of both species. These increases are small, however, when compared to the total energy absorbed by the stratosphere.

POTENTIAL CLIMATIC IMPACT

The climatic impact of changes in stratospheric composition depends upon both the solar and longwave effects of the perturbation. Changes in temperature, in addition to affecting the transfer of longwave radiation, also affect atmospheric stability and transport. Here we will consider only the global impact of the solar and longwave effects and neglect any potential feedback on transport.

When evaluating the computed change in global mean surface temperature, changes on the order of several tenths of a degree Kelvin may be a significant climatic perturbation since regional changes in temperature might be several times greater than the global mean. Pollack et al. (1976) suggest that 0.1 K is a threshold

FIGURE C-3. The change in NO₂ concentration due to an NO_x injection of 1000 molecules cm⁻³s⁻¹ and H₂O injection of 177,000 molecules cm⁻³s⁻¹ over a 1-km thick layer at 17 or 20 km.

value for considering the change in global mean surface temperature to be significant. Computing the change in global mean surface temperature associated with past major changes in climate, they infer that values below 0.1 K would not have major consequences.

A previous assessment of the effect of changes in O₃ and NO₂ on surface temperature by Ramanathan et al. (1976) showed a cooling at the surface associated with a reduction in O₃ due to an NO_x injection. Only reductions in O₃ were

considered (not increases), and it was assumed that the changes in O_3 and NO_2 were uniform (percentagewise) between 12 and 40 km. Our present results differ from these modeling assumptions in that the changes in O_3 and NO_2 concentrations are not uniform with altitude, and there is a net increase in O_3 column density rather than a decrease. Nevertheless, the work of Ramanathan et al. (1976) is useful because it demonstrates the importance of the longwave effect of the perturbation. The reduction in total O_3 tended to warm the troposphere by increasing the transmissivity of the stratosphere for solar radiation. The reduction in stratospheric temperature due to reduced O_3 , however, had a greater effect on the longwave radiation emitted downward from the stratosphere. The net result was a slight reduction in surface temperature.

A similar calculation using our current modeling results would predict an increase in temperature in the lower stratosphere (Luther and Duewer, 1978). It is possible that the longwave effect would also dominate in this case. Although the net change in temperature is uncertain, it is clear that the longwave effect would tend to warm the troposphere, whereas the solar effect would tend to cool.

In attempting to assess the effect of changes in stratospheric composition on the global mean surface temperature, it is desirable that the same model be used throughout the study. Since we do not have a climate model that may be applied to this study, we will rely on the results of other researchers.

According to Ramanathan's model (Ramanathan et al., 1976), the change in surface temperature is related to the change in ozone by

$$\Delta T_s = (0.009 \text{ to } 0.014 \text{ K}) \Delta O_3, \quad (C.1)$$

where ΔO_3 is the percent change in ozone concentration applied uniformly over the altitude region 12-40 km. The first coefficient applies to the assumption of constant cloud top altitude whereas the second coefficient applies to the assumption of constant cloud top temperature. A similar expression relates the change in surface temperature to the percent change in NO_2 concentration between 12 and 40 km:

$$\Delta T_s = (3 \times 10^{-4} \text{ to } 6 \times 10^{-4} \text{ K}) \Delta NO_2. \quad (C.2)$$

The expressions are not applicable directly to our results, but they may be used to

estimate an approximate value for ΔT_s . Using the method described in Luther (1978), the change in surface temperature is estimated to be less than 0.1 K for both the 17- and 20-km injection altitudes.

A recent analysis of the effect of changes in ozone on the earth's radiation balance by Ramanathan and Dickinson (1979) indicates that a vertical redistribution of ozone can produce larger perturbations to the tropospheric energy balance than do uniform changes in ozone. The change in the net radiative flux possibly can be of the opposite sign as well. Changes in the tropospheric lapse rates, which were not included in the calculations, could also affect the magnitude of ΔT_s .

We now consider the potential climatic effect of the water vapor injected into the stratosphere along with the NO_x from engine emissions. According to our model calculations in which the stratospheric water vapor profile is computed, the increase in the stratospheric water vapor mixing ratio would be 0.10 ppmv for a 17-km injection and 0.31 ppmv for a 20-km injection. Ramanathan's model was also used in the CIAP study to estimate the change in surface temperature resulting from a change in stratospheric water vapor mixing ratio (Grobecker et al., 1974):

$$\Delta T_s = (0.2 \text{ to } 0.3 \text{ K}) \Delta \text{H}_2\text{O} (\text{ppmv}) \quad . \quad (\text{C.3})$$

The estimated change in surface temperature as a result of these changes in stratospheric water vapor are given in Table C-2. These changes in temperature are also estimated to be less than 0.1 K.

In addition to NO_x and water vapor, aircraft engines also emit SO_2 , which is converted to sulfate aerosols. Assuming an emission index of 1.0 g/kg fuel, the SO_2 injection rate would be 3.4×10^7 kg/yr when the NO_x injection rate is

TABLE C-2. Change in surface temperature due to an increase in stratospheric water vapor.

Altitude of Injection (km)	$\Delta \text{H}_2\text{O}$ in Stratosphere (ppmv)	ΔT_s (K)
17	0.10	0.02-0.03
20	0.31	0.06-0.09

6.2×10^8 kg/yr. The change in surface temperature due to increased stratospheric aerosols (75% H_2SO_4) has been computed by Pollack et al. (1976). Using a radiative-convective model, they find

$$\Delta T_s = (-6.3 \text{ to } -10 \text{ K}) \Delta \tau, \quad (\text{C.4})$$

where $\Delta \tau$ is the increase in the stratospheric optical depth. Pollack et al. find that $\Delta \tau$ is related to the mass density (m) of sulfate aerosols in $\mu\text{g}/\text{m}^3$ averaged over a 10-km thick layer by the expression $\Delta \tau = 0.031 m$. The expression $\Delta \tau = 0.038 m$ was used in the CIAP Report of Findings (Grobecker et al., 1974). The aerosol mass density is obtained from the expression

$$m = \frac{HFtc(M_a/M_c)}{A\ell},$$

where H is the fraction of the aerosols deposited in a given hemisphere, F is the SO_2 emission rate, t is the residence time, c is the conversion efficiency, M_a is the molecular weight of the aerosol, M_c is the molecular weight of SO_2 , A is the area of a hemisphere of the earth, and ℓ is the depth of the layer (10 km). For a sulfuric acid solution that is 75% H_2SO_4 by weight, $M_a/M_c = 1.6$. Values for the various quantities used by Pollack et al. (1976) and used in the CIAP Report of Findings are shown in Table C-3. The resulting values for $\Delta \tau$ are considerably smaller (by approximately a factor of 2) using Pollack et al.'s values. In both cases the values for ΔT_s are estimated to be less than -0.01 K for a 17-km injection altitude and less than -0.02 for a 20-km injection altitude. Using the criterion that changes a surface temperature less than 0.1 K would not have major consequences, none of the SST engine emissions (NO_x , H_2O , and SO_2) are estimated to have a major climatic effect. The largest individual effect on surface temperature is that of water vapor, which is estimated to cause a temperature increase of 0.06 – 0.09 K for a 20-km injection at 4.3×10^{10} kg/yr. The combined effect of all engine emissions on climate is likely to be an increase in global mean temperature of less than 0.1 K for these injection rates.

TABLE C-3. Factors used in calculating the change in surface temperature due to an SO₂ emission rate of 3.44×10^7 kg/yr in the Northern Hemisphere.

Source	Altitude of injection (km)	Residence time, years	Conversion efficiency	Fraction in hemisphere	$\Delta\tau$	ΔT_s^a (K)
Pollack et al., 1976	17	0.978	0.869	0.7	3.9×10^{-4}	-0.002 to -0.004
$\Delta\tau = 0.031 \text{ m}^b$	20	1.715	0.945	0.7	7.6×10^{-4}	-0.005 to -0.008
CIAP Report of Findings, 1974	17	1.70	0.83	1.0	1.1×10^{-3}	-0.07 to -0.11
$\Delta\tau = 0.038 \text{ m}$	20	1.00	0.93	1.0	2.3×10^{-3}	-0.014 to -0.023

$aT_s = (-6.3 \text{ to } -10 \text{ K}) \Delta\tau$.

b_m is the mass density of sulfate aerosols in $\mu\text{g}/\text{m}^3$ averaged over a 10-km-thick shell.

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APPENDIX D.
THE RELATION BETWEEN ATMOSPHERIC TRACE SPECIES
VARIABILITIES AND SOLAR UV VARIABILITY*

We provide here a discussion of calculated trace species variations due to solar UV variability. Our purpose is to examine those species whose variations may be observable and thus help confirm the supposed solar variations.

LONG-TERM VARIATIONS IN ODD-OXYGEN AND TEMPERATURE

Figure D-1 shows the percent changes in O_3 , $O(^3P)$, $O(^1D)$ and temperature from maximum to minimum in solar UV flux variations. The percent changes are computed by dividing the differences of species concentrations corresponding to the solar UV flux maximum and minimum by the concentration at the minimum. The change in the solar flux was specified as described in Penner and Chang (1978). The changes in species concentrations are due primarily to changes in the photolysis rates for odd-oxygen production and O_3 destruction according to

and

The changes in ozone concentration are sensitive to the calculated temperature increase in the stratosphere because of the temperature dependence of the reactions

and

both of which tend to change in the direction of reducing ozone concentrations as temperature is raised. The increase in UV flux at solar maximum causes increased

*See Penner and Chang (1978, 1979).

FIGURE D-1. Change in temperature (top scale) and percent change in O_3 , $\text{O}(^3\text{P})$, and $\text{O}(^1\text{D})$ from solar minimum to solar maximum [(max-min)/min $\times$ 100] (bottom scale). The dashed line shows the calculated change in O_3 when hydrostatic equilibrium is not included.

solar absorption in the Hartley and Huggins bands of O_3 , resulting in an increase in temperature. The temperature increase is further enhanced by the increases in local ozone concentrations. The present model also includes the changes in cooling rates associated with changes in stratospheric water distribution. Local H_2O remains almost constant throughout the solar cycle and the feedback on the temperature is quite small.

Changes in the temperature profile are expected to lead to changes in the background atmosphere as it adjusts to hydrostatic equilibrium (Chandra et al., 1978). Only minor differences in the variation for most species is observed when hydrostatic adjustment is included. Larger changes, however, occur in the variation of O_3 , NO_2 , and $O(^1D)$. Without hydrostatic adjustment, O_3 is decreased at solar maximum at high altitude due to the combined effects of increases in the rate of photolysis of O_3 and increases in the temperature (dashed line in Fig. D-1). O_3 is approximately given by

$$[O_3]^2 = \frac{J_1 k_1 [O_2]^2 [M]}{J_2 k_2 (1 + A)} \quad , \quad (D.5)$$

where A represents changes introduced by minor species in the NO_x , HO_x and ClO_x families (Nicolet, 1975). With hydrostatic adjustment, increases in $[O_2]$ and $[M]$ at high altitude tend to increase O_3 . Eventually, the increase in O_3 due to hydrostatic adjustment will offset decreases in O_3 caused by an increase in J_1 and a decrease in k_1/k_2 . As shown in Fig. D-1 for the present case, O_3 increased by approximately 4% at 55 km, whereas without hydrostatic adjustment, it decreased 7%.

NO_2 variations also become positive at high altitude with hydrostatic adjustment. These changes are introduced mainly because O_3 has increased, leading to a larger role for the reaction

Changes in the variations of other species due to the inclusion of hydrostatic adjustment are rather minor. The results of Penner and Chang (1978) which compare calculated ozone and temperature variations to observations are shown in

Figs. D-2 to D-4. The comparisons of variations in O_3 and temperature with observations are not significantly affected by including hydrostatic adjustment since the comparisons are for an O_3 change averaged over the altitudes 32-46 km, and the changes are dominated by the higher O_3 concentrations at the lower altitudes within this range. As shown here, however, it is necessary to include hydrostatic adjustment when discussing local ozone variations above about 37 km.

The concentration of $O(^3P)$ is determined by the balance

$$[O(^3P)] = \frac{J_2[O_3]}{k_1[O_2] [M]} \quad (D.7)$$

FIGURE D-2. Comparison of calculated total ozone deviations to the analysis of data by Angell and Korshover (1978a).

FIGURE D-3. Comparison of calculated layer-mean ozone variations to the analysis of ozone data by Angell and Korshover (1978b).

FIGURE D-4. Comparison of calculated layer-mean ozone variations to the analysis of ozone data by Angell and Korshover (1978c).

Combining Eq. (D.5) with (D.7) shows that $O(^3P)$ is only proportional to $M^{-1/2}$ so its concentration is not very sensitive to changes in M resulting from hydrostatic adjustment. $O(^3P)$ increases more than 25% above 40 km (Fig. D-1) at solar maximum due to the increase in J_2 . The $O(^1D)$ concentration, also shown in Fig. D-1, is directly proportional to $J_3[O_3]$, where J_3 refers specifically to photolysis of O_3 leading to $O(^1D)$ production,

The increases in O_3 and J_3 both drive increases in $O(^1D)$. At the highest altitudes this is offset somewhat by increased deactivation of $O(^1D)$ by collision with O_2 and N_2 . It should be noted that the maximum changes of $O(^1D)$ are in the altitude range of 30 to 40 km, i.e., the principal production region of odd-nitrogen and odd-hydrogen from reactions of $O(^1D)$ with N_2O , CH_4 and H_2O . Therefore, one might expect similar variations in the trace species families NO_x and HO_x at this altitude. However, for N_2O and CH_4 the local concentrations are decreased at solar maximum so that the local rate of production of radicals is almost unchanged in the present model.

The time variations of $O(^3P)$ and $O(^1D)$ follow that of the driving function without significant time lag in the altitude range above 20 km. Below 20 km a noticeable time lag in $O(^3P)$ of a few months develops following the time lag of ozone (Fig. D-5). The response time of the total ozone column to variations in solar UV flux is less than two months, reflecting the behavior near the ozone peak around 25 km. These time lags are a function of the 1-D model transport parameterization and should be used with caution since they are sensitive to K_z .

The temperature trend is shown to be in reasonable agreement with radiosonde and rocketsonde temperature data in Fig. D-6, although there remain unexplained details (Penner and Chang, 1978; Angell and Korshover, 1978b). As a test of our understanding of ozone and temperature variations, it is of interest to examine whether the observed temperature variations might drive ozone variations, independent of changes in the solar flux. In order to study this question, we specified the temperature profile in our model and perturbed the calculated ambient temperature profile by $\pm 2.5^\circ K$ and $\pm 5.0^\circ K$ about the average value above 30 km with a linear variation in the perturbed temperature between 20 and 30 km. We calculated trace species concentrations consistent with each temperature profile.

FIGURE D-5. Time variation of O_3 at selected altitudes. Solar maximum and minimum were at 2.75 and 8.25 years, respectively.

This choice of temperature perturbation provides a reasonable fit to the observed temperature variations (Quiroz, 1979; Angell and Korshover, 1978). The background atmosphere was adjusted to hydrostatic equilibrium in each case.

The results of this calculation are shown in Fig. D-7. The calculated ozone decreased below 40 km, consistent with Eq. (D.5) and the temperature dependence of reactions k_1 and k_2 . Above 40 km, hydrostatic adjustment increases $[O_2]$ and $[M]$ so that the O_3 variation becomes positive when the temperature is increased. Observations of ozone and temperature variations below 32 km show an in-phase relationship, which is contrary to the model calculations. Given the present evidence we believe that temperature changes in the stratosphere are insufficient to account for the variations in ozone. We caution, however, that these conclusions are based on a comparison of ozonesonde-derived ozone trends in Europe with radiosonde-derived temperature trends in the Western Hemisphere. These regions were chosen for comparison because they had the largest number of stations and thus provided the most precise trend estimates. Angell and Korshover's (1978a)

FIGURE D-6. Comparison of calculated layer-mean temperature changes to the analysis of rocketsonde measured temperature changes for the Western Hemisphere north subtropics by Angell and Korshover (1978b).

analysis of ozonesonde trends in North America indicated an increase in ozone in the layer from 24-32 km at the same time the temperature was decreasing. The North American trend was based on only 2 stations reporting for the entire time period which may not be sufficient to properly delineate a small long-term regional trend.

FIGURE D-7. Percent change in O_3 for a temperature perturbation of $\pm 1.5^{\circ}\text{K}$ and $\pm 5.0^{\circ}\text{K}$ above 30 km from the average calculated temperature. The temperature perturbation is decreased linearly to zero at 20 km and the background atmospheric pressure is adjusted to hydrostatic equilibrium in each case.

Stanulonis and Chamberlain (1978) looked at ozone and temperature fluctuations from 4 stations near 32°N and found positive, though small, correlations. Thus, a final conclusion in this matter must await further analysis.

LONG-LIVED TRACE SPECIES

The so-called long-lived trace species such as N_2O , CCl_4 , CF_2Cl_2 , $CFCI_3$, CH_3Cl , H_2O and CH_4 are destroyed in the stratosphere either by radiation at wavelengths shorter than 300 nm or by reactions with $O(^1D)$ and OH . Their time variations are in phase with the assumed 11-year variations in solar UV fluxes at altitudes above 35 km. Under the influence of the assumed variations in solar UV fluxes, CF_2Cl_2 , $CFCI_3$, CCl_4 and N_2O all have variations of 40% or larger above 30 or 40 km. Since CF_2Cl_2 and $CFCI_3$ are not in steady state, their expected variations are not the same for every solar cycle. A detailed examination of their possible variations at this time is not warranted. Although CCl_4 is in quasi-steady-state, the absolute accuracies of current measurement techniques for CCl_4 ($\pm 100\%$ (WMO, 1977)) are not adequate for detecting the estimated time variations.

The percent changes of H_2O , CH_4 and N_2O are shown in Fig. D-8. The calculation shows a change of less than 3% for H_2O throughout the stratosphere. Although the destruction rate of H_2O increases at solar maximum (more $O(^1D)$ and photolysis), the increase in production rate from the methane cycle more than compensates for this change in loss rate, so H_2O increases slightly at all altitudes in the stratosphere.

CH_4 shows a solar cycle variation of up to -24% (max to min) around 50 km. This is mainly the result of the variations in $O(^1D)$ and HO concentrations. Since the upward flux of CH_4 from the troposphere is fixed and the chemical lifetime of CH_4 is relatively short above 35 km, any change in the loss rate coefficients affects the local CH_4 concentrations directly. Below 50 km the reaction with HO molecules is the dominate loss mechanism for CH_4 . At altitudes below 30 km, CH_4 also has very little variation since HO changes very little (Fig. D-9). Observational data of CH_4 below 40 km are highly sensitive to variations in transport (Ehhalt et al., 1975). This sensitivity and the small variations expected below 40 km make it difficult to detect CH_4 time variations below 40 km. Only rocket or satellite measurements at the top of the stratosphere offer possibilities of detecting any possible trend.

The large variations in N_2O are caused by changes in its photolysis rate. In the lower and middle stratosphere its variation over a solar cycle is very similar to that of CH_4 and is also difficult to measure. However, above 40 km it is expected

FIGURE D-8. Percent change for N₂O, CH₄, and H₂O from solar minimum to solar maximum [(max-min)/min x 100].

to vary by as much as -46% (max to min), and current measurement techniques with a gaschromatograph and grab sample have an accuracy of a few percent (WMO, 1977). Because of the large reservoir and long lifetime of N₂O in the atmosphere, its atmospheric budget is expected to remain constant for many decades. Therefore, it should be straightforward to use upper stratospheric N₂O data as a test for solar-terrestrial coupling through solar UV variations.

The time variation of N₂O concentrations for several altitudes is shown in Fig. D-10. The variation in N₂O is nearly in phase with the solar forcing function

FIGURE D-9. Percent change for selected species in the HO_x family from solar minimum to solar maximum $[(\text{max-min})/\text{min} \times 100]$.

at altitudes above 40 km. Below that level, the maximum and minimum concentrations occur well after the solar flux minimum and solar flux maximum. Near 35 km, the calculated delay is about 5 months. At 25 km it is 12 months, and below 20 km it becomes longer than 18 months, although at these levels the calculated variation is quite small (less than 1.4%). Because of this difference in

FIGURE D-10. Time variation of N_2O at selected altitudes. Solar maximum and minimum were at 2.75 and 8.25 years, respectively.

phase-lag at different altitudes, the integrated column density shows a much less clear signal for observation purposes. Similar remarks apply to the time variations of CH_3Cl and CH_4 . Delays for CH_4 are somewhat longer than those of N_2O , but below 20 km the N_2O response is more delayed reflecting its longer chemical lifetime in the lower stratosphere. The delay response for CH_3Cl is less than that of either N_2O or CH_4 at all altitudes because its chemical lifetime is shorter. As with the discussion of O_3 , these time lags below 30 km are a function of our one-dimensional parameterization of eddy transport and should not be interpreted as quantitative estimates of true atmospheric time lags.

OTHER TRACE SPECIES

HO_x ($H + HO + HO_2 + 2H_2O_2$) is increased throughout the stratosphere as a result of the increase in $O(^1D)$. The main sources of HO_x are the reactions

and

followed by the subsequent degradation of CH_3 (see Table A-2). This results in increases for all of the species in the HO_x family throughout most of the stratosphere from solar minimum to solar maximum. The same is not true for the other families, NO_x ($N + NO + NO_2 + HNO_3 + NO_3 + 2N_2O_5 + ClONO_2$) and ClX ($Cl + ClO + HCl + ClONO_2$). The source of NO_x is approximately given by $2k_{67}[O(^1D)][N_2O]$. A comparison of the variation for $O(^1D)$ and N_2O in Figs. D-1 and D-8 shows that the net effect of increases in $O(^1D)$ and decreases in N_2O is a very slight increase in the production rate for NO_x . Total NO_x is increased by less than 4% at 40 km. The behavior of ClX is similar to that of NO_x . The enhanced photolysis coefficients for the source species, CF_2Cl_2 , CCl_4 , CH_3Cl , $CFCl_3$ at solar maximum is accompanied by a corresponding decrease in the source molecule concentrations resulting in only about $\pm 1\%$ variation in ClO_x at all altitudes.

Even though the NO_x and ClX family concentrations are not greatly changed, large changes in individual trace species are calculated (Figs. D-11 and D-12). The reasons for the changes in local chemical balances among the short-lived species in each family can be fairly subtle because, in general, a large number of coupling reactions must be considered simultaneously. For example, consider the changes associated with the major NO_x species, HNO_3 , NO , and NO_2 . HNO_3 is decreased at solar maximum above 22 km due to increased photolysis, a major pathway for loss,

Although the source of HNO_3 , the three-body recombination of HO and NO_2 ,

FIGURE D-11. Percent change for selected species in the NO_x family from solar minimum to solar maximum $[(\text{max}-\text{min})/\text{min} \times 100]$.

is also larger at solar maximum (see changes in HO and NO_2 in Figs. D-9 and D-12), the increased rate of photolysis of HNO_3 actually dominates. Since total NO_{x3} remains almost constant, a 10 to 20% decrease in HNO_3 will lead to an increase in the combined sum of NO and NO_2 above 22 km. The local partitioning of NO and NO_2 is given by

FIGURE D-12. Percent change for selected species in the ClX family from solar minimum to solar maximum $[(\text{max-min})/\text{min} \times 100]$.

$$\frac{\text{NO}}{\text{NO}_2} = \frac{J_4 + k_4 [\text{O}]}{k_3 [\text{O}_3] + k_{36} [\text{ClO}] + k_{24} [\text{HO}_2]}$$

from the reactions,

The net results of all the couplings are small increases for NO_2 at all altitudes and small decreases for NO between 30 and 40 km with increases above 40 km. These changes are mainly the result of the changes in O_3 concentrations and in J_4 . For these species and others in the ClX and HO_x families, the magnitude of individual time variations are usually too small to be detected since they are often quite variable even on a diurnal and seasonal time scale. Even ratios such as NO/NO_2 , Cl/ClO , HO/HO_2 , etc. are not significantly better for long-term trend detection.

Changes in the concentrations of the major species in the ClO_x family are also driven by changes in several reactions and species. For example, increases in HO and HO_2 affect both the production and removal of HCl . Only direct fully coupled model calculations can provide the quantitative information represented in Fig. D-12. Although ClONO_2 shows a large percentage variation above 40 km, there is little ClONO_2 at these altitudes for detection. Similar general observations can also be made for the variations in HO , HO_2 and H_2O_2 .

None of the short-lived species show significant solar cycle variations that are easily detectable because of the presence of all the coupling reactions and the balancing of many variations in reaction rates of similar magnitudes. Furthermore, the available instrumental accuracies for these species are in the range of 10-30% (WMO, 1977) which are either worse than or comparable to the expected maximum variations. Other species such as ClNO_2 , NO_3 , N_2O_5 , H , and N included in this study are very difficult to measure. Therefore, they are of minor interest in the present analysis.

CONCLUSIONS

The variations of stratospheric trace species under the influence of hypothetical solar UV flux variations have been studied. The results may be used to guide observation strategies with a view toward verifying the validity of the assumed 11-year solar cycle influence on the earth's atmosphere. The possible candidates for this use are those species with the largest local solar cycle variations and whose response is directly due to the changing solar UV fluxes, such as N_2O , O_3 , CH_4 , HNO_3 , CCl_4 , $CFCl_3$, CF_2Cl_2 , and CH_3Cl . The lifetimes for these species above 40 km are sufficiently short so their response is in phase with the changes in solar UV fluxes. Of course, seasonal variations of these trace species in the upper stratosphere will also be fairly large and may partially obscure the expected variations. Since the seasonal change in solar conditions is well quantified, we can monitor this change and remove its effect from the trend analysis. Due to the currently available instrumental accuracy and the changing source functions for CFMs, N_2O is the best candidate.

The possibility of long-term temperature variations driving ozone variations independent of solar UV is far from settled because different data appear to give conflicting results. For this reason and in order to further validate the solar variations, long-term monitoring of high altitude (above 40 km) N_2O is particularly attractive.

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APPENDIX E.
A THEORETICAL STUDY OF STRATOSPHERIC TRACE
SPECIES VARIATIONS DURING A SOLAR ECLIPSE*

INTRODUCTION

Solar eclipses are known to affect measurable quantities in the upper atmosphere. Various workers have discussed the response of ionospheric electron and positive ion densities to an eclipse (Landmark et al., 1970; Marriott et al., 1972; Anastassiades, 1970).

Other studies have investigated the possibility of changes in stratospheric and mesospheric ozone during an eclipse. Stranz (1961), using a Dobson ozonometer, measured approximately a 4% increase in total ozone shortly after the maximum phase of an eclipse in which only about 80% of totality was reached. Hunt (1965) attempted to explain this total ozone increase by using Chapman reactions and the solar flux changes expected in the path of totality. Hunt found that at most an increase of only 0.6% is to be expected, and that ozone should be affected only above 45 km. In later observations, Randhawa (1968), Ballard et al. (1969), Randhawa (1973), Gramnick et al. (1974), and Osherovich et al. (1974) had come to mutually contradictory conclusions on ozone changes during solar eclipses; some observed ozone increases while others detected no changes. Clearly inconsistencies exist in the observations and in their utilization for validating ozone-related atmospheric chemistry as it is understood at present.

In addition to ozone observations, measurements of other minor constituents during a solar eclipse could provide validation of the short-lifetime chemistry in atmospheric models. Consequently, experiments for upcoming solar eclipses, when properly supported by theoretical analysis, could contribute significantly to our understanding of atmospheric chemistry. In fact, given the proper data on trace species concentrations during an eclipse, such measurements could provide a direct demonstration that currently proposed NO_x , HO_x and ClO_x catalytic cycles are indeed concurrently functioning in the stratosphere in the manner suggested by

*See Wuebbles and Chang (1979).

laboratory chemistry. While detailed measurements of diurnal variations could provide similar knowledge, the difference in time scale between the diurnal cycle and a solar eclipse event suggests that the latter event may provide a clearer picture for understanding.

The purpose of this study is to examine theoretically the expected effect of a solar eclipse on stratospheric minor constituents. Primary emphasis is given to the total eclipse which will occur over North America on February 26, 1979 (Fiala and Lukac, 1977). Variations similar to those computed for this particular case should be expected for other total eclipses.

METHODOLOGY

Fifty degrees north is the latitude at which totality is the longest (~3 minutes) for the February 1979 eclipse. In attempting to simulate typical expected atmospheric conditions for the February 26, 1979 solar eclipse, we modified the model by setting the temperature (Louis, 1974), tropospheric water vapor (Oort and Rasmussen, 1971), and the ozone distribution (Wilcox and Belmont, 1977) to 50°N winter conditions. The latitude and the solar declination angle, necessary to calculate the solar zenith angle for photodissociation coefficients, were set to 50° and -8.8°, respectively.

While ozone in the model was held fixed for most calculations in order to simulate February 50°N conditions, the model was also run with calculated ozone to examine the expected response of ozone to an eclipse. Our analysis has shown that fixing the ozone distribution does not significantly affect the temporal variations calculated for other species during the eclipse.

Assuming fixed total odd nitrogen and odd chlorine as calculated for midlatitudes, the model was run diurnally to equilibrium. The calculated daytime total column for NO₂ at 50°N of 1.9×10^{15} molecules/cm² is consistent with the observations of Noxon (1979). The model had approximately 1.7 ppb of ClX and 17 ppb of NO_x at 40 km.

Solar flux variations during the eclipse were parameterized based on Hunt (1965). The eclipse was assumed to start at 9:30 a.m. and end at 12:00 noon, corresponding to the February 1979 eclipse for 50°N in southern Canada. Totality

was assumed to occur for three minutes beginning at 10:43:30 a.m. Based on measurements of sky brightness during an eclipse (Velasquez, 1971; Dandekar and Turtle, 1971), the solar flux at totality was uniformly reduced to 10^{-4} of the unobscured flux. During the eclipse we assumed the solar flux to be proportional to the area of the unocculted sun. Limb darkening is a secondary effect that becomes important only near totality at which time the changes in trace species concentrations that are of interest are all near completion.

RESULTS AND DISCUSSION

Those species having chemical lifetimes less than a few hours should be expected to vary significantly from normal diurnal behavior during a solar eclipse. In this study, we emphasize the variations expected for those species most important to the chemistry of stratospheric ozone. Local concentrations of the species could be quite variable, and therefore we should focus on relative effects rather than their absolute magnitudes.

The model calculated response of ozone during an eclipse essentially agrees with Hunt (1965). A significant increase in O_3 is to be expected in the upper stratosphere and in the mesosphere because of the conversion of $O(^3P)$ to ozone through the reaction $O(^3P) + O_2 + M \rightarrow O_3 + M$ accompanied by decreased photolysis of O_2 and O_3 . The maximum increase in O_3 , found at the end of totality, was computed to be 15% and 45% at 50 and 55 km, respectively. Larger percent changes should be expected in the mesosphere. Since most of the atmospheric ozone is at lower altitudes in the stratosphere, an insignificant change in the total ozone column is to be expected.

Figure E-1 shows the variations expected during the eclipse in the concentration of NO and NO_2 at altitudes of 20, 30, and 40 km. The solid line indicates normal behavior from 9:00 a.m. to 2:00 p.m. local time, while the dotted line shows the change in concentration expected during the eclipse. The decreased solar flux results in the NO_2 photolysis rate decreasing during the eclipse. Also the rapid conversion of $O(^3P)$ to O_3 decreases the importance of $NO_2 + O(^3P) \rightarrow NO + O_2$. NO is then rapidly converted to NO_2 during the eclipse primarily by the reactions $NO + O_3 \rightarrow NO_2 + O_2$ and $NO + ClO \rightarrow NO_2 + Cl$.

FIGURE E-1. Calculated responses of NO and NO₂ to a solar eclipse. The solid line indicates normal diurnal behavior; the dotted line shows the expected solar eclipse effect.

By the end of totality, over a factor of 10 decrease is calculated for NO at 20 and 30 km, with a factor of 6.5 decrease at 40 km. The maximum NO₂ concentration also occurs at the end of totality with values ranging from a factor of 1.4 higher than normal at 20 km to 6.4 at 40 km.

Except in the upper stratosphere (i.e., above 40 km), the NO₂ increase is not directly proportional to the NO decrease. This is due to the relatively slow, yet significant, formation rates for ClONO₂ and N₂O₅ from NO₂. The peak increase in the ClONO₂ concentration occurs approximately 15 minutes after totality due to its slow formation rate. ClONO₂ is increased by 20% at 20 km and 42% at 30 km. The N₂O₅ concentration increases by 11% at 20 km and 20% at 30 km. After the eclipse, the slow reconversion of stored ClONO₂ and N₂O₅ back to NO₂ lags behind the NO₂ to NO inversion causing the NO₂ to fall below the normal diurnal concentration. The NO to NO₂ conversion is not affected in the upper stratosphere where neither ClONO₂ nor N₂O₅ is important as a temporary sink for NO₂.

The expected variations for Cl and ClO are shown in Fig. E-2. Rapid conversion of Cl to ClO during the eclipse occurs primarily through $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$. However, as a result of the increased formation rate of ClONO₂ caused by increased NO₂, the net effect on the ClO concentration is a decrease. The

FIGURE E-2. Calculated response of Cl and ClO to a solar eclipse.

minimum in ClO occurs approximately 25 minutes after totality. This time lag is caused by the relatively slow formation rate of ClONO_2 when compared to the rate of change for NO_2 . As the solar flux increases after totality, the ClO concentration increases due to increased photolysis of ClONO_2 . Little change in ClO is expected at 40 km where ClONO_2 formulation is not important and Cl is only about 1% of ClO.

Both OH and HO_2 should decrease in concentration during an eclipse, as shown in Fig. E-3. OH concentrations were reduced relative to the normal diurnal

FIGURE E-3. Calculated response of OH and HO_2 to a solar eclipse.

concentrations by factors of 2.7, 17.0, and 5.9 at 20, 30, and 40 km, respectively, with the minimum occurring at the end of totality. Smaller decreases are calculated for HO_2 , with the minimum in HO_2 occurring approximately 15 minutes after totality. With the decreased importance of $\text{O}(^3\text{P})$ and NO during the eclipse, a balance between OH and HO_2 is maintained by the rapidly occurring reaction $\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$ and the slightly slower reaction $\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$. Odd hydrogen (OH and HO_2) loss occurs at a slower rate through conversion to H_2O ($\text{OH} + \text{HO}_2$), H_2O_2 ($\text{HO}_2 + \text{HO}_2$) and HNO_3 ($\text{OH} + \text{NO}_2 + \text{M}$). Because of the relative abundance of HNO_3 and H_2O_2 when compared to OH and HO_2 , insignificant changes in the concentrations of H_2O_2 and HNO_3 were calculated. At 40 km, the relative speed of reactions for $\text{HO}_2 + \text{O}_3$ and $\text{OH} + \text{O}_3$ is at least a factor of 3 less than at 20 and 30 km. Because of this, a slight, probably artificial and not measurable, increase in HO_2 is calculated at totality (Fig. E-3).

Although we have focused mainly on the local changes at individual altitudes, clearly total column changes are also observable. Since the variations for individual species at all altitudes all follow the same general individual trends, the total column for them also varies in the same manner. For example, the ClO column shows the same approximately 25-minute delay in reaching minimum as is shown in Fig. E-2 with a factor 1.8 decrease. The NO_2 column shows a factor 2 increase at totality and the same overshoot phenomenon after totality by as much as 10%. OH and HO_2 columns at minimum are factors of 3.4 and 2.5 less with the HO_2 column showing a slight phase lag from totality. The Cl and NO columns obviously provide the most notable changes (disappear completely) and should be most easily observed.

SUMMARY AND CONCLUSIONS

The results from this study suggest that significant and detectable variations are expected for some of the important stratospheric minor constituents during a solar eclipse. Such observations, particularly simultaneous observations of trace species, would demonstrate clearly the simultaneous functioning of the various important photochemical catalytic cycles in the stratosphere. In principle, similar

information can be obtained by observations during a normal diurnal cycle, especially during sunrise and sunset. However, observations during a solar eclipse offer several advantages over that of the diurnal cycle. First, the relatively short time duration for the event allows a more clear identification of some of the major reactions in the important catalytic cycles. The same short time duration (2-3 hours) also minimizes the influence of atmospheric transport process in altering the local trace species concentrations. Measuring the full diurnal cycle would involve a much longer observation period (at least 14 and as much as 24 hours) subjecting the local chemistry to the influence of significant and usually unquantifiable mixing processes. Thus it is difficult to assess the relative role of chemistry and dynamics in determining the observation data. Also, because of the longer time scale, more interference through conversion to such temporary sinks as ClONO_2 , N_2O_5 and HNO_3 should be expected. This increased interference makes it even more difficult to sort out the effects of the catalytic cycle reactions. Also, at sunrise and sunset there is considerable uncertainty on the proper treatment for the direct and scattered solar flux as a function of altitude. This then leads to uncertainty in the representation of photodissociation processes in the theoretical calculations. For the present calculation this will not be a limitation on the model, i.e., the eclipse takes place near local noontime.

We would like to emphasize the point that the present theoretical predictions should be viewed mostly in a qualitative sense. The relative changes in magnitudes at totality and the phase lag in maximum effect from the time of totality are the interesting parameters. Of course the precise predictions are totally dependent upon the local conditions such as temperature, total NO_x , ClO_x , HO_x , etc. direct and scattered radiation, time of the day, and local atmospheric motions (which must be measured). Depending on the measurement technique the individual data may be more dependent upon a particular set of local variables. For example, surface instruments would be highly sensitive to atmospheric transport of air masses while airborne instruments are much less so, and the rate of observed changes in NO_2 are sensitive to the yet to be measured rate of change of near ultraviolet solar fluxes while Cl and ClO are not.

We have pointed out the potential usefulness of solar eclipse events in testing our understanding of stratospheric chemistry. But the quality of the test depends upon the measurement program established. Given sufficient data on local

conditions, more precise calculations than our present preliminary results might be carried out to more fully test our understanding of stratospheric chemistry.

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APPENDIX F.

THE ATMOSPHERIC NUCLEAR TESTS OF THE 1950's AND 1960's:
A POSSIBLE TEST OF OZONE DEPLETION THEORIES*

INTRODUCTION

It was suggested by Foley and Ruderman (1973) that the atmospheric nuclear tests of the late 1950's and early 1960's should have caused a stratospheric ozone reduction of more than 10% if then current models of the effect on stratospheric ozone of NO_x from SST's were correct. However, their analysis failed to consider the difference in the effect to be expected from a pulse injection of NO_x in contrast to the effect of a continuous NO_x source active over a more restricted altitude range. In 1973, Chang and Duewer, using a one-dimensional time-dependent model, calculated the effect on ozone of the nuclear tests (using a production of NO_x /megaton yield about half that used by Foley and Ruderman, but spread over only the Northern Hemisphere rather than the world) and obtained a calculated Northern Hemispheric annual mean ozone reduction of roughly 4% for 1963. Using a different technique Johnston et al. (1973) had calculated a 1-6% decrease at peak ozone reduction where the range cited refers to their estimated uncertainty in NO_x production. Chang and Duewer concluded that the calculated reduction was not inconsistent with the observed variability of atmospheric ozone as analyzed by Johnston et al. (1973). The effects of the test series were also investigated by Goldsmith et al. (1973), COMESA (1975), and Bauer and Gilmore (1975). On the basis of calculations of the ozone depletion expected from operation of Concorde made with their then current models, Goldsmith et al. and the COMESA Report concluded that ozone reductions of several percent (Goldsmith et al., 1973) but less than 2% (COMESA, 1975) would have been expected, and that no reduction was apparent in the ozone record. The differences between these estimates reflected differences between their 1973 and 1975 models, largely in chemical reactions and rate coefficients. Bauer and Gilmore reviewed the calculations and analyses

*See Chang et al. (1979).

available in 1975 and concluded that the predicted ozone reductions fall within the variability of the ozone record.

In the years since 1975, significant changes have occurred in the formulation of one-dimensional models of the stratosphere and in the experimental values of chemical reaction rate constants used as model input. Also, substantially more analysis of the ozone record has been carried out. In this paper, we discuss the effect several of these advances have on the computed effect of the atmospheric nuclear test series on stratospheric ozone. Although the present discussion focuses only on the nuclear test series and the long-term ozone trend in the 1960's, there have been other studies of the near-term effect of individual nuclear NO_x clouds on ozone on the time scale of days to weeks (Christie, 1976; Johnston, 1977). Furthermore, analysis of the potential effects of large scale nuclear exchange in a doomsday scenario have been performed (Hampson, 1974; MacCracken and Chang, 1975; NRC, 1975; Whitten et al., 1975; Duewer et al., 1978).

DESCRIPTION OF THE NO_x PERTURBATION

Several workers have investigated the problem of NO_x production from a nuclear fireball (see Table F-1). The most recent and comprehensive of these are those of Gilmore (1975) and COMESA (1975). As can be seen in Table F-1, these two studies are in good agreement as to their estimates for the total NO_x produced by a nuclear explosion. However, the COMESA study included an estimate of loss of NO_x from the rising debris cloud (i.e., 20% loss). In this work we accept the COMESA estimate of the total NO_x injection per megaton, but note that this value should be considered uncertain by roughly $\pm 50\%$. A related question is that of the yields of the various nuclear devices. Table F-2 gives several published estimates of the total yield for the period of active testing.

We have followed the procedure of taking unclassified qualitative yield descriptions and assigning them quantitative values consistent with other available data. Our integrated yield estimate for the period 1961-1962 is consistent with the estimates given by COMESA (1975) and Foley and Ruderman (1973) but roughly 10% larger than those cited by Johnston et al. (1976) or Seitz et al. (1968).

TABLE F-1. Estimates of NO yield per MT

		10 ³² molecules/MT
Zeldovich and Razier	(1967)	0.5
Foley and Ruderman	(1972)	0.3-1.5
Johnston et al.	(1973)	0.17-1.0
Chang and Duewer	(1973)	0.5
Goldsmith et al.	(1973)	1.0
Gilmore	(1975)	0.4-1.5 (.9)
COMESA - (Goldsmith et al.)	(1975)	0.6-1.1 (.84)
COMESA - after allowance for disentrainment	(1975)	0.5-0.9 (.67)
This work uses		0.67

During the test period, a few nuclear devices were exploded in or above the stratosphere and generated clouds that stabilized in or above the mesosphere. These tests may have created more NO_x/megaton than low altitude tests because a low density fireball can be expected to depart from equilibrium composition at a higher temperature than a higher-density fireball. Thus, it might be argued (Hampson, 1977) that these devices could have produced a very high yield of NO at altitudes of 70-200 km. However, in that altitude range, NO_x has a lifetime on the order of a day (Gerard and Barth, 1977), and it is unlikely that any significant fraction of NO_x produced at high altitudes reached the stratosphere. Further, while energetic particles escaping from a high-altitude fireball might produce NO_x in the stratosphere, it is unlikely that this process had a significant effect on the yields of NO_x summed over all tests.

The model perturbations are small enough that model response to variation of the total NO_x injection is approximately linear for most chemistries. Thus, if a readjustment of the NO_x yield should be dictated by future work, our computed ozone perturbations would, to a fair approximation, scale linearly. Post-1977 one-dimensional models display near-linear response to NO_x perturbation over a more limited range than earlier models. For NO_x perturbations somewhat larger

TABLE F-2. Approximate total yield of high yield* atmospheric nuclear tests by year.

	COMESA (1975)	Foley & Ruderman (1973)	Johnston et al. (1976)	Seitz et al. (1968)	This** Work
Pre-1956	61.6	62	—	—	—
1956	26.0	26	—	—	20
1957	13.5	—	—	—	16
1958	61.9	85	—	—	58
1959	0	0	—	—	0
1960	0	0	—	—	0
1961	120.6	—	99.7	97	119
1962	213.5	340	204	206	216
1963	—	—	—	—	—
1964	—	—	—	—	—
1965	—	—	—	—	—
1966	1.4	—	—	—	—
1967	3.5	—	—	—	—
1968	7.6	—	—	—	—
1969	3.0	—	—	—	—
1970	6.1	—	—	—	—
Total 1961-62	334	340	304	303	335
Total 1956-62	435	451	—	—	429

*1 megaton TNT equivalent (4.2×10^{15} joules).

**These yield figures were estimated by taking the unclassified qualitative yield descriptions and assigning them quantitative values consistent with other available data in the open literature.

than those reported here, nonlinear feedback must be analyzed in detail. The onset of this nonlinear behavior depends on the altitude of injection, vertical diffusion coefficients, photochemical kinetics systems, rate coefficients and other model input parameters.

Foley and Ruderman (1972; 1973) gave a parameterization for the top and bottom of the stabilized cloud versus device yield such that

$$CT = 21.64Y^{(0.2)}$$

$$CB = 13.41Y^{(0.2)}$$

where CT - cloud top (km)

CB - cloud bottom (km)

Y - yield (megatons TNT equivalent) .

This parameterization was largely based on direct observations of United States tests (Peterson, 1970) and was only inferred to be valid for the Soviet tests.

Seitz et al. (1968) estimated cloud tops and bases from measurements of the radioactive debris a few days after the 1961-1962 tests. Few of the debris measurements extended above 24 km, and the cloud tops for most of the higher yield tests were not directly measured. When samples were taken near 30 km shortly after a high-yield test, the cloud top was estimated to be above 30 km. However, when no data above 24 km were available, a cloud top near 24 km was given (Seitz et al., 1968). This procedure is quite arbitrary and may not be consistent with other available results. For example, from an analysis of the ratio of ^{14}C to ^{90}Sr , Telegadas and List (1969) concluded that the very large Soviet test of October 1961 probably stabilized almost entirely above the region examined by Seitz et al. Also, mesospheric lithium, ^7Li , increased after this test implying a cloud top above the stratopause (Martell, 1970; Sullivan and Hunten, 1964). Nevertheless, the data of Seitz et al. provide the only published systematic estimates of the debris cloud stabilization heights of the Soviet tests in the 1960's and as such must be considered along with any other choices. We believe that these data systematically underestimate (at least) the cloud tops, and we view them as probably a lower limit to the true stabilization heights.

The height parameterization of Foley and Ruderman (1973) as used in earlier reports (Chang and Duewer, 1973; MacCracken and Chang, 1975) may over-estimate the height of stabilization since it is based almost exclusively on data from the tropics. However, it provides a reasonable fit to data for moderate-yield mid-latitude tests (Telegadas, 1976). Figure F-1 presents the stabilization estimates from the two different methodologies.

We assumed the injection to result in a uniform increase in concentration between cloud top and cloud bottom. When we used Seitz et al. (1968) injection

FIGURE F-1. Cloud top and cloud base vs. yield for the treatments used. The curves defining the shaded area give the cloud top and cloud base according to the parameterization of Foley and Ruderman (1972). The vertical bars extend from cloud base to cloud top for the data cited by Seitz et al. (1968) after adjustment to height above a variable tropopause as discussed in the text. The number of tests of a particular yield at high latitudes (indicated with a P) and at low latitudes (indicated with a T) is also given on the figure.

altitudes, we assumed that it was appropriate to adjust the injection to a constant height above the tropopause corrected to mid-latitude conditions (Johnston et al., 1976). Thus, we increased CT and CB by 4 km for polar tests and reduced them by 2 km for tropical tests. This was not done when the Foley and Ruderman parameterization was used because that parameterization was designed for mid-latitude applications and thus contains an implicit adjustment. We believe that these two treatments of the stabilization heights provide approximate upper and lower bounds for the stabilization altitudes of the test debris. As we will show (Fig. F-2 and Table F-3), the computed ozone reductions in the peak year (1963) are larger by about 1-2% of total O_3 when we use the Foley and Ruderman (1973) parameterization than when we use Seitz et al. (1968) estimates.

FIGURE F-2. Calculated change in O₃ vs. date showing the effect of the treatment of cloud stabilization height. - · - · - Seitz et al. (1968) stabilization height, 1977 chemistry; - - - Seitz et al. (1968) stabilization height, 1976 chemistry; ——— Foley and Ruderman (1973) stabilization height, 1977 chemistry; — — — Foley and Ruderman (1973) stabilization height, 1976 chemistry. All calculations used the Chang (1976) K_z and diurnal averaging.

In all calculations the injection was assumed to be mixed throughout the Northern Hemisphere, and no further dilution was considered. Mixing into the Southern Hemisphere might have reduced the NO_x perturbation by 15-25% in 1963-64 (Johnston et al., 1976). A simplified treatment of mixing within the Northern Hemisphere is necessary in one-dimensional models. With such approximations short-term effects (in weeks or months) of individual tests could not be analyzed. But on the time scale of years to a decade, individual initialization error in horizontal spreading would have decayed. Thus the uniform horizontal spreading approximation seems reasonable.

TABLE F-3. Effects Calculated for Various Model Inputs.

Chemistry	K ₂	Stabilization Parameterization	Other Variations	$\Delta O_3_{\max}$	$\langle \Delta O_3 \rangle_{1963}$	$\langle \Delta O_3 \rangle_{1964}$
1973	Chang (1974)	Foley & Ruderman	0.5×10^{31} NO (megaton, Bates & Hayes (1967) N ₂ O, NO multiple scattering)	-5.0	-4.0	-3.3
1973	Chang (1974)	Foley & Ruderman	0.5×10^{31} NO/megaton	-4.8	-3.8	-3.1
1973	Hunten (1975)	Foley & Ruderman	0.5×10^{31} NO/megaton	-5.3	-4.5	-3.9
1974	Chang (1974)	Foley & Ruderman	—	-8.2	-7.1	-6.2
1976	Chang (1976)	Foley & Ruderman	Diurnal averaging	-6.8	-4.5	-2.7
1976	Chang (1976)	Seitz et al.	Diurnal averaging	-5.1	-4.3	-2.6
1976	Chang (1976)	Foley & Ruderman	No diurnal averaging	-6.1	-4.2	-2.6
1976	Hunten (1975)	Foley & Ruderman	No diurnal averaging	-5.0	-3.9	-2.8
1976	Chang (1976)	Seitz et al.	No diurnal averaging	-4.3	-3.8	-2.5
1977	Chang (1976)	Foley & Ruderman	Diurnal averaging	-4.2	-3.0	-1.4
1977	Chang (1976)	Seitz et al.	Diurnal averaging	-1.9	-1.5	-0.8
1977	Hunten (1975)	Seitz et al.	Diurnal averaging	-1.8	-1.4	-0.7

THE MODEL

The general structure of the model used has been described elsewhere (Chang et al., 1974; Luther et al., 1978; NRC, 1976, Appendix D). We will describe only those features that have evolved significantly since 1973.

1. Model Chemistry

The model chemistry used in our 1973 calculation contained 33 reactions of HO_x , NO_x and O_x , with rate constants based primarily on Garvin and Gevantman (1972). These are given in Table F-4 as 1973 chemistry. When the CIAP calculations were carried out (1974) we incorporated the 41 reactions listed as 1974 chemistry in Table F-4. Most rate constants were taken from Garvin and Hampson (1974).

Our 1976 chemistry (Table F-4) incorporated ClX reactions and was nearly the same as was used in the NAS chlorofluoromethane report (NRC, 1976). Most of the rate constants were derived from Hampson and Garvin (1975), but several had been revised to reflect 1975 or 1976 measurements (NRC, 1976; DeMore et al., 1977). Our 1977 chemistry (Table F-4) contains the same reactions as our 1976 chemistry, but several rate constants were adjusted to reflect recent evaluations (DeMore et al., 1977; Watson, 1977) and measurements (Howard and Evenson, 1977; Burrows et al., 1977; Chang and Kaufman, 1978). There are some known processes of potential importance (e.g., HOCl and HOONO_2 formation) that we do not include because the important subsequent processes (e.g., photolysis rates and products) are insufficiently well characterized.

As we will show, the predicted effect of the nuclear test series is quite sensitive to model chemistry. For this study the model contained 1.1-1.3 ppb of ClX (the precise amount is a function of the transport parameterization) from CH_3Cl and CCl_4 , but chlorofluoromethanes were neglected.

TABLE F-4. Chemistries Used in This Study.

<u>Reaction</u>	<u>Rate 1977</u>	<u>Rate 1976</u>	<u>Rate 1974</u>	<u>Rate 1973</u>
$O_2 + h\nu \rightarrow O + O$	QJ(1)*	QJ(1)	Same	QJ(1) x 2
$O_3 + h\nu \rightarrow O + O_2$	QJ(2)*	QJ(2)	Same	QJ(2) x 2
$O_3 + h\nu \rightarrow O(^1D) + O_2$	QJ(3)*	QJ(3)	Same	QJ(3) x 2
$O + O_2 + M \rightarrow O_3 + M$	$1.10 \times 10^{-34} e^{510/T}$	$1.07 \times 10^{-34} e^{510/T}$	Same	Same
$O + O_3 \rightarrow 2O_2$	$1.9 \times 10^{-11} e^{-2300/T}$	Same	Same	Same
$NO_2 + h\nu \rightarrow NO + O$	QJ(4)*	QJ(4)	Same	QJ(4) x 2
$O_3 + NO \rightarrow NO_2 + O_2$	$2.1 \times 10^{-12} e^{-1450/T}$	$9.0 \times 10^{-13} e^{-1200/T}$	Same	Same
$O + NO_2 \rightarrow NO + O_2$	9.1×10^{-12}	Same	Same	Same
$N_2O + h\nu \rightarrow N_2 + O(^1D)$	QJ(5)*	QJ(5)	Cross sections were larger	QJ(5) x 2 (larger cross sections)
$N_2O + O(^1D) \rightarrow N_2 + O_2$	5.5×10^{-11}	7×10^{-11}	1.1×10^{-10}	6.6×10^{-11}
$N_2O + O(^1D) \rightarrow 2NO$	5.5×10^{-11}	7×10^{-11}	1.1×10^{-10}	6.6×10^{-11}
$NO + h\nu \rightarrow N + O$	QJ(6)	QJ(6)	Same	QJ(6) x 2
$N + O_2 \rightarrow NO + O$	$5.5 \times 10^{-12} e^{-3220/T}$	$1.1 \times 10^{-14} T e^{-3150/T}$	Same	$1.02 \times 10^{-14} T e^{-3130/T}$
$N + NO \rightarrow N_2 + O$	$8.2 \times 10^{-11} e^{-410/T}$	2.7×10^{-11}	Same	$5.1 \times 10^{-11} e^{-170/T}$
$O(^1D) + H_2O \rightarrow 2OH$	2.3×10^{-10}	2.1×10^{-10}	3.5×10^{-10}	2.8×10^{-10}
$O(^1D) + CH_4 \rightarrow OH + CH_3$	1.3×10^{-10}	Same	4.0×10^{-10}	2.4×10^{-10}

TABLE F-4. Continued

Reaction	Rate 1977	Rate 1976	Rate 1974	Rate 1973
$\text{HNO}_3 + h\nu \rightarrow \text{OH} + \text{NO}_2$	QJ(7)*	QJ(7)	Same	QJ(7) x 2
$\text{O}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{O}_2$	$1.5 \times 10^{-12} e^{-1000/T}$	$1.6 \times 10^{-12} e^{-1000/T}$	Same	$1.3 \times 10^{-12} e^{-956/T}$
$\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$	4.2×10^{-11}	Same	Same	Same
$\text{O}_3 + \text{HO}_2 \rightarrow \text{OH} + 2\text{O}_2$	$1.0 \times 10^{-13} e^{-1250/T}$	Same	Same	$1.0 \times 10^{-12} e^{-1875/T}$
$\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$	3×10^{-11}	Same	$8 \times 10^{-11} e^{-500/T}$	1.0×10^{-11}
$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	$2.08 \times 10^{-32} e^{290/T}$	Same	Same	$1.1 \times 10^{-32} e^{407/T}$
$\text{O}_3 + \text{H} \rightarrow \text{OH} + \text{O}_2$	$1.23 \times 10^{-10} e^{-562/T}$	Same	2.6×10^{-11}	2.6×10^{-11}
$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$1.7 \times 10^{-11} e^{-500/T}$	Same	$3 \times 10^{-11} e^{-500/T}$	$3 \times 10^{-11} e^{-500/T}$
$\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	2×10^{-11}	Same	2×10^{-10}	2×10^{-10}
$\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	Parameterization given in NASA (1977)	$2.76 \times 10^{-13} e^{880/T}$ $1.166 \times 10^{18} e^{222/T + M}$	4×10^{-11} $1.12 \times 10^{18} + M$	10^{-11} $1.5 \times 10^{20} e^{-750/T + M}$
$\text{OH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3$	8.9×10^{-14}	Same	1.3×10^{-13}	1.3×10^{-13}
$\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{OH}$	QJ(8)*	QJ(8)	Same	Same
$\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$	$1.0 \times 10^{-11} e^{-750/T}$	$1.7 \times 10^{-11} e^{-910/T}$	Same	Same
$\text{N}_2 + \text{Q}(\text{I}D) + \text{M} \rightarrow \text{N}_2\text{O} + \text{M}$	3.5×10^{-37}	2.8×10^{-36}	Same	Same
$\text{N} + \text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{O}$	$2 \times 10^{-11} e^{-800/T}$	1.4×10^{-12}	9×10^{-12}	9×10^{-12}
$\text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M}$	$1.6 \times 10^{-32} e^{584/T}$	$3.96 \times 10^{-33} e^{940/T}$	Same	N. I.
$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$	$4.28 \times 10^{-11} e^{-500/T}$	2.0×10^{-13}	Same	N. I.

TABLE F-4. Continued

<u>Reaction</u>	<u>Rate 1977</u>	<u>Rate 1976</u>	<u>Rate 1974</u>	<u>Rate 1973</u>
$H_2 + O(^1D) \rightarrow OH + H$	9.9×10^{-11}	2.9×10^{-10}	Same	N. I.
$OH + OH \rightarrow H_2O + O$	$1.0 \times 10^{-11} e^{-550/T}$	Same	Same	N. I.*
$N + O_3 \rightarrow NO + O_2$	$5 \times 10^{-12} e^{-650/T}$	5.7×10^{-13}	Same	N. I.*
$NO_2 + O_3 \rightarrow NO_3 + O_2$	$1.2 \times 10^{-13} e^{-2450/T}$	Same	$1.23 \times 10^{-13} e^{-2470/T}$	N. I.
$HO_2 + h\nu \rightarrow OH + O$	QJ(9)*	QJ(9)	N. I.	N. I.
$OH + CH_4 \rightarrow H_2O + CH_3$	$2.36 \times 10^{-12} e^{-1710/T}$	Same	N. I.	N. I.*
$OH + OH + M \rightarrow H_2O_2 + M$	$1.2 \times 10^{-32} e^{900/T}$	$2.5 \times 10^{-33} e^{2500/T}$	N. I.	N. I.
$H_2O_2 + O \rightarrow OH + HO_2$	$2.75 \times 10^{-12} e^{-2125/T}$	Same	N. I.	N. I.
$O + CH_4 \rightarrow OH + CH_3$	$3.5 \times 10^{-11} e^{-4550/T}$	Same	N. I.	N. I.
$CO + OH \rightarrow H + CO_2$	1.4×10^{-13}	Same	N. I.	N. I.*
$O(^1D) + M \rightarrow O + M$	$2.2 \times 10^{-11} e^{99/T}$	$2.2 \times 10^{-11} e^{92/T}$	5.85×10^{-11}	3.2×10^{-11} *
$NO_3 + h\nu \rightarrow NO_2 + O$	10^{-1}	10^{-1}	0.	0.
$NO_3 + h\nu \rightarrow NO + O_2$	4×10^{-2}	5×10^{-2}	1.	1.
$N + NO_2 \rightarrow 2NO$	N. I.	N. I.	6×10^{-12}	6×10^{-12}
$NO + NO_3 \rightarrow 2NO_2$	8.7×10^{-12}	N. I.	N. I.	N. I.
$NO_2 + O + M \rightarrow NO_3 + M$	1.0×10^{-31}	N. I.	N. I.	N. I.
$NO_2 + NO_3 \rightarrow NO + O_2 + NO_2$	2.0×10^{-13}	N. I.	N. I.	N. I.

TABLE F-4. Continued

<u>Reaction</u>	<u>Rate 1977</u>	<u>Rate 1976</u>	<u>Rate 1974</u>	<u>Rate 1973</u>
$\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$	$\frac{2.92 \times 10^{-12}}{7 \times 10^{21} e^{-2670/T} + \text{M}}$	N. I.	N. I.	N. I.
$\text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M}$	$\frac{6.0 \times 10^{14} e^{-10700/T}}{7.0 \times 10^{21} e^{-2670/T} + \text{M}}$	N. I.	N. I.	N. I.
$\text{N}_2\text{O}_5 + \text{O} \rightarrow 2\text{NO}_2 + \text{O}_2$	1.0×10^{-14}	N. I.	N. I.	N. I.
$\text{N}_2\text{O}_5 + \text{H}_2 \rightarrow 2\text{HNO}_3$	1.0×10^{-20}	N. I.	N. I.	N. I.
$\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \text{O}$	$\text{QJ}(10)^*$	N. I.	N. I.	N. I.
$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	$2.7 \times 10^{-11} e^{-257/T}$	$2.97 \times 10^{-11} e^{-243/T}$	(No ClX reactions were included in 1973 or 1974 chemistries)	
$\text{Cl} + \text{OCIO} \rightarrow 2\text{ClO}$	5.9×10^{-11}	Same		
$\text{Cl} + \text{O}_2 + \text{M} \rightarrow \text{ClO}_2 + \text{M}$	N. I.	$1.7 \times 10^{-33} (300/T)$		
$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$	$7.3 \times 10^{-12} e^{-1260/T}$	$5.4 \times 10^{-12} e^{-1133/T}$		
$\text{Cl} + \text{ClO}_2 \rightarrow \text{Cl}_2 + \text{O}_2$	N. I.	5.0×10^{-11}		
$\text{Cl} + \text{ClO}_2 \rightarrow 2\text{ClO}$	N. I.	1.4×10^{-12}		
$\text{Cl} + \text{NO} + \text{M} \rightarrow \text{ClNO} + \text{M}$	N. I.	$1.7 \times 10^{-32} e^{553/T}$		
$\text{Cl} + \text{ClNO} \rightarrow \text{Cl}_2 + \text{NO}$	N. I.	3.0×10^{-11}		
$\text{Cl} + \text{NO}_2 + \text{M} \rightarrow \text{ClNO}_2 + \text{M}$	$6.9 \times 10^{-34} e^{2115/T}$	Same		
$\text{Cl} + \text{ClNO}_2 \rightarrow \text{Cl}_2 + \text{NO}_2$	3×10^{-12}	Same		
$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$	$7.7 \times 10^{-11} e^{-130/T}$	5.3×10^{-11}		

TABLE F-4. Continued

<u>Reaction</u>	<u>Rate 1977</u>	<u>Rate 1976</u>	<u>Rate 1974</u>	<u>Rate 1973</u>
$\text{NO} + \text{ClO} \rightarrow \text{NO}_2 + \text{Cl}$	2.2×10^{-11}	$2.6 \times 10^{-11} e^{-50/T}$	(No ClX reactions were included in 1973 or 1974 chemistries)	
$\text{ClO} + \text{O}_3 \rightarrow \text{ClO}_2 + \text{O}_2$	$1.0 \times 10^{-12} e^{-4000/T}$	$1.0 \times 10^{-12} e^{-2763/T}$		
$\text{ClO} + \text{O}_3 \rightarrow \text{OCIO} + \text{O}_2$	$1.0 \times 10^{-12} e^{-4000/T}$	$1.0 \times 10^{-12} e^{-2763/T}$		
$\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}$	$5.1 \times 10^{-33} e^{1030/T}$	Same		
$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{OCIO}$	$2.1 \times 10^{-12} e^{-2200/T}$	$2.0 \times 10^{-12} e^{-2300/T}$		
$\text{ClO} + \text{ClO} + 2\text{Cl} + \text{O}_2$	$1.5 \times 10^{-12} e^{-1230/T}$	$2.0 \times 10^{-13} e^{-1260/T}$		
$\text{HCl} + \text{O}(^1\text{D}) \rightarrow \text{Cl} + \text{OH}$	1.4×10^{-10}	2×10^{-10}		
$\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$	$3.0 \times 10^{-12} e^{-425/T}$	$2 \times 10^{-12} e^{-310/T}$		
$\text{O} + \text{HCl} \rightarrow \text{OH} + \text{Cl}$	$1.14 \times 10^{-11} e^{-3370/T}$	$1.75 \times 10^{-12} e^{-2273/T}$		
$\text{O} + \text{OCIO} \rightarrow \text{ClO} + \text{O}_2$	$2 \times 10^{-11} e^{-1100/T}$	5.0×10^{-13}		
$\text{NO} + \text{OCIO} \rightarrow \text{NO}_2 + \text{ClO}$	3.4×10^{-13}	Same		
$\text{N} + \text{OCIO} \rightarrow \text{NO} + \text{ClO}$	6.0×10^{-13}	Same		
$\text{H} + \text{OCIO} \rightarrow \text{OH} + \text{ClO}$	5.7×10^{-11}	Same		
$\text{Cl} + \text{OH} \rightarrow \text{HCl} + \text{O}$	$1.0 \times 10^{-11} e^{-2970/T}$	$2.0 \times 10^{-12} e^{-1878/T}$		
$\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2$	3×10^{-11}	Same		
$\text{Cl} + \text{HNO}_3 \rightarrow \text{HCl} + \text{NO}_3$	$1.0 \times 10^{-11} e^{-2170/T}$	$4.0 \times 10^{-12} e^{-1500/T}$		
$\text{ClONO}_2 + \text{O} \rightarrow \text{ClO} + \text{NO}_3$	$4.5 \times 10^{-12} e^{-840/T}$	Same		

TABLE F-4. Continued

<u>Reaction</u>	<u>Rate 1977</u>	<u>Rate 1976</u>	<u>Rate 1974</u>	<u>Rate 1973</u>
$\text{ClO}_2 + \text{HO}_2 \rightarrow \text{HCl} + 2\text{O}_2$	N. I.	3.0×10^{-12}	(No ClX reactions were included in 1973 or 1974 chemistries)	
$\text{CH}_3\text{Cl} + \text{OH} \rightarrow \text{Cl} + \text{H}_2\text{O} + \text{HO}_2$	$2.2 \times 10^{-12} e^{-1142/T}$	Same		
$\text{CH}_3\text{Cl} + 2\text{HO}_2 \rightarrow \text{CO} + \text{Cl}$	QCJ(1)*	QCJ(1)		
$\text{HCl} + h\nu \rightarrow \text{H} + \text{Cl}$	QCJ(2)*	QCJ(2)		
$\text{ClONO}_2 \rightarrow \text{ClO} + \text{NO}_2$	QCJ(3)*	QCJ(3)		
$\text{ClO} + h\nu \rightarrow \text{Cl} + \text{O}$	QCJ(4)*	QCJ(4)		
$\text{ClO} + h\nu \rightarrow \text{Cl} + \text{O}(^1\text{D})$	QCJ(5)*	QCJ(5)		
$\text{ClNO}_2 + h\nu \rightarrow \text{Cl} + \text{NO}_2$	QCJ(7)*	QCJ(7)		
$\text{OCIO} + h\nu \rightarrow \text{ClO} + \text{O}(^1\text{D})$	QCJ(8)*	QCJ(8)		
$\text{OCIO} + h\nu \rightarrow \text{ClO} + \text{O}$	QCJ(9)*	QCJ(9)		
$\text{CF}_2\text{Cl}_2 + h\nu \rightarrow 2\text{Cl}$	QCJ(10)*	QCJ(10)		
$\text{CFCl}_3 + h\nu \rightarrow 2.5 \text{ Cl}$	QCJ(11)*	QCJ(11)		
$\text{CCl}_4 + h\nu \rightarrow 2\text{Cl}$	QCJ(12)*	QCJ(12)		
$\text{CFCl}_3 + \text{O}(^1\text{D}) \rightarrow 2\text{Cl}$	2.3×10^{-10}	3.0×10^{-10}		
$\text{CF}_2\text{Cl}_2 + \text{O}(^1\text{D}) \rightarrow 2\text{Cl}$	2.0×10^{-10}	2.5×10^{-10}		
$\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$	$4.7 \times 10^{-11} e^{-2340/T}$	$5.7 \times 10^{-11} e^{-2400/T}$		
$\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{H} + \text{HO}_2$	$1.6 \times 10^{-12} e^{-384/T}$	$1.0 \times 10^{-11} e^{-810/T}$		

N. I. - Not included in model

*Multiple scattering effects included.

2. Rainout and Boundary Conditions

The 1973 model (Chang and Duewer, 1973) did not include rainout processes. All subsequent models included rainout losses below 8 km using rainout coefficients of $2.31 \times 10^{-6} \text{ sec}^{-1}$ for HNO_3 , HCl and ClO (for models including chlorine chemistry) and 1.16×10^{-6} for NO_2 . The major effect of rainout is to uncouple surface boundary conditions for NO_x and ClO_x from stratospheric and upper tropospheric concentrations. Calculated stratospheric perturbations are not strongly sensitive to the precise rainout rates chosen.

The model uses fixed concentration boundary conditions at the surface (Chang et al., 1974). For versions incorporating rainout, the model stratosphere has significant sensitivity to the boundary conditions for only N_2O (320 ppb), CH_4 (1.3 ppm), CH_3Cl (750 ppt), and CCl_4 (92 ppt). The 1973 model was also influenced by the surface boundary conditions for NO , NO_2 and HNO_3 , which produced a nearly uniform 3.7 ppb NO_x mixing ratio in the troposphere. In current models treating rainout processes, the NO_x mixing ratio in the upper troposphere (which is about 0.1 ppb at 10 km) is dependent on the vertical transport coefficient, K_z . The upper boundary conditions are all flux boundary conditions, and all present calculations are very insensitive to them.

3. Treatment of Photolysis

In our 1973 calculation, we neglected multiple scattering effects, diurnal variation of species concentrations and used then-current values for the N_2O photodissociation cross sections (Bates and Hays, 1967). In all of the current calculations, we used Johnston and Selwyn (1975) photodissociation cross sections for N_2O . The 1974 and 1976 models approximated diurnal variations in solar flux by using 1/2 of noontime photodissociation rates. The chlorine nitrate formation rate was adjusted to be consistent with a fully diurnal calculation for the 1976 model. The 1977 model uses reaction rates at each level averaged over a diurnal cycle (Luther, 1977; Chang et al., 1978). Limited calculations were made using the 1976 chemistry and diurnal averaging. The 1976, 1977, and 1978 models included multiple scattering effects (Luther et al., 1978).

The response of the model is little affected by the change in N_2O absorption cross sections or multiple scattering (together they resulted in a 0.2% change in total ozone reduction for a calculated maximum depletion of roughly 5% using the 1973 chemistry). The incorporation of diurnal averaging of reaction rates increased the ozone reduction for 1976 chemistry by ~0.5 to 1% of total ozone when the Seitz injection scheme was used (see Table F-3).

4. Parameterization of Vertical Transport

In our 1973 paper, the Chang (1974) transport coefficient K_z was used. In this paper we considered the effects of different K_z choices by performing calculations using the Chang (1974), Chang (1976), and Hunten (1975) K_z 's. Only the recovery time had a strong sensitivity to K_z (see Fig. F-3 and Table F-3).

INTERPRETATION OF THE OZONE RECORD

Johnston et al. (1973) analyzed the global ozone record for 1960-1970 and found a statistically insignificant decrease of 2.2% from 1960-1962 followed by a statistically significant increase of 3.7% in 1963-1970. They viewed this increase as consistent with recovery from an ozone reduction of "a few percent" induced by the nuclear tests. The same data have been analyzed by several other authors (Komhyr et al., 1971; Angell and Korshover, 1973, 1976, 1978; Goldsmith et al., 1973; Christie, 1973; COMESA, 1975; London and Kelley, 1974). Although most of these analyses, and some analyses restricted to individual stations (e.g., Birrer, 1974; Pittcock, 1974a and b, 1976, 1977) find similar trends in ozone over the decade of the 1960's, the decrease in ozone appears to have occurred before the tests (Angell and Korshover, 1976; Christie, 1973; London and Kelley, 1974; COMESA, 1975), while the subsequent increase appears to have reached ozone concentrations larger than the long-term mean. Birrer (1974) in an analysis of the Arosa data from 1926-1971 found several periods with trends comparable to those observed during the 1960's. Birrer concluded that human influence on the stratosphere could only be inferred from the analysis of all stations in the network with continuous records of at least

FIGURE F-3. Calculated change in O₃ vs. date showing the effect of the choice of chemistry. — 1977 chemistry, Chang (1976) K_Z; - - - 1976 chemistry, Chang (1976) K_Z; - · - · - 1974 chemistry, Chang (1974) K_Z. All calculations used the Foley and Ruderman stabilization parameterization.

ten years and that a change of 5% would have to persist 10 years to be significant in the Arcsa data. This viewpoint seems consistent with the analyses of Pittock, and London and Kelley, but in some contrast to the analyses of Angell and Korshover (1973, 1976, 1978), Goldsmith et al. (1973), COMESA (1975), Christie (1973), Hill et al. (1977), Johnston et al. (1973), and Komhyr et al. (1971). This is not to suggest that these studies in any group are all in total agreement. It is clear that there is considerable trend structure in the past ozone data, and existing divergent interpretations of such trend structures are yet to be resolved (e.g., Pittock, 1974a and b; Angell and Korshover, 1974, 1976, 1978; Komhyr et al., 1971; Birrer et al., 1974; Johnston et al., 1973). For the detection of possible effects on ozone from past nuclear tests, the most restrictive interpretation would appear to be that of Angell and Korshover (1976). They concluded any such effect must have been less

than 1-2%. On the other hand Johnston et al. (1973) have estimated that a perturbation of about 4-5% would be consistent with their analysis.

The 1-2% limit cited by Angell and Korshover (1976) seems to refer to the maximum trend actually found in the data. If the 2σ error bars on the data as estimated by Angell and Korshover (1978) are considered, a trend of up to about 4% would not be inconsistent. Moreover, the ozone record contains unexplained long-term fluctuations with an amplitude of roughly 5%. Some of these long-term fluctuations may be related to solar variability (Heath and Thekaekara, 1977; Callis and Nealy, 1978; Penner and Chang, 1978) volcanic activity (either as an effect on ozone or via a measurement artifact (Angell and Korshover, 1973, 1976, 1978; Cadle, 1975; Kulkarni, 1974), solar proton events (Crutzen et al., 1975), and chlorofluoromethanes (Rowland and Molina, 1974). Indeed, Johnston (1974) has suggested that the nuclear test series may account for a "missing" ozone maximum in 1963. The case for a link between ozone and solar cycle variability is somewhat ambiguous (Penner and Chang, 1978). It would appear that the data may offer some support (possibly statistically insignificant) for a 1-2% ozone reduction in 1963-1964 (with a larger reduction of unexplained origin in early 1961). Given the imprecision of the data elements as analyzed by Angell and Korshover (1978), the data would not rule out an effect of as much as 4%, and the presence of incompletely explained fluctuations in the ozone record could be used to argue for broader error bars. Although such arguments have some ad hoc character, it would appear that ozone depletions of 4-5% could be reconciled with the data, although much larger depletions (or increases) would be more difficult to reconcile with the O_3 record.

RESULTS AND DISCUSSION

1. Effect of K_z 's

Calculations were carried out using the Foley and Ruderman stabilization parameterization for 1973, 1974, 1976 and 1977 chemistries. The Chang (1976) K_z was used with the 1974, 1976 and 1977 chemistries, the Chang (1974) K_z was used with the 1973 and 1974 chemistries and the Hunten K_z (1975) was used with the 1973, 1976, and 1977 chemistries. The Seitz et al. (1968) stabilization estimates

were considered using 1976 and 1977 chemistries with the Chang (1976) K_z and for the 1977 chemistry using the Hunten K_z .

In the calculation of the nuclear test series effects, the total NO_x injection is determined by the device yield and is independent of K_z . Most of the injection occurred over a fairly short time. Therefore, unlike SST calculations, the maximum change in NO_x is nearly independent of K_z . As Figure F-3 and Table F-3 show, the ozone depletions in 1963-1964 were only weakly dependent on K_z . For pre-1977 model chemistries, there is a substantial difference in recovery time based on the effective removal rate of excess stratospheric NO_x . For the 1977 model chemistry, the apparent recovery time is initially determined by the rate of vertical redistribution of the injection, although at later times recovery is controlled by the rate of removal of excess NO_x from the stratosphere. The Hunten K_z differs from the Chang K_z in that there is a sharp break at 14 km rather than a relatively slow decline in K_z values between 10 and 22 km. As a result excess NO_x between 13 and 25 km remains in excess for a longer time when the Hunten K_z is used than when the Chang K_z is used. Consequently, the ozone increases that are calculated in this altitude range persist longer, and net reductions (difference between high altitude decrease and low altitude increase, see below) disappear more rapidly. In no case would the choice of K_z alone cause the calculated perturbation to become in conflict with observation or vice versa.

2. Effect of Stabilization Estimates

As Fig. F-2 and Table F-3 show, the procedure used to estimate the stabilization altitude does have a significant effect on the calculation. However, for the model chemistries studied, the differences in the effects computed using these two stabilization estimates were less dramatic than the differences between model computations using different chemistries (Fig. F-4).

The estimated stabilization heights for the polar tests remain a significant source of uncertainty in the calculations. For reasons discussed above, we find the published information ambiguous and somewhat unsatisfactory. The two methods of estimation used provide a probable upper and lower bound to the true stabilization heights, but the Foley and Ruderman parameterization may be the more nearly accurate of the two. Chang (1975) and Mahlman (1977) have discussed the

FIGURE F-4. Calculated O₃ change vs. date showing the effect of choice of K_z. - - - Hunten (1975) K_z; — Chang (1976) K_z. Upper curves use the 1977 chemistry and diurnal averaging. Lower curves use the 1976 chemistry without diurnal averaging.

information available from tracer calculations based on ¹⁴C and ⁹⁰Sr. At present, we will note that these results further strengthen the need to accept the uncertainty in cloud stabilization heights as inherent uncertainties in such analysis.

3. Effect of Model Chemistries

The model representation of atmospheric chemistry has evolved substantially since early 1973. Between 1973 and 1974 several reactions involving HO_x species were added to the model, the effect of which should have been reduced model sensitivity to NO_x perturbations. However, in addition, the reaction of N atoms with O₃ was included, substantially increasing model sensitivity to high altitude NO_x injections (because of its effect on the lifetime of NO_x near 50 km). Also, the treatment of solar fluxes was modified (in 1973 we used photolysis rates characteristic of a 45° zenith angle; in 1974 we halved the photolysis rates),

rainout processes for NO and NO₂ were neglected in 1973 but included in 1974, and the estimated NO_x injection per megaton yield was increased from 5×10^{31} to 6.7×10^{31} molecules/megaton. The net effect of these changes was that the calculated peak ozone reduction (January of 1963) increased from 4.9% to 8.2% for otherwise equivalent calculations (the 4.9% reduction for 1973 chemistry would have been 6.6% if the NO_x injections had been the same as for later calculations).

Between the calculations used in support of the CIAP Report of Findings (Grobecker et al., 1974) made with our 1974 chemistry and the NRC (1976) chlorofluoromethane report, the model was modified to include a representation of stratospheric CLX chemistry, several fairly minor reactions of HO_x were added, the rate of

was revised (from 2×10^{-10} to $2 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$), and numerous comparatively minor changes in rate constants were entered (see Table F-4). As a result of these changes, the computed effects declined by roughly 30% of the computed change, but remained larger than 5% of the total ozone.

Our 1977 chemistry reflects the measurement of Howard and Evenson (1977), i.e., the rate of

was increased by roughly a factor of 40. Also, there were a few comparatively minor changes in other rate coefficients (see Table F-4). The dramatic results of these changes were almost completely due to reaction (2). Reaction (2) strongly couples NO_x and HO_x reaction systems. As a result of the large change in the rate constant for reaction (2) used in the model, the interference by NO_x with HO_x catalyzed ozone destruction, important between 10-25 km, became much stronger.

Recently, Howard (1978) has reported a negative activation energy for reaction (2) and has also reported a first direct measurement for the reaction

When this is considered along with the measurement of Cox (1978) for the rate constant for the reaction

the above-mentioned coupling becomes stronger and further enhances the role of HO_x in the lower stratosphere. A preliminary estimate indicates that the calculated best estimate of O_3 change in 1963 would be more positive and may even be a small increase in ozone. This new development is very complex, and a full analysis of it may demand a better understanding of stratospheric and tropospheric exchange processes that have been heavily parameterized in all current models as well as further refinement of the chemical reaction rate data.

4. Calculated Ozone Trend

The sharp decrease immediately following the large tests is due to the initialization procedure used. The source term consisted of pulse injections primarily at high latitudes, most of them in a period of ~4 months in late 1962. Thus, at least for the several months before horizontal mixing in the Northern Hemisphere became extensive, the one-dimensional approximation is expected to be poor and to overestimate the ozone depletions (Bauer and Gilmore, 1975). When the Foley and Ruderman (1973) stabilization height estimates were used with 1977 chemistry, we computed ozone decreases for all years during the period of active atmospheric testing, and the reductions calculated in 1963 (3% annual average ozone reduction in the Northern Hemisphere) are slightly larger than the limit to the perturbation cited by Angell and Korshover (1976) but consistent with Johnston et al. (1973) or Angell and Korshover (1978). The effect we now predict is smaller than the error bars in the ozone data as estimated by Angell and Korshover (1978) and should not be detectable in any case.

The model calculation can provide estimates of the local ozone changes at each altitude. Figure F-5 presents the ozone changes computed at various altitudes when we use 1977 chemistry, the Foley and Ruderman injection parameterization and the Chang (1976) K_z . Because these detailed trends are very sensitive to

variations in the input parameters, all such details should only be viewed qualitatively.

Figure F-5 does show several features of qualitative importance, however. Although recent chemistries predict net perturbations in column ozone that are small relative to the changes predicted using earlier chemistries, these small column changes result from the partial cancellation of larger local changes in ozone. That is, there are local increases in ozone below ~ 24 km, and local decreases in ozone

FIGURE F-5. Calculated change in local ozone concentration vs. date for several altitudes. — — — 10 km; — — — 20 km; - - - - 30 km; - - - - 40 km. The Chang (1976) K_2 , Foley and Ruderman stabilization parameterization and our 1977 chemistry were used in this calculation.

above 25 km, and the magnitudes of these local changes are comparable (but of opposite sign). The ozone decreases at higher altitudes result largely from the well known NO_x catalyzed ozone destruction via the reactions

and

The ozone increases at lower altitudes result because

1. in the lower stratosphere there is a comparatively low oxygen atom concentration which makes the rate of reaction (6) very slow relative to

so that the efficiency of NO_x catalyzed ozone destruction is low.

2. Reactions such as

and

that result in an HO_x catalyzed ozone destruction have a reduced efficiency if HO_2 reacts with NO by reaction (2) (and this is followed by reaction (7)) rather than reacting with ozone via reaction (3).

3. The reactions

and

are a major sink for HO_x radicals in the lower stratosphere.

4. The reactions

and

are analogs to reactions (2) and (10) involving chlorine species. The net effect of the slow direct catalysis of ozone destruction by NO_x via reactions 5 and 6 (and some other processes) and the interference with ozone destruction catalyzed by HO_x and ClX species is that ozone increases are calculated in portions of the lower stratosphere.

However, the magnitude and vertical extent of this increase are quite strongly dependent on the ambient concentrations of HO_x species and precursors, the details of exchange between the troposphere and the stratosphere, and the rate constants for several difficult to study chemical reactions. Unfortunately, there are no published measurements of HO or HO_2 in the 12-27 km region, and most reactive species that have been measured in this region seem highly variable. Thus, model results continue to be quite sensitive to poorly known input parameters, and the possibility that future models will have significantly different sensitivity to NO_x than our current model is quite real.

It should be noted that the problems related to high latitude injections (i.e., much of the injected material may be removed from the stratosphere before it affects middle or low latitudes) and the initial dispersion of pollutant are also present in calculations of the effects of SST flight since more than half of projected SST emissions occur north of 50°N (Oliver et al., 1977). Thus, some of the potential sources of error introduced by the use of one-dimensional models in the calculation of the test series effects also exist for calculations of SST's.

It may appear that the difficulty of dealing with initial cloud spread could be dealt with in two-dimensional models. However, for the simple reason that all two-dimensional models derive their transport from long-term averaged observation data of stratospheric tracers, it is not clear that such models can correctly represent transport on the time scale of weeks to months. Furthermore, limited spatial resolution in two- and three-dimensional models as required by practical computational considerations also requires parameterization of initial debris cloud spread and its effects are yet to be studied. Nevertheless, two- or three-dimensional calculations of both effects are to be desired, but present

multi-dimensional models are expensive to run, and the likely rapid evolution of model chemistry may act to discourage extensive calculations.

CONCLUSIONS

Several conclusions may be drawn from these calculations. Most important is that our current (1977) one-dimensional model calculates ozone depletions that seem reconcilable with observations, and that the 1960's tests may provide a useful if largely negative test of stratospheric models (i.e., a test that some past models could have met only by presuming all uncertainties near their limits, and that some future calculations might encounter similar difficulties in meeting). The calculations reported here demonstrate that a one-dimensional calculation of the effects of the nuclear tests is relatively insensitive to K_z and only moderately sensitive to the treatment of cloud stabilization heights. Unexpected changes in model chemistry have produced major reductions in the predicted effects on atmospheric ozone of nuclear weapons and SST's (Luther, 1977; Broderick, 1977), more than five years after major programs designed to predict the effects of NO_x on ozone were instituted and more than two years after reports of findings were issued. These major changes came as a result of measurements of parameters not affecting the major NO_x catalytic cycles directly.

The calculations reported here reflect current best estimates of many input parameters, some of which (especially reaction rate constants involving HO_2) are admittedly rather uncertain (DeMore et al., 1977; Duewer et al., 1977). Thus, when new measurements become available, it is likely that some model inputs and model predictions will change again.

The major changes in model chemistry, and those changes that most strongly affect model sensitivities have been in the treatment of reactions that affect HO_x species or link NO_x to minor species other than odd oxygen, rather than in the major catalytic odd oxygen destruction cycles involving NO_x (see also Duewer et al., 1977). Because this secondary chemistry has such a strong effect on one-dimensional model sensitivity to NO_x injection, it will be necessary to closely examine the representation of the chemistry used in multi-dimensional models when interpreting their results.

We believe that ozone changes of the magnitude of 4% are reconcilable with observation if one accepts the analysis of either Angell and Korshover (1978) or Johnston et al. (1973). Any model that predicts a response to the nuclear weapons tests of the 1950's and 1960's significantly larger than 4% (Northern Hemisphere annual average) may be in error in a way that seriously affects its reliability in other prognostic applications, although the case for this may be rendered ambiguous by the possible existence of other sources of long-term O_3 variability. In the above application model errors could result from the basic model formulation (e.g., dimensionality, resolution, numerical method), the detailed representation of chemistry or transport (e.g., input rate constants), or the treatment of the perturbation (e.g., NO_x yield, stabilization heights). In the case of the calculations described here using 1973, 1974 and 1976 chemistries, relatively large perturbations were predicted, and new measurements of chemical rate constants have led to a much smaller predicted response to the nuclear tests.

As the above discussion indicates, the nuclear test series do not appear to provide a positive test or calibration point for models of the stratosphere. However, they would appear to provide a negative test of such models. This test may be overly stringent when applied to steady-state effects, such as those from SST and CFM's. However, if any current or future stratospheric model should predict large ozone changes from the tests of the 1950's and 1960's, it would be necessary to understand this apparent conflict with observation before accepting other predictions of that model.

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PERFORMANCE OF THE LAWRENCE LIVERMORE LABORATORY
ZONAL ATMOSPHERIC MODEL*

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1. Introduction

The two-dimensional zonal atmospheric model developed at the Lawrence Livermore Laboratory uses basic (primitive) conservation equations and is designed to assess the potential climatic effects of various atmospheric and surface perturbations. The model was originally designed to test climatic theories regarding ice ages (MacCracken, 1968). The model has since undergone substantial improvement and modification (MacCracken and Luther, 1974; Luther and MacCracken, 1974), and has been used to study climatic feedback mechanisms induced by changes in the radiative and moisture properties of the earth's surface and atmosphere (MacCracken, 1975; Potter *et al.*, 1975; Ellsaesser *et al.*, 1976).

2. Model Description

2.1. General structure

The model is divided vertically into nine pressure layers, with the temperature and moisture computed at 10, 20, 50, 100, 200, 400, 600, 850, and 1000 mb, and winds computed midway between these levels; horizontally the model uses a 10° latitude grid. The boundary layer between the lowest atmospheric level and the earth's surface is assumed to have no storage capacity with respect to vertical transports of sensible heat or water vapor. Similarly, the wind velocity of this layer allows no divergence of the angular momentum fluxes. The surface at each latitude is divided proportionally into land (of differing types and elevations)

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and ocean (which may be partially ice-covered or ice-free). Although the model does not have the spatial coherence of a continental structure, it does allow realistic treatment of the boundary layer at each latitude. Figures 1 and 2 show the basic grid structure with the various surface types: mountains, sea-level land, ocean, and sea-ice.

The prognostic variables of the model are temperature, water vapor mixing ratio, surface pressure and the two horizontal components of wind velocity. The horizontal velocity equations are based on the conservation of angular momentum and are formulated in a flux-divergence form with eddy diffusion terms included to simulate subgrid scale transport (including in this case transport by wave cyclones). Since there is no longitudinal resolution, velocity divergence need only be considered in latitude and pressure coordinates for the conservation of mass. Advective fluxes are calculated by determining the net transport across a plane, assuming that the transport velocity is constant and the transported quantity varies linearly between grid points.

2.2. *Physical processes*

Surface fluxes of sensible heat and moisture are calculated using vertical gradients of temperature and water vapor, the surface wind velocity, and appropriate bulk transfer coefficients. The surface fluxes are also a function of low-level convective intensity so that there is increased transport under unstable atmospheric conditions.

At each latitude, fractional cloud cover is calculated at the 200, 400, 600, and 850 mb levels based on a function of relative humidity. The relationship has been calibrated at each height and latitude using the London (1957) data. The clouds are assumed to be randomly correlated vertically.

Because precipitation and convection usually occur on too small a horizontal scale to be computed explicitly in this model, a parameterization for convection is included that also accounts for convective precipitation and heat transport. The convection parameterization is a function of cloud overlap, vertical stability (departure from neutral moist adiabatic stability), vertical motion, and moisture content. The mechanism does not force the model instantaneously to a prescribed fixed

Fig. 1. Vertical and horizontal grid system for the zonal model. The lower figure depicts a mountain at latitude ℓ although sea level land or ocean may also be present in the appropriate fractional coverage. The upper figure shows a more detailed view of the vertical structure near the boundary layer.

Fig. 2. Conceptual view of the sub-division of the surface at one latitude into distinct surface types for calculation of vertical fluxes. Figure shows ocean, sea-ice, land and mountains.

lapse rate but rather relates the rate of adjustment to the departure from the local moist adiabatic lapse rate. The model assumes that cloud air is saturated and rising, and that clear air is descending with a differential velocity that is the product of the convective intensity and a height-dependent, prescribed vertical velocity typical of observed cumulus convection. As the cloud fraction rises it cools, moisture is precipitated, latent heat is released, and the temperature is adjusted. Precipitation can also occur when an entire grid becomes saturated; this occurs primarily at the tropical tropopause in this model. A portion of the rain that is forced out at higher altitudes is re-evaporated as it falls through lower layers.

Validation of the radiation prescriptions can be found in Luther and MacCracken (1975) and Ellsaesser *et al.* (1976).

2.3. Surface treatment

The land surface boundary is divided into up to 10 layers of variable depth. The upper layers are thinner (typically 20 cm) to better match their thermal inertia to diurnal and seasonal forcing. The layers, starting from the top, may be snow, ice or land. The number of snow and ice layers depends on the total accumulated depth. Surface temperature is calculated for each surface type (e.g., tundra, savanna, etc.) based upon the radiative and energy fluxes from the atmosphere and from the lower surface layers. As the local atmospheric conditions change at each latitude, the surface conditions also respond. The ground may become wetter or drier (affecting albedo) and snow and ice may accumulate or melt.

The ocean is presently treated as an isothermal layer of prescribed depth (e.g., 50m), the temperature of which is dependent on the surface energy balance and a prescribed meridional ocean heat flux. Sea-ice cover and thickness is determined by the temperature and the energy balance of both the ocean and the sea-ice. The ice forms first as a layer 20 cm thick of limited extent; it spreads, up to a maximum extent, depending upon the energy balance of the open water; it thickens according to the energy balance of the ice itself. Melting of the ice occurs in the reverse sequence.

3. Model Performance

The annual-average version of the zonal model has previously been shown to compare favorably with observational data (MacCracken, 1975). That version is similar to the seasonal version with the exception that a latitudinally-dependent fixed annual-average solar flux and a reduced thermocline depth (i.e., reduced oceanic heat capacity) are imposed in order to permit convergence to a pseudo-equilibrium state.

The data presented here are some of the results from a two-year integration of the seasonal version of the model. Since we are concerned with model performance and intercomparison, the data for January were used for comparison with the data collected by Kahle and Haurwitz (1973).

The resulting analysis consists of comparison of the radiative energy terms that are most readily comparable with the zonal averages of the Mintz-Arakawa (as presented by Kahle and Haurwitz (1973)) and the Holloway and Manabe (1971) GCM experiments and observational data compiled by Schutz and Gates (1972). The January data for the zonal model are based on 30-day averages for the temperature, cloudiness, etc., and on the last 7.5 days for the energy balance parameters.

3.1. Meteorology

One of the most important model parameterizations as far as radiation is concerned is cloudiness. Although the net effect of changes in cloudiness is currently under scrutiny (Cess, 1976), the proper distribution of climatological cloud cover is quite important. Generally, the zonal model compares quite favorably with the cloud data as presented by Kahle and Haurwitz (1973) in Fig. 3.* The higher than observed cloudiness in the northern latitudes is due to the high values that are computed for humidity. The lack of definite minima in total cloudiness in the subtropics may be related to the grid size and the position of the

*In all comparisons, GCM's are labeled with **, radiative convective models with *, the LLL Zonal Atmospheric Model with the label ZAM2, and observations are indicated by a reference alone.

Fig. 3. The zonally averaged total cloud cover, from Kahle and Haurwitz (1973).

Fig. 4. The zonally averaged precipitable water, from Kahle and Haurwitz (1973).

two Hadley cells present in this model version. This lack of a subtropical minimum in cloudiness has a noticeable effect on various radiation parameters.

Precipitable water is shown in Fig. 4. There is quite good agreement with observation in the middle and high latitudes, but there is insufficient moisture in the tropics and subtropics. The relative minimum around 30°S is also evident in the cloud cover, precipitation and the surface longwave flux. The paradox here is that the tropical and subtropical minimum in precipitable water should be in the winter hemisphere where the downward arm of the Hadley cell is strongest (in this case 30°N). The model, however, does not reproduce this well, and we are still searching for a plausible explanation.

Surface temperatures from the model (Fig. 5) are the average surface or top-layer temperatures (as distinguished from shelter height temperature). Although Kahle and Haurwitz (1973) attribute the warmer than observed temperatures in high latitudes in the Mintz-Arakawa model to a generally too low surface albedo, this is not likely the case for the zonal model. The high temperatures may possibly be due to the minimum fraction of open leads specified in the sea-ice at these high latitudes. The relatively high temperature in the south polar regions may be due to the relatively low amount of cloud cover or to excessive diffusive transport of heat. This is corroborated by the high longwave loss to space discussed below.

The rate of evaporation from the surface appears to be generally acceptable in the middle and high latitudes (Fig. 6), but it is too high in the tropics and subtropics. The reason for this may be that evaporation is functionally tied to low-level convective activity which, in turn, is high in the tropics. Precipitation (Fig. 7) shows a strong relationship to evaporation. Higher than observed evaporation rates in low latitudes appear to provide moisture, which, due to the unstable lapse rates, causes a positive departure in small-scale precipitation. Subtropical precipitation minima appear in both hemispheres, but for January we should expect the dip to be more accentuated in the Northern Hemisphere than in the Southern Hemisphere. The general structure, however, is consistent with observations.

Fig. 5. The zonally averaged ground and surface air temperature, from Kahle and Haurwitz (1973).

Fig. 6. The zonally averaged evaporation, from Kahle and Haurwitz (1973).

Fig. 7. The zonally averaged precipitation, from Kahle and Haurwitz (1973).

Fig. 8. The zonally averaged sensible heat flux, from Kahle and Haurwitz (1973).

The sensible heat flux from the surface to the atmosphere (Fig. 8) agrees generally with the data from Budyko (1973), although his data are taken as a residual from the heat balance equation. The average sensible heat flux is near zero in the high northern latitudes.

3.2. Radiation

Figure 9 shows the solar radiation reflected to space by the earth-atmosphere system. Although the computed values appear low in the higher latitudes and subtropics, recent satellite observations indicate that the planetary albedo of 35% as given by Sellers (1965) is somewhat high. The lower than observed values in the southern subtropics can be attributed to the lower than observed cloudiness at those latitudes. Differences in cloud cover appear to be the most significant factor controlling shortwave radiation scattered to space, as indicated by the surface absorbed solar radiation (Fig. 10).

The planetary albedo (Fig. 11) shows general agreement with the satellite observations. This parameter integrates the effects of a number of processes, including atmospheric absorption and scattering, cloud amount, surface albedo and cloud albedo. The percentage of the incoming solar radiation that is scattered back to space appears to be in quite good agreement with the other models as well.

Longwave loss out the top of the atmosphere (Fig. 12) again suggests that the Hadley cell does not have the proper structure. The double peaks in observed data and various other models are due to Hadley cell control of cloud cover in the subtropical latitudes, but since the zonal model fails to reproduce this feature satisfactorily, only slight peaks are apparent. The higher than observed values of longwave loss at higher latitudes are probably due to the surface temperature being too high, as shown in Fig. 5.

The longwave flux at the earth's surface (Fig. 13) gives another indication of the effect of cloud cover on the radiation balance. The low values in the high northern latitudes are probably due to the high polar night cloud cover. The general structure, however, is quite consistent with the various other models.

Fig. 9. The zonally averaged solar radiation reflected and scattered back to space from the earth-atmosphere system, from Kahle and Haurwitz (1973).

Fig. 10. The zonally averaged solar radiation absorbed by the earth's surface, from Kahle and Haurwitz (1973).

Fig. 11. The zonally averaged planetary albedo, from Kahle and Haurwitz (1973).

Fig. 12. The zonally averaged net longwave flux at the 200 mb level [for Mintz-Arakawa, Katayama (1967), Haurwitz (1972)] or for the outgoing long-wave radiative flux at the top of the atmosphere [for London (1957), Holloway and Manabe (1971), Vonder Haar (1969), Sasamori *et al.* (1972), Raschke *et al.* (1973) and ZAM2], from Kahle and Haurwitz (1973).

Fig. 13. The zonally averaged net long-wave radiative flux at the earth's surface, from Kahle and Haurwitz (1973).

Fig. 14. The zonally averaged net radiative flux through the top of the atmosphere [for London (1957), Sasamori *et al.* (1972), Vonder Haar and Suomi (1971) and ZAM2] or the 200 mb level for Mintz-Arakawa and Katayama (1967), from Kahle and Haurwitz (1973).

The net radiative flux at the top of the atmosphere is compared in Fig. 14. In spite of the deviation from other models, the zonal model reproduces the net flux at the top of the atmosphere quite well. The excessive negative values in the northern latitudes are the result of the large longwave loss to space shown in Fig. 12. More recent observational data from Ellis and Vonder Haar (1976) show that the zonal model is quite close to the observed longwave flux to space while the solar absorption is probably too low in the subtropics (Fig. 15).

4. Conclusions

Results from the zonal model indicate quite reasonable agreement with observation in terms of the parameters and processes that influence the radiation and energy balance calculations. The model produces zonal statistics similar to those from general circulation models, and has also been shown to produce similar responses in sensitivity studies (e.g., Ellsaesser *et al.*, 1976). Further studies of model performance are planned, including:

1. Comparison with July data.
2. Comparison of temperature and moisture transport and wind fields for winter and summer months.
3. A tabulation of atmospheric energetics.

Based on these preliminary performance studies, however, it appears that the zonal model can be used in conjunction with more complex models to help unravel the problems of understanding the processes governing present climate and climate change. As can be seen in a subsequent paper on model sensitivity studies, in addition to reduced cost of computation, the zonal model facilitates analysis of feedback mechanisms and simplifies analysis of the interactions between processes.

Fig. 15. The upper portion of the figure shows the zonally averaged solar radiation absorbed by the atmosphere from London (1957) and Sasamori *et al.* (1972), from Kahle and Haurwitz (1973) and from ZAM2. The lower portion shows the zonally averaged longwave radiation lost to space from Ellis and Vonder Haar (1976) and from ZAM2.

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