**QUANTIFIED ESTIMATES OF TOTAL GWPS FOR
GREENHOUSE GASES TAKING INTO ACCOUNT
TROPOSPHERIC CHEMISTRY**

by

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1. Introduction

A number of infrared absorbing gases, referred to as greenhouse gases, are being studied because of their potential for directly influencing climate through radiative forcing. In addition, indirect effects on radiative forcing resulting from chemical interactions in the troposphere and stratosphere are likely to be important to determining the impact of human-related activities on climate change. Such indirect effects can occur through chemical effects on concentrations of ozone in the troposphere and stratosphere, through effects on hydroxyl concentrations in the troposphere, and through effects on water vapor in the stratosphere. A list of atmospheric constituents with recognized direct and indirect effects on climatic forcing is given in Table 1.1. The 1990 Intergovernmental Panel on Climate Change (IPCC) scientific assessment on climate change demonstrated that indirect effects can have a significant effect on calculations of Global Warming Potentials (GWPs). Since GWPs are a relative measure of the integrated radiative (or climatic) forcing resulting from greenhouse gases, the IPCC calculations suggest that effects from atmospheric chemical processes need to be carefully analyzed in determining future climate changes.

Table 1.1. Partial listing of direct and indirect effects related to radiative forcing on climate.

Species	Description	Type of effect	Sign of effect on radiative forcing
INORGANICS			
CO ₂	CO ₂	direct	+
	Stratospheric O ₃ increase via stratospheric cooling	indirect	-
CO	Tropospheric O ₃	indirect	+
	Tropospheric CH ₄ increase via reduced OH sink	indirect	+
	CO ₂	indirect	+
COS	Stratospheric aerosol	indirect	-
	Stratospheric aerosol/sulfate/O ₃ reduction	indirect	-
H ₂	Increase in stratospheric H ₂ O vapor	indirect	+
H ₂ O	Troposphere	direct	+
	Stratosphere	direct	+
	Aircraft in the Stratosphere	direct	+
N ₂ O	N ₂ O	direct	+
	Stratospheric O ₃ depletion	indirect	+
NO _x	Tropospheric O ₃	indirect	+
	Stratospheric O ₃ reduction	indirect	-
	Tropospheric CH ₄ increase via reduced OH sink	indirect	?
	Aircraft emissions/Upper tropospheric O ₃	indirect	+
	Aircraft emissions/Lower stratospheric O ₃	indirect	-
ORGANICS			
CH ₄	CH ₄	direct	+
	Effect on tropospheric O ₃	indirect	+
	Effect on stratospheric O ₃	indirect	+
	Stratospheric O ₃ increase via Cl _x /Br _x deactivation	indirect	+
	Effect on Stratospheric H ₂ O vapor	indirect	+

Table 1.1. Partial listing of direct and indirect effects related to radiative forcing on

Species	Description	Type of effect	Sign of effect on radiative forcing
	Effect on stratospheric H ₂ O vapor; increasing polar strat. clouds; then O ₃ depletion	indirect	-
	CO ₂	indirect	+
Non-methane Hydrocarbons (NMHCs)	Effect on tropospheric O ₃	indirect	+
	Tropospheric CH ₄ increase via reduced OH sink	indirect	+
	Effect on Stratospheric O ₃	indirect	+
	Stratospheric O ₃ increase via Cl _x /Br _x deactivation	indirect	+
	Effect on CO ₂	indirect	+
Halogenated Organics (selected)	CFC-11	direct	+
	CFC-12	direct	+
	CFC-113	direct	+
	CFC-22	direct	+
	Halons	direct	+
	CH ₃ Br	direct	+
	Cl _x & Br _x /Lower Stratospheric O ₃ depletion	indirect	-
	Cl _x & Br _x /Upper Stratospheric O ₃ depletion	indirect	+
AEROSOLS			
Aerosols	Sulfates in Stratosphere/Troposphere	direct	-
	Tropospheric sulfates	indirect	-
	Carbonaceous aerosols in Troposphere	direct	+
	Stratospheric O ₃ depletion from heterogenous chemistry	indirect	-
	Sulfates from Aircraft; Stratosphere/Troposphere	direct	-
	Aircraft-related sulfates; Stratospheric O ₃ depletion	indirect	-

The IPCC report had determined the indirect effects on GWPs resulting from changes in tropospheric ozone from surface emissions of methane (CH₄), nitrogen oxides (NO_x), carbon monoxide (CO), and non-methane hydrocarbons (NMHCs). These GWPs were based on calculations from the two-dimensional tropospheric model developed at Harwell in the U.K. (Derwent, 1990; Hough, 1991). The recent update of GWPs in the international assessments by the World Meteorological Organization (WMO, 1991) and by IPCC (1992) determined that the existing incomplete understanding of atmospheric chemical processes infer that the indirect GWPs determined in the 1990 IPCC report should be withdrawn. There are also recognized limitations with the model used in determining the indirect effects for the 1990 report.

Many uncertainties exist in the published GWPs. For example, direct radiative forcing effects are influenced by uncertainties in the lifetimes in the gases of concern. The effect of uncertainties in the carbon cycle have a significant effect on the integrated radiative forcing from CO₂ (since GWPs for any given gas by definition are relative to the radiative forcing from CO₂, uncertainties in CO₂ affect the GWPs for all other gases). Indirect effects on GWPs are particularly subject to uncertainties in atmospheric

chemistry. The concept of a GWP for a short-lived heterogeneously distributed constituent is complicated by the dependence on location of the emission; such constituents include NO_x and some NMHCs.

Nonetheless, Global Warming Potentials are being used extensively nationally and internationally in policy analyses relating to the concerns about climate change. Accurate determination of potential indirect effects are crucial to such analyses. Although many uncertainties remain in the theoretical understanding and modeling of atmospheric chemical and physical processes, it is important that steps be taken towards reducing these uncertainties and towards deriving better estimates of the potential direct and indirect effects on climate.

The purpose of this report is to give an interim account of the progress being made at Lawrence Livermore National Laboratory (LLNL) in developing an improved capability for assessing the direct and indirect effects on Global Warming Potentials. Much of our current efforts are being devoted to improving the capability for modeling of global tropospheric processes in our state-of-the-art zonally-averaged chemical-radiative-transport model of the troposphere and stratosphere. These efforts are in preparation for an improved evaluation and better quantification of the indirect GWPs resulting from effects on tropospheric ozone from methane and other gases with significant human-related emissions.

Chapter 2 describes the LLNL two-dimensional chemical-radiative-transport model, including the enhanced capabilities resulting from this project. Chapter 3 describes the derived current atmosphere as calculated with the model. Included is a discussion of our efforts to validate the model with available observational data in the troposphere. Previous published studies (e.g., Wuebbles *et al.*, 1991; Miller *et al.*, 1992; Kinnison, 1989) have been aimed at validation of stratospheric processes in the model. Chapter 4 describes initial perturbation studies with the enhanced model, including analysis of the effects of increased emissions of methane and NO_x on tropospheric ozone and hydroxyl. Chapter 5 describes the studies evaluating the effect of defined uncertainties on direct GWPs. Chapter 6 presents the philosophy and calculations we are doing to determine indirect Global Warming Potentials. Chapter 7 summarizes the findings from this report, while Chapter 8 describes the needs for future work.

The evaluation and analysis of the derived current atmosphere provides an important test of the capability to represent: (1) the complexity of tropospheric chemical processes in existing models; and (2) the zonal average of the spatially varying tropospheric chemical processes in a two-dimensional chemical-transport model. The evaluation and analysis of the perturbation studies are important to examining the capabilities of the model to represent effects on ozone from various emissions. These results are compared to the published results from other 2-D and 3-D chemical-transport models. The perturbation results are a forerunner to the studies of the indirect Global Warming Potentials.

Our studies of direct effects on climate forcing currently are focusing on some of the key uncertainties associated with determining GWPs. Chapter 5 describes the significant progress we have made in evaluating the effects of uncertainties on GWPs associated with the CO_2 decay rate, with the atmospheric lifetimes of other greenhouse gases, and with the assumption of an equilibrium background atmosphere made in the IPCC assessments.

There are three major findings that should result from this project that should have significant impacts on EPA and its programs. First, the current and ongoing studies of the direct and indirect GWPs should have a significant influence on the continuing national and international assessments of climate change. Second, the

improved capability for modeling of chemical and physical processes should lead to enhanced understanding of the controlling factors influencing ozone, hydroxyl and other key tropospheric constituents. Third, the enhanced modeling capability should be important to future studies of human-related influences on tropospheric and stratospheric chemical processes.

2. Description of Two-Dimensional Model

Atmospheric chemical-radiative-transport models are used to investigate the role trace gases have on both chemical and physical processes that determine the distribution of ozone and other trace constituents. A two-dimensional model includes transport in the meridional direction. Therefore, such models offer a more realistic representation of the feedbacks that dynamics can have on the distribution of trace species such as NO_x , HO_x , and Cl_x . Since these chemical families control ozone production and loss processes, the role of transport can be extremely important in determining the distribution of ozone in the atmosphere. This version of the LLNL zonally-averaged two-dimensional chemical-radiative-transport model currently determines the atmospheric distributions of 81 chemically active atmospheric trace constituents in the troposphere and stratosphere. The model domain extends from pole to pole and from the ground to 60 km. The sine of latitude is used as the horizontal coordinate with uneven increments corresponding to approximately 10 degrees in latitude. The vertical coordinate corresponds to the natural logarithm of pressure; the scale height is 7.2 km and surface pressure is 1013 mb. The vertical resolution is 1.5 km in the troposphere and 3 km in the stratosphere.

2.1. Model Transport

In the dynamics portion of the two-dimensional model, the circulation field is obtained using the approach of Garcia and Solomon (1983). Since this approach has not been fully implemented in the model yet, we use known temperature and zonal mean wind fields. Both the temperature and zonal mean wind field varies continuously over the annual cycle. The temperature field is based on the reference model of Barnett and Corney (1985), while the zonal mean wind is based on data of Fleming *et al.* (1988). The method used to obtain the circulation is based on combining the zonal mean momentum equation and the thermodynamic equation into a form that, along with the thermal wind equation, yields a second-order diagnostic equation for the residual mean meridional stream function. This stream function is defined so that the continuity equation is solved exactly. The coefficients of the stream function terms on the left side of the equation are functions of known quantities: the coriolis force, zonal mean wind, scale height, temperature field, a global reference altitude-dependent temperature field, and the Brunt-Vaisala frequency. The model seasonally averages the known temperature fields to provide an altitude-dependent reference temperature field from which an altitude-dependent Brunt-Vaisala frequency is calculated. The right-hand side of the stream function equation includes the net heating rate term and the Eliassen-Palm flux representing wave driving. The net heating rate is calculated knowing the temperature and chemical specie distribution and includes latent heating. The present code does not include a separate planetary or gravity wave calculation, but instead calculates the Eliassen-Palm flux directly from the zonal mean momentum equation. This is done by simply calculating the left-hand side of the zonal mean momentum equation using the known zonal mean wind field and approximate values of v^* and w^* . These approximate values of v^* and w^* are obtained from a diagnostic approach of iteration between the continuity and thermodynamic equations with a known temperature field. The right-hand side also includes a very small value of Rayleigh friction (value of about 0.1 day^{-1}) to account for small-scale disturbances. With all terms known, the second-order equation for the stream function is evaluated from which the velocity fields are then obtained.

The transport of chemical species is accomplished through advection and turbulent eddy transport. Advection terms are treated using the second-order two-dimensional transport algorithm of Smolarkiewicz (1984). The transport caused by eddy motion is parameterized through the diffusion coefficients K_{yy} and K_{zz} . Values of K_{zz} do

not vary with annual cycle, but are different within the troposphere and stratosphere. The value of K_{zz} in the troposphere is $4 \text{ m}^2/\text{sec}$, while K_{zz} in the stratosphere has values of $0.1 \text{ m}^2/\text{sec}$ in the lower stratosphere increasing to $0.25 \text{ m}^2/\text{sec}$ near the middle stratosphere and returning to $0.1 \text{ m}^2/\text{sec}$ at the stratopause. Values of K_{yy} in the stratosphere are calculated using a method similar to that of Newman (1988) by dividing the zonal mean momentum equation (i.e., the Eliassen-Palm flux) by the horizontal gradient of the quasi-geostrophic potential vorticity. In the stratosphere, a minimum value of K_{yy} has been established as $1 \times 10^5 \text{ m}^2/\text{sec}$. The values of K_{yy} in the troposphere for the current model are assigned a value of $2 \times 10^6 \text{ m}^2/\text{sec}$. The tropopause is treated as an annual mean, but latitude-dependent, function of the temperature field. The height of the tropopause varies from 8 km near the poles to 14 km at the equator.

Two physical removal processes are included in the model. Surface deposition occurs in the first layer of the model. Most species are assigned a standard deposition velocity of 1 cm/sec. Nitric oxide, nitrogen dioxide, ozone, molecular hydrogen, and formaldehyde are assigned unique deposition velocities. Also, source gases emitted at the surface (e.g., methane) are assigned a deposition velocity of zero. Rainout is parameterized in the model as a first-order loss process that occurs in the first 6-7 altitude layers. There is no latitudinal or seasonal dependence.

2.2. Radiative transfer models

2.2.1. Solar model

To capture the spectral detail needed for photodissociation calculations, our two-stream multiple-layer UV-visible model uses 126 wavelength bins between 175 nm and 735 nm. The two-stream approach was chosen because of the requirements for computational efficiency placed on radiative transfer models designed for inclusion in atmospheric chemistry models. In this approach, solar radiation is effectively divided into direct solar radiation, downward diffuse radiation, and upward diffuse radiation. The scattering of energy from the direct solar beam within each individual layer is treated using the delta-Eddington algorithm, which includes the dependence of scattering and absorption on the solar zenith angle. The scattering of diffuse radiation (i.e., previously scattered radiation) from each individual layer is modeled using the simpler Sagan-Pollack algorithm. Both algorithms allow inclusion of the bulk optical properties of clouds and aerosols. Finally, the adding method is used to calculate irradiances throughout the vertically inhomogeneous atmosphere.

2.2.2. Infrared Model

The RADIR infrared model that we have been using for several years is a version of the model described by Harshvardhan *et al.* (1987). For our usage, it has been modified to improve the accuracy in the upper stratosphere. It includes absorption and emission by CO_2 , O_3 , and H_2O . It is based on wide-band parameterizations fit to line-by-line calculations. Inhomogeneous absorption paths are included by pressure- and temperature-weighted scaling of trace gas absorber amounts. The model provides for specification of fractional cloud cover within each vertical model layer. Separate fractions can be specified for convective (deep, overlapping) and randomly overlapped clouds.

As part of our focus effort to develop a new infrared radiative transfer model based on the correlated-k distribution technique, we have acquired a substantial capability to calculate the absorption properties of common trace gases. We have the HITRAN-91 spectroscopic database. Temperature-dependent absorption cross-section data for a

number of chlorofluorocarbons (CFCs) are included with these data. To make use of these data, we have a version of FASCODE modified to facilitate the calculation of pressure- and temperature-dependent absorption coefficients. A final processing program is available to calculate absorption coefficient frequency distributions from these data. The new correlated-k distribution infrared model, when completed, should greatly enhance our capabilities to model radiative and climatic processes and should push the state-of-the-art for modeling of infrared processes.

2.3. Model Chemistry

As part of this project with EPA, we have put significant effort into enhancing the capabilities for modeling of tropospheric chemical processes. The mechanism we are currently using in the LLNL two-dimensional model has the following characteristics:

- A total of 81 species are allowed to vary with time in the troposphere and stratosphere. There are 38 non-methane hydrocarbon species and their oxidation products. Eleven of the precursor organic compounds have surface emission sources.
- There are 176 thermal (i.e., two- and three-body) reactions in the mechanism, 64 of which involve the NMHCs.
- There are 59 photolysis reactions, 12 of which involve the NMHCs.
- PAN chemistry is explicitly represented.
- Isoprene chemistry is included in a condensed mechanism.
- A complete representation of known stratospheric chemical processes.

The mechanism is listed in its entirety in Table 2.1. The reactions are classified by type: thermal, three-body, and photolytic. The kinetic parameters and/or the literature references are included as well.

Table 2.1. Chemical reaction mechanism for LLNL two-dimensional model.

(a) Thermal Reactions $\left(\text{Arrhenius rate constant expression } k = A \cdot \exp\left(\frac{-E}{RT}\right) \right)$				
No.	Reaction	A ¹	-E/R ²	Reference
1	$\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$	8.00E-12	-2,060	1
2	$\text{O}(^1\text{D}) + \text{O}_3 \rightarrow 2\text{O}_2$	1.20E-10	0	1
3	$\text{O}(^1\text{D}) + \text{O}_3 \rightarrow \text{O}_2 + \text{O} + \text{O}$	1.20E-10	0	1
4	$\text{N}_2\text{O} + \text{O}(^1\text{D}) \rightarrow \text{N}_2 + \text{O}_2$	4.90E-11	0	1
5	$\text{N}_2\text{O} + \text{O}(^1\text{D}) \rightarrow 2\text{NO}$	6.70E-11	0	1
6	$\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$	2.20E-10	0	1
7	$\text{H}_2 + \text{O}(^1\text{D}) \rightarrow \text{OH} + \text{H}$	1.00E-10	0	1
8	$\text{O}(^1\text{D}) + \text{CH}_4 \rightarrow \text{CH}_2\text{O} + \text{H}_2$	1.40E-11	0	1
9	$\text{O}(^1\text{D}) + \text{CH}_4 \rightarrow \text{CH}_3\text{O}_2 + \text{OH}$	1.40E-10	0	1
10	$\text{CF}_2\text{Cl}_2 + \text{O}(^1\text{D}) \rightarrow 2\text{Cl}$	1.12E-10	0	1
11	$\text{O}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{O}_2$	1.60E-12	-940	1
12	$\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$	2.20E-11	120	1
13	$\text{O}_3 + \text{HO}_2 \rightarrow \text{OH} + 2\text{O}_2$	1.10E-14	-500	1
14	$\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$	3.00E-11	200	1
15	$\text{O}_3 + \text{H} \rightarrow \text{OH} + \text{O}_2$	1.40E-10	-470	1
16	$\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	4.80E-11	250	1
17	$\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$	2.90E-12	-160	1
18	$\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$	5.50E-12	-2,000	1
19	$\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$	2.00E-12	-1,400	1
20	$\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$	6.50E-12	120	1
21	$\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$	1.50E-11	-3,600	1
22	$\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$	3.40E-11	0	1
23	$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	1.20E-13	-2,450	1
24	$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$	5.00E-22	0	1
25	$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$	3.70E-12	240	1
26	$\text{OH} + \text{HNO}_4 \rightarrow \text{H}_2\text{O} + \text{NO}_2 + \text{O}_2$	1.30E-12	380	1
27	$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	2.90E-11	-260	1
28	$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$	3.00E-11	70	1
29	$\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$	2.60E-12	-350	1
30	$\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2$	1.80E-11	170	1
31	$\text{CH}_3\text{Cl} + \text{OH} \rightarrow \text{Cl} + \text{H}_2\text{O} + \text{HO}_2$	2.10E-12	-1,150	1
32	$\text{HO}_2 + \text{ClO} \rightarrow \text{O}_2 + \text{HOCl}$	4.80E-13	700	1
33	$\text{OH} + \text{HOCl} \rightarrow \text{H}_2\text{O} + \text{ClO}$	3.00E-12	-500	1
34	$\text{Cl} + \text{HO}_2 \rightarrow \text{OH} + \text{ClO}$	4.10E-11	-450	1
35	$\text{OH} + \text{CH}_3\text{CCl}_3 \rightarrow \text{H}_2\text{O} + 3\text{Cl}$	5.00E-12	-1,800	1
36	$\text{NO} + \text{ClO} \rightarrow \text{NO}_2 + \text{Cl}$	6.40E-12	290	1
37	$\text{ClONO}_2 + \text{O} \rightarrow \text{ClO} + \text{NO} + \text{O}_2$	2.90E-12	-800	1
38	$\text{ClONO}_2 + \text{O} \rightarrow \text{ClO} + \text{NO}_2 + \text{O}$	2.90E-12	-800	1
39	$\text{OH} + \text{ClONO}_2 \rightarrow \text{HOCl} + \text{NO} + \text{O}_2$	1.20E-12	-333	1
40	$\text{OH} + \text{ClONO}_2 \rightarrow \text{HOCl} + \text{NO}_2 + \text{O}$	1.20E-12	-333	1
41	$\text{Cl} + \text{ClONO}_2 \rightarrow 2\text{Cl} + \text{NO} + \text{O}_2$	6.80E-12	160	1
42	$\text{Cl} + \text{ClONO}_2 \rightarrow 2\text{Cl} + \text{NO}_2 + \text{O}$	6.80E-12	160	1
43	$\text{CH}_3\text{O}_2 + \text{O} \rightarrow \text{CH}_2\text{O} + \text{HO}_2$	3.00E-11	0	1
44	$\text{O} + \text{CH}_2\text{O} \rightarrow \text{OH} + \text{HO}_2 + \text{CO}$	3.40E-11	-1,600	1
45	$\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{O}_2$	3.90E-12	-1,885	1
46	$\text{OH} + \text{CH}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{HO}_2 + \text{CO}$	1.00E-11	0	1
47	$\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{HO}_2 + \text{CH}_2\text{O} + \text{NO}_2$	4.20E-12	180	1
48	$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3\text{O}_2$	1.10E-11	-1,400	1
49	$\text{Cl} + \text{CH}_2\text{O} \rightarrow \text{HCl} + \text{HO}_2 + \text{CO}$	8.10E-11	-30	1

Table 2.1. Chemical reaction mechanism for LLNL two-dimensional model.

(a) Thermal Reactions $\left(\text{Arrhenius rate constant expression } k = A \cdot \exp\left(\frac{-E}{RT}\right) \right)$				
No.	Reaction	A	-E/R	Reference
50	$\text{Cl} + \text{CH}_3\text{Cl} \rightarrow \text{HO}_2 + \text{CO} + 2\text{HCl}$	3.30E-11	-1,250	1
51	$\text{CCl}_3\text{CF}_3 + \text{O}(^1\text{D}) \rightarrow 3\text{Cl}$	1.60E-10	0	1
52	$\text{CHF}_2\text{Cl} + \text{OH} \rightarrow \text{Cl}$	1.20E-12	-1,650	1
53	$\text{CHF}_2\text{Cl} + \text{O}(^1\text{D}) \rightarrow \text{Cl}$	1.00E-10	0	1
54	$\text{O}(^1\text{D}) + \text{N}_2 \rightarrow \text{O} + \text{N}_2$	1.80E-11	110	1
55	$\text{O}(^1\text{D}) + \text{O}_2 \rightarrow \text{O} + \text{O}_2$	3.20E-11	70	1
56	$\text{Cl} + \text{ClOO} \rightarrow 2\text{Cl} + \text{O}_2$	1.40E-10	0	1
57	$\text{Cl} + \text{OCIO} \rightarrow 2\text{ClO}$	3.40E-11	160	1
58	$\text{O} + \text{OCIO} \rightarrow \text{ClO} + \text{O}_2$	2.80E-11	-1,200	1
59	$\text{OH} + \text{OCIO} \rightarrow \text{HOCl} + \text{O}_2$	4.50E-13	800	1
60	$\text{OCIO} + \text{NO} \rightarrow \text{NO}_2 + \text{ClO}$	2.50E-12	-600	1
61	$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{ClOO}$	4.00E-13	-1,250	1
62	$\text{ClO} + \text{ClO} \rightarrow 2\text{Cl} + \text{O}_2$	4.00E-13	-1,250	1
63	$\text{Cl} + \text{Cl}_2\text{O}_2 \rightarrow \text{Cl}_2 + \text{ClOO}$	1.00E-10	0	1
64	$\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2$	1.70E-11	-800	1
65	$\text{Br} + \text{CH}_2\text{O} \rightarrow \text{HBr} + \text{H} + \text{CO}$	1.70E-11	-800	1
66	$\text{Br} + \text{HO}_2 \rightarrow \text{HBr} + \text{O}_2$	1.50E-11	-600	1
67	$\text{Br} + \text{OCIO} \rightarrow \text{BrO} + \text{ClO}$	2.60E-11	-1,300	1
68	$\text{Br} + \text{Cl}_2\text{O}_2 \rightarrow \text{Cl} + \text{Br} + \text{ClOO}$	3.00E-12	0	1
69	$\text{BrO} + \text{O} \rightarrow \text{Br} + \text{O}_2$	3.00E-11	0	1
70	$\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{OCIO}$	1.60E-12	430	1
71	$\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{ClOO}$	2.90E-12	220	1
72	$\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{Cl} + \text{O}_2$	5.80E-13	170	1
73	$\text{BrO} + \text{NO} \rightarrow \text{NO}_2 + \text{Br}$	8.80E-12	260	1
74	$\text{BrO} + \text{BrO} \rightarrow 2\text{Br} + \text{O}_2$	1.50E-12	180	1
75	$\text{BrO} + \text{HO}_2 \rightarrow \text{HOBr} + \text{O}_2$	5.00E-12	0	1
76	$\text{BrO} + \text{OH} \rightarrow \text{Br} + \text{HO}_2$	1.00E-11	0	1
77	$\text{OH} + \text{HBr} \rightarrow \text{H}_2\text{O} + \text{Br}$	1.10E-11	0	1
78	$\text{OH} + \text{CH}_3\text{Br} \rightarrow \text{Br} + \text{H}_2\text{O}$	6.80E-13	-850	1
79	$\text{O} + \text{HBr} \rightarrow \text{OH} + \text{Br}$	5.80E-12	-1,500	1
80	$\text{NO}_3 + \text{Br} \rightarrow \text{BrO} + \text{NO}_2$	1.60E-11	0	1
81	$\text{NO}_3 + \text{BrO} \rightarrow \text{NO}_2 + \text{Br} + \text{O}_2$	1.00E-12	0	1
82	$\text{CFCl}_2\text{CF}_3 + \text{O}(^1\text{D}) \rightarrow 2\text{Cl}$	1.28E-10	0	1
83	$\text{CF}_3\text{CF}_2\text{Cl} + \text{O}(^1\text{D}) \rightarrow \text{Cl}$	7.12E-11	0	1
84	$\text{OH} + \text{CH}_3\text{OOH} \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} + \text{OH}$	1.10E-12	200	1
85	$\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2$	3.30E-13	800	1
86	$\text{OH} + \text{CH}_3\text{OOH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$	2.70E-12	200	1
87	$\text{CH}_2\text{O} + \text{NO}_3 \rightarrow \text{CO} + \text{HO}_2 + \text{HNO}_3$	5.80E-16	0	1
88	$\text{CH}_3\text{CHO} + \text{OH} \rightarrow \text{CH}_3\text{COO}_2$	6.00E-12	250	1
89	$\text{CH}_3\text{CHO} + \text{NO}_3 \rightarrow \text{CH}_3\text{COO}_2 + \text{HNO}_3$	1.40E-12	-1,900	1
90	$\text{CH}_3\text{COO}_2\text{NO}_2 + \text{OH} \rightarrow \text{CH}_2\text{O} + \text{NO}_2$	1.20E-12	-650	2
91	$\text{CH}_3\text{COO}_2 + \text{NO} \rightarrow \text{CH}_3\text{O}_2 + \text{NO}_2$	2.10E-11	0	3
92	$\text{C}_2\text{H}_5\text{O}_3 + \text{NO} \rightarrow f_a^3\text{CH}_2\text{O} + f_b^4\text{CH}_3\text{CHO} + \text{HO}_2 + \text{NO}_2$	4.20E-12	180	7
93	$\text{C}_2\text{H}_4 + \text{O}_3 \rightarrow \text{CH}_2\text{O} + .42\text{CO} + .12\text{H}_2 + .12\text{HO}_2$	1.20E-14	-2,630	1
94	$\text{C}_2\text{H}_5\text{O}_3 + \text{HO}_2 \rightarrow f_a\text{CH}_2\text{O} + f_b\text{CH}_3\text{CHO} + \text{HO}_2 + \text{OH}$	6.50E-13	650	7
95	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{COO}_2 \rightarrow \text{CH}_2\text{O} + .5\text{CH}_3\text{O}_2 + .5\text{HO}_2$	5.50E-12	0	2,7

Table 2.1. Chemical reaction mechanism for LLNL two-dimensional model.

(a) Thermal Reactions $\left(\text{Arrhenius rate constant expression } k = A \cdot \exp\left(\frac{-E}{RT}\right) \right)$				
No.	Reaction	A	-E/R	Reference
96	$\text{CH}_3\text{COO}_2 + \text{CH}_3\text{COO}_2 \rightarrow 2\text{CH}_3\text{O}_2$	2.80E-12	530	2
97	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow 1.8\text{CH}_2\text{O} + 1.25\text{HO}_2$	2.20E-13	220	1
98	$\text{CH}_3\text{COO}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{COO}_2\text{H}$	4.30E-13	1,040	5
99	$\text{CH}_3\text{COO}_2\text{H} + \text{OH} \rightarrow \text{CH}_3\text{COO}_2$	5.00E-12	0	7
100	$\text{C}_2\text{H}_6 + \text{OH} \rightarrow \text{C}_2\text{H}_5\text{O}_2$	1.10E-11	-1,100	1
101	$\text{C}_3\text{H}_8 + \text{OH} \rightarrow 0.33\text{C}_2\text{H}_5\text{O}_2 + 0.58\text{C}_4\text{H}_9\text{O}_2$	1.40E-11	-750	1
102	$\text{C}_6\text{H}_{14} + \text{OH} \rightarrow 0.24\text{C}_2\text{H}_5\text{O}_2 + 0.71\text{C}_4\text{H}_9\text{O}_2$ $+ 0.45\text{C}_6\text{H}_{13}\text{O}_2$	1.35E-11	-262	6
103	$\text{C}_2\text{H}_5\text{O}_2 + \text{NO} \rightarrow 0.985\text{CH}_3\text{CHO} +$ $0.985\text{HO}_2 + 0.985\text{NO}_2$	4.87E-12	180	7
104	$\text{C}_4\text{H}_9\text{O}_2 + \text{NO} \rightarrow 0.91\text{R}_1\text{COCH}_3 + 0.91\text{NO}_2$ $+ 0.91\text{HO}_2$	4.87E-12	180	7
105	$\text{RO}_2\text{COCH}_3 + \text{NO} \rightarrow 0.92\text{CH}_3\text{CHO} +$ $0.92\text{CH}_3\text{COO}_2 + 0.92\text{NO}_2$	4.20E-12	180	7
106	$\text{C}_6\text{H}_{13}\text{O}_2 + \text{NO} \rightarrow 0.96\text{C}_2\text{H}_5\text{O}_2 +$ $0.96\text{R}_1\text{COCH}_3 + 0.96\text{NO}_2$	4.87E-12	180	7
107	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow 0.525\text{CH}_2\text{O} + 0.5\text{CH}_3\text{CHO}$ $+ 0.06\text{CH}_4 + 0.06\text{H}_2 + 0.33\text{CO} + 0.23\text{HO}_2$ $+ 0.095\text{OH} + 0.215\text{CH}_3\text{O}_2$	6.50E-15	-1,900	1
108	$\text{C}_6\text{H}_6 + \text{OH} \rightarrow 0.64\text{ARO}_2$	2.47E-12	-207	6
109	$\text{C}_7\text{H}_8 + \text{OH} \rightarrow 0.76\text{ARO}_2$	1.81E-12	355	6
110	$\text{ARO}_2 + \text{NO} \rightarrow \text{CH}_3\text{COCHO} + \text{R}_2\text{CHO} +$ $\text{HO}_2 + \text{NO}_2$	4.87E-12	180	7
111	$\text{R}_2\text{CHO} + \text{OH} \rightarrow \text{R}_2\text{COO}_2$	3.00E-11	0	7
112	$\text{R}_2\text{COO}_2 + \text{NO} \rightarrow \text{HCOCHO} + 3\text{NO}_2 + \text{CO} +$ HO_2	4.20E-12	180	7
113	$\text{HCOCHO} + \text{OH} \rightarrow \text{HO}_2 + 2\text{CO}$	1.12E-11	0	2
114	$\text{CH}_3\text{COCHO} + \text{OH} \rightarrow \text{CH}_3\text{COO}_2 + \text{CO}$	1.70E-11	0	2
115	$\text{C}_2\text{H}_5\text{O}_2 + \text{HO}_2 \rightarrow \text{C}_2\text{H}_5\text{OOH}$	6.50E-13	650	7
116	$\text{C}_4\text{H}_9\text{O}_2 + \text{HO}_2 \rightarrow \text{C}_4\text{H}_9\text{OOH}$	6.50E-13	650	7
117	$\text{C}_6\text{H}_{13}\text{O}_2 + \text{HO}_2 \rightarrow \text{C}_6\text{H}_{13}\text{OOH}$	6.50E-13	650	7
118	$\text{RO}_2\text{COCH}_3 + \text{HO}_2 \rightarrow \text{CH}_3\text{CHO} +$ $\text{CH}_3\text{COO}_2 + \text{OH}$	6.50E-13	650	7
119	$\text{RO}_2\text{CH}_2\text{OH} + \text{HO}_2 \rightarrow \text{CH}_3\text{CHO} + \text{CH}_2\text{O} +$ $\text{HO}_2 + \text{OH}$	6.50E-13	650	7
120	$\text{ARO}_2 + \text{HO}_2 \rightarrow \text{Sink}$	6.50E-13	650	7
121	$\text{R}_2\text{COO}_2 + \text{HO}_2 \rightarrow \text{Sink}$	6.50E-13	650	7
122	$\text{C}_2\text{H}_5\text{OOH} + \text{OH} \rightarrow 0.75\text{CH}_3\text{CHO} +$ $0.75\text{OH} + 0.25\text{C}_2\text{H}_5\text{O}_2$	2.00E-11	0	7
123	$\text{C}_4\text{H}_9\text{OOH} + \text{OH} \rightarrow \text{R}_1\text{COCH}_3 + \text{OH}$	2.00E-11	0	7
124	$\text{C}_6\text{H}_{13}\text{OOH} + \text{OH} \rightarrow \text{C}_6\text{H}_{13}\text{O}_2$	3.00E-12	0	8
125	$\text{Isoprene} + \text{OH} \rightarrow \text{IsopO}_2$	2.54E-11	410	2,9
126	$\text{IsopO}_2 + \text{NO} \rightarrow .9\text{NO}_2 + .9\text{HO}_2 + 0.6\text{CH}_2\text{O}$ $+ 0.35\text{Mvk} + 0.25\text{Mac} + 0.37\text{Sink}$	4.20E-12	180	8,9
127	$\text{Isoprene} + \text{O}_3 \rightarrow 0.8\text{CH}_2\text{O} + 0.26\text{Mvk} +$ $0.67\text{Mac} + 0.19\text{CO} + 0.06\text{HO}_2 + 0.68\text{OH} +$ $0.07\text{C}_3\text{H}_6 + 0.13\text{Sink}$	1.23E-14	-2,013	8,10
128	$\text{Mvk} + \text{OH} \rightarrow \text{MvkO}_2$	4.13E-12	452	2
129	$\text{MvkO}_2 + \text{NO} \rightarrow 0.92\text{NO}_2 + 0.66\text{CH}_3\text{COO}_2$ $+ 0.66\text{CH}_3\text{CHO} + 0.26\text{HO}_2 + 0.26\text{CH}_2\text{O} +$ $0.26\text{CH}_3\text{COCHO} + 0.08\text{Sink}$	4.20E-12	180	8,9

Table 2.1. Chemical reaction mechanism for LLNL two-dimensional model.

(a) Thermal Reactions $\left(\text{Arrhenius rate constant expression } k = A \cdot \exp\left(\frac{-E}{RT}\right) \right)$				
No.	Reaction	A	-E/R	Reference
130	Mvk + O ₃ → 0.5CH ₂ O + 0.21HO ₂ + 0.15CH ₃ CHO + 0.15CH ₃ COO ₂ + 0.5CH ₃ COCHO + 0.2CO + 0.06H ₂	4.00E-15	-2,000	10
131	Mac + OH → 0.5MacRO ₂ + 0.5Sink	1.86E-11	175	2,9
132	MacRO ₂ + NO → 0.92NO ₂ + 0.92HO ₂ + 0.92CH ₂ O + 0.15CH ₃ COCHO + 0.77CO + 0.85Sink	4.20E-12	180	8,9
133	Mac + O ₃ → 0.65CH ₂ O + 0.36HO ₂ + 0.5CH ₃ COCHO + 0.35CO + 0.06H ₂ + 0.15CH ₃ O ₂	4.40E-15	-2,500	10
134	RO ₂ CH ₂ OH + NO → CH ₃ CHO + CH ₂ O + HO ₂ + NO ₂	4.20E-12	180	7
135	C ₂ H ₆ + Cl → HCl + C ₂ H ₅ O ₂	7.70E-11	-90	1
136	C ₃ H ₈ + Cl → HCl + 0.5C ₂ H ₅ O ₂ + 0.5C ₄ H ₉ O ₂	1.40E-10	40	1

¹Units are cm³/molecule-sec.²Unit is degrees Kelvin.³fa = 2(1 - fb)⁴fb = $\frac{a O_2}{(1 + a O_2)}$, where a = 5.4 · 10⁻²⁰**(b) Three-body reactions (special rate constant expressions such as Troë equation)**

Number	Reaction	Reference
1	O + O ₂ → O ₃	1
2	H + O ₂ → HO ₂	1
3	HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	1
4	HO ₂ + HO ₂ + H ₂ O → H ₂ O ₂ + O ₂ + H ₂ O	1
5	NO ₂ + NO ₃ → N ₂ O ₅	1
6	N ₂ O ₅ → NO ₂ + NO ₃	1
7	OH + NO ₂ → HNO ₃	1
8	OH + HNO ₃ → H ₂ O + NO + O ₂	1
9	OH + HNO ₃ → H ₂ O + NO ₂ + O	1
10	HO ₂ + NO ₂ → HNO ₄	1
11	HNO ₄ → HO ₂ + NO ₂	1
12	ClO + NO ₂ → ClONO ₂	1
13	CO + OH → H + CO ₂	1
14	N ₂ O ₅ → 2HNO ₃	1
15	ClONO ₂ → HNO ₃ + HOCl	1
16	ClO + ClO → Cl ₂ O ₂	1
17	ClOO → Cl + O ₂	1
18	Cl ₂ O ₂ → Cl ₂ + O ₂	1
19	BrO + NO ₂ → BrONO ₂	1
20	CH ₃ O ₂ + NO ₂ → CH ₃ O ₂ NO ₂	1
21	CH ₃ O ₂ NO ₂ → CH ₃ O ₂ + NO ₂	1
22	CH ₃ COO ₂ + NO ₂ → CH ₃ COO ₂ NO ₂	4
23	C ₂ H ₄ + OH → C ₂ H ₅ O ₃	1
24	C ₅ H ₁₂ + OH → 0.25C ₂ H ₅ O ₂ + 0.66C ₄ H ₉ O ₂ + 0.31C ₆ H ₁₃ O ₂	6
25	R ₁ COCH ₃ + OH → RO ₂ COCH ₃	6

Table 2.1. Chemical reaction mechanism for LLNL two-dimensional model.

(b) Three-body reactions (special rate constant expressions such as Troë equation)

Number	Reaction	Reference
26	$C_3H_6 + OH \rightarrow RO_2CH_2OH$	2
27	$C_2H_2 + OH \rightarrow HCOCHO + OH$	2
28	$CH_3COO_2NO_2 \rightarrow CH_3COO_2 + NO_2$	4
29	$C_2H_2 + Cl \rightarrow Sink + Cl$	1
30	$C_4H_{10} + OH \rightarrow 0.28C_2H_5O_2 + 0.59C_4H_9O_2 + 0.18C_6H_{13}O_2$	6

(c) Photolysis Reactions

No.	Reaction	Reference
1.	$O_2 + hv \rightarrow O + O$	1 in Herzberg continuum, 11 in Schumann-Runge band
2.	$O_3 + hv \rightarrow O + O_2$	1
3.	$O_3 + hv \rightarrow O(^1D) + O_2$	1
4.	$H_2O_2 + hv \rightarrow 2OH$	1
5.	$H_2O + hv \rightarrow H + OH$	1
6.	$NO_2 + hv \rightarrow NO + O$	1
7.	$N_2O + hv \rightarrow N_2 + O(^1D)$	1
8.	$NO + hv \rightarrow N + O$	11
9.	$NO_3 + hv \rightarrow NO_2 + O$	1
10.	$NO_3 + hv \rightarrow NO + O_2$	1
11.	$N_2O_5 + hv \rightarrow NO_2 + NO + O_2$	1
12.	$N_2O_5 + hv \rightarrow 2NO_2 + O$	1
13.	$HNO_3 + hv \rightarrow OH + NO_2$	1
14.	$HNO_4 + hv \rightarrow OH + NO + O_2$	1
15.	$HNO_4 + hv \rightarrow OH + NO_2 + O$	1
16.	$ClO + hv \rightarrow Cl + O$	1
17.	$ClO + hv \rightarrow Cl + O(^1D)$	1
18.	$CH_3Cl + hv \rightarrow Cl + CH_3O_2$	1
19.	$CCl_4 + hv \rightarrow 4Cl$	1
20.	$CH_3CCl_3 + hv \rightarrow 3Cl$	1
21.	$CFCl_3 + hv \rightarrow 3Cl$	1
22.	$CF_2Cl_2 + hv \rightarrow 2Cl$	1
23.	$HOCl + hv \rightarrow OH + Cl$	1
24.	$ClONO_2 + hv \rightarrow Cl + NO + O_2$	1
25.	$ClONO_2 + hv \rightarrow Cl + NO_2 + O$	1
26.	$CH_2O + hv \rightarrow CO + H_2$	1
27.	$CH_2O + hv \rightarrow H + HO_2 + CO$	1
28.	$CCl_3CF_3 + hv \rightarrow 3Cl$	1
29.	$CHF_2Cl + hv \rightarrow Cl$	1
30.	$Cl_2 + hv \rightarrow 2Cl$	1
31.	$OCIO + hv \rightarrow ClO + O$	1
32.	$ClOO + hv \rightarrow ClO + O$	1
33.	$Cl_2O_2 + hv \rightarrow Cl + ClOO$	1
34.	$BrO + hv \rightarrow Br + O$	1
35.	$HOBr + hv \rightarrow Br + OH$	1
36.	$BrONO_2 + hv \rightarrow Br + NO_2 + O$	1

Table 2.1. Chemical reaction mechanism for LLNL two-dimensional model.**(c) Photolysis Reactions**

No.	Reaction	Reference
37.	$\text{BrONO}_2 + h\nu \rightarrow \text{Br} + \text{NO} + \text{O}_2$	1
38.	$\text{HBr} + h\nu \rightarrow \text{H} + \text{Br}$	1
39.	$\text{CFCl}_2\text{CF}_3 + h\nu \rightarrow 2\text{Cl}$	1
40.	$\text{CF}_3\text{CF}_2\text{Cl} + h\nu \rightarrow \text{Cl}$	1
41.	$\text{CH}_3\text{Br} + h\nu \rightarrow \text{Br}$	1
42.	$\text{CF}_3\text{Br} + h\nu \rightarrow \text{Br}$	1
43.	$\text{CF}_2\text{ClBr} + h\nu \rightarrow \text{Cl} + \text{Br}$	1
44.	$\text{N}_2\text{O}_5 + h\nu \rightarrow \text{NO}_2 + \text{NO} + 2\text{O}$	1
45.	$\text{N}_2\text{O}_5 + h\nu \rightarrow 2\text{NO} + \text{O}_2 + \text{O}$	1
46.	$\text{HNO}_4 + h\nu \rightarrow \text{HO}_2 + \text{NO}_2$	1
47.	$\text{ClONO}_2 + h\nu \rightarrow \text{Cl} + \text{O} + \text{NO}_2$	1
48.	$\text{CH}_3\text{O}_2\text{NO}_2 + h\nu \rightarrow \text{CH}_3\text{O}_2 + \text{NO}_2$	1 (see HO_2NO_2)
49.	$\text{CH}_3\text{CHO} + h\nu \rightarrow \text{CH}_3\text{O}_2 + \text{CO} + \text{HO}_2$	12
50.	$\text{CH}_3\text{CHO} + h\nu \rightarrow \text{CH}_4 + \text{CO}$	12
51.	$\text{CH}_3\text{COO}_2\text{NO}_2 + h\nu \rightarrow \text{CH}_3\text{COO}_2 + \text{NO}_2$	2
52.	$\text{R}_1\text{COCH}_3 + h\nu \rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{CH}_3\text{COO}_2$	2
53.	$\text{HCOCHO} + h\nu \rightarrow 0.13\text{CH}_2\text{O} + 0.87\text{H}_2 + 1.87\text{CO}$	2
54.	$\text{CH}_3\text{COCHO} + h\nu \rightarrow \text{CH}_3\text{COO}_2 + \text{HO}_2 + \text{CO}$	2
55.	$\text{C}_2\text{H}_5\text{OOH} + h\nu \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2 + \text{OH}$	2 (see CH_3OOH)
56.	$\text{C}_4\text{H}_9\text{OOH} + h\nu \rightarrow \text{R}_1\text{COCH}_3 + \text{HO}_2 + \text{OH}$	2 (see CH_3OOH)
57.	$\text{C}_6\text{H}_{13}\text{OOH} + h\nu \rightarrow \text{R}_1\text{COCH}_3 + \text{C}_2\text{H}_5\text{O}_2 + \text{OH}$	2 (see CH_3OOH)
58.	$\text{CH}_3\text{COO}_2\text{H} + h\nu \rightarrow \text{CH}_3\text{O}_2 + \text{OH}$	2 (see CH_3OOH)
59.	$\text{R}_2\text{CHO} + h\nu \rightarrow \text{R}_2\text{COO}_2 + \text{HO}_2$	2 (see CH_3OOH)

(d) Nonstandard chemical species names used in the reaction mechanism.

Mechanism Name	Name or Chemical Formula
HNO_4	HO_2NO_2
$\text{C}_2\text{H}_5\text{O}_3$	$\text{HOCH}_2\text{CH}_2\text{O}_2$
R_1COCH_3	$\text{C}_2\text{H}_5\text{COCH}_3$
RO_2COCH_3	$\text{CH}_3\text{CH}(\text{O}_2)\text{COCH}_3$
$\text{RO}_2\text{CH}_2\text{OH}$	$\text{CH}_3\text{CH}(\text{O}_2)\text{CH}_2\text{OH}$
C_7H_8	$\text{C}_6\text{H}_5\text{CH}_3$
ARO_2	Oxidized aromatic intermediate species
R_2CHO	HCOCHCHCHO
R_2COO_2	HCOCHCHCOO_2
Isoprene	$\text{CH}_2\text{C}(\text{CH}_3)\text{CHCH}_2$
Isop O_2	Isoprene peroxy radical
Mvk	$\text{CH}_3\text{C}(\text{O})\text{CHCH}_2$
Mvk O_2	Methylvinylketone peroxy radical
Mac	$\text{CH}_2\text{C}(\text{CH}_3)\text{CHO}$
Mac RO_2	Methylacrolein peroxy radical
Sink	Surrogate for unknown reaction products

(e) List of references cited for kinetic parameters

Table 2.1. Chemical reaction mechanism for LLNL two-dimensional model.

(d) Nonstandard chemical species names used in the reaction mechanism.	
Mechanism Name	Name or Chemical Formula
1. Demore, W.B., S.P. Sander, R.F. Hampson, M.J. Kurylo, D.M. Golden, C.J. Howard, A.R. Ravishankara, and M.J. Molina, <i>Chemical kinetics and photochemical data for use in stratospheric modeling: Evaluation number 9</i> , Jet Propulsion Laboratory, California Institute Of Technology, Pasadena, CA, 1990.	
2. Atkinson, R., D.L. Baulch, R.A. Cox, R.F. Hampson, J.A. Kerr, and J. Troë, Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement III, <i>J. Phys. Chem. Ref. Data</i> , 18, 881-1097, 1989.	
3. Kirchner, F., F. Zabel, and K.H. Becker, Determination of the rate constant ratio for the reactions of the acetylperoxy radical with NO And NO ₂ , <i>Ber. Bunsenges. Phys. Chem.</i> , 94, 1379-1382, 1990.	
4. Bridier, I., F. Caralp, H. Loirat, R. Lesclaux, B. Veyret, K.H. Becker, A. Reimer, and F. Zabel, Kinetic and theoretical studies of the reactions CH ₃ C(O)O ₂ + NO ₂ + M = CH ₃ C(O)O ₂ NO ₂ + M between 248 and 393 K and between 30 and 760 torr, <i>J. Phys. Chem.</i> , 95, 3594-3600, 1991.	
5. Moortgat, G.K., B. Veyret, and R. Lesclaux, Kinetics of the reaction of HO ₂ With CH ₃ C(O)O ₂ in the temperature range 253-368 K, <i>Chem. Phys. Ltrs.</i> , 160, 443-447, 1989.	
6. Atkinson, R., Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds, <i>J. Phys. Chem. Ref. Data, Monograph No. 1</i> , 1-246, 1989.	
7. Hough, A.M., The development of a two-dimensional global tropospheric model: the model chemistry, <i>J. Geophys. Res.</i> , 96, 7325-7362, 1991.	
8. Atkinson, R., Gas-phase tropospheric chemistry of organic compounds: a review, <i>Atmos. Environ.</i> , 24a, 1-41, 1990.	
9. Paulson, S.E., R.C. Flagan, J.H. Seinfeld, Atmospheric photooxidation of isoprene part I: the hydroxyl radical and ground state atomic oxygen reactions, <i>Intl. J. Chem. Kin.</i> , 24, 79-101, 1992.	
10. Paulson, S.E., R.C. Flagan, J.H. Seinfeld, Atmospheric photooxidation of isoprene part II: the ozone-isoprene reaction, <i>Intl. J. Chem. Kin.</i> , 24, 103-125, 1992.	
11. Allen, M. and J.E. Frederick, 1982: Effective photodissociation cross sections for molecular oxygen and nitric oxide in the Schumann-Runge bands, <i>J. Atmos. Sci.</i> , 39, 2066-2075.	
12. Martinez, R.D., A.A. Buitrago, N.W. Howell, C.H. Hearn, and J.A. Joens, 1992: The near U.V. absorption spectra of several aliphatic aldehydes and ketones at 300K, <i>Atm. Env.</i> , 26A, 785-792.	

2.3.1. Description of basic mechanism

The basic photochemistry represents the tropospheric and stratospheric interactions of actinic solar flux with the individual species in the families O_x , NO_y , ClO_y , HO_y , BrO_y , as well as with CH_4 and its oxidation products. This part of the mechanism incorporates 43 transported species and 4 species for which abundance is determined through the assumption of instantaneous equilibrium. The thermal reactions considered number 103, the photolytic reactions number 47. Source gases used include NO_x , N_2O , CH_4 , CO_2 , CO , the chlorine compounds CFC-11, CFC-12, CFC-113, CFC-114, CFC-115, HCFC-22, CCl_4 , CH_3CCl_3 , CH_3Cl , and the bromine compounds CH_3Br , CF_2ClBr , and CF_3Br . Most of the thermal reaction rates were taken from the NASA Panel recommendations provided in DeMore *et al.*, 1990. However, the rate constant for $CH_4 + OH$ circulated by Vaghjiani and Ravishankara (1991) was used because it represents the most recent work. Absorption cross section information has been assembled primarily from DeMore *et al.* (1990) and Gillotay and Simon (1991a,b). Water vapor is dealt with in a unique way compared to the other chemical species. The level of water vapor is assigned its climatological value, following the specific humidity of the Oort climatology, everywhere below the tropopause. Above the tropopause, water vapor treated as a transported species; methane oxidation is its major source in this region of the atmosphere.

The photolytic loss rate constants are calculated by integrating the product of absorption coefficient, quantum yield, and solar flux over wavelength (i.e., from 175 nm to 760 nm). The exoatmospheric solar flux is from WMO, 1985. The solar flux is then calculated as a function of altitude, latitude, and season at each time step, including the effects of absorption by O_2 and O_3 and multiple molecular (Rayleigh) scattering. The absorption cross sections and quantum yields include temperature and pressure dependence where appropriate and available. The Schumann-Runge band region of the O_2 absorption is treated using the technique of Allen and Frederick (1982), modified to match the more recent lower cross sections of the O_2 Herzberg continuum region. The photolysis of NO is also treated through the parameterization technique of Allen and Frederick (1982).

The nonlinearity of the photochemistry with respect to diurnal averaging is accounted for through the calculation of individual altitude, latitude, and seasonally varying factors for each photochemical process. Full diurnal variability of each species is calculated off-line for four seasons. The factors, relating individual process rates from the full diurnal calculation to the diurnally averaged values, are then spline interpolated for each time step.

Members of the ClO_y family currently thought to play a role in the Antarctic spring, such as the ClO dimer, are included but polar stratospheric aerosol surface is not included currently. A representation of background stratospheric sulfuric acid aerosol surface is incorporated into the model, following the recommendations from the WMO, 1989 report. The reactions of N_2O_5 and $ClONO_2$ with H_2O on the aerosol surface are parameterized as first-order loss processes with rate constants determined by specified surface area density, collision frequency, and reaction probability.

2.3.2. Description of hydrocarbon mechanism

The hydrocarbon mechanism originally was adapted from Hough (1991). However, we have made many refinements. First, we removed (x) NO_2 - (y) NO from the product side of reactions. The term (x) NO_2 - (y) NO indicates that the reaction is in fact a sum of elementary reactions. The (x) and (y) represent stoichiometric coefficients. We found that the reaction of methacrolein with ozone was so fast that it was completely depleting NO in the lower troposphere during the winter months. Our solution was to rederive the

reaction to determine the steps where NO is converted to NO₂. In each of these steps, we found that the RO₂ radical responsible for the conversion was CH₃O₂. Therefore, we substituted CH₃O₂ for the -(y) NO product and allowed the NO - NO₂ conversion to occur via the CH₃O₂ + NO reaction. In reactions where NO appears as a reactant, we include the term -(y) NO in the NO mass balance differential equation. This solves the problem. Jacob and Wofsy (1988) comment that the use of (x) NO₂ - (y) NO in their boundary layer modeling of isoprene oxidation in the Amazon led to problems similar to our own. Such pseudo-products were designed for use in urban photochemical modelling applications where the NO_x levels are very high.

Also, we have added the Cl chemistry of ethane, propane, and acetylene. A one-dimensional modeling study by Singh and Kasting (1988) showed that these reactions played an important role in the destruction of non-methane hydrocarbons in the stratosphere. We observed a decrease of several orders of magnitude in the mixing ratios of these species in the stratosphere when we added these reactions to the mechanism. The products for the ethane and propane reactions are known; they are not identified for acetylene. We assume that the Cl atom catalyzes the degradation of acetylene. The carbon in acetylene is put into a sink species and thus is lost from further reaction. For ethane and propane, HCl and the appropriate peroxy radicals are formed. We have updated the isoprene chemistry using Paulson *et al.* (1992a,b) and Tuazon and Atkinson (1989; 1990a,b). Essentially, our isoprene mechanism is a condensed version of the mechanism Paulson uses in her study. The kinetic parameters are primarily from Paulson's study. Lastly, the RO₂ + HO₂ reactions have been removed from the isoprene-methylvinylketone-methacrolein chemistry; Hough originally included these reactions by analogy to CH₃O₂ + HO₂.

The kinetic parameters and photolysis data have been revised using the latest references (see Table 2.1.e). Although most of the changes are minor, the thermal decomposition of peroxyacetylnitrate (PAN) has been measured recently (Bridier *et al.*, 1991) and the values did change significantly.

2.4. Emissions and Boundary Conditions

In our modeling of the current and possible future atmospheres, we need to represent the surface (as well as atmospheric) emissions and concentrations of a number of constituents that affect tropospheric and stratospheric chemistry. This section describes the approach currently being used in the model and the uncertainties associated with emission inventories.

A great deal of evidence indicates that surface emissions and concentrations of globally important trace gases are increasing (see WMO, 1991 for an overview). During the last ten years, scientists have been measuring the concentrations and emission rates of a variety of trace species (e.g., hydrocarbons and carbon monoxide) on a regional as well as global scale. These trace gases can affect the tropospheric oxidizing capacity due to changes in the levels of ozone and hydroxyl. To quantify these effects, researchers use global atmospheric models to investigate the effects of trace species. Emission inventories and measurements of the source gases are required for the initialization as well as validation of these models. The source gas fluxes must be estimated correctly in order for the models to calculate accurate species concentrations. Discrepancies between measured and calculated species concentrations can be used to check the consistency of emissions inventories, assuming all other model parameters are correct. The emphasis up to now has been to use global models to study these effects. One goal of these studies is to investigate the impact on the troposphere—ozone, hydroxyl, and oxidizing capacity.

Efforts to measure important trace species in the atmosphere have been underway for several decades. Most of these investigations are performed at a particular place or within a small region. Typically, the vertical profiles at different sites are measured in these studies. In contrast, Fishman *et al.* (1990) have used satellite data to analyze the distribution of tropospheric ozone. A few investigators, most notably D.H. Ehhalt, J. Rudolph, H.B. Singh, and their colleagues have conducted measurement campaigns that involve airborne or shipboard platforms for gathering concentration data for a wide variety of species (e.g., ozone, peroxyacetylnitrate, and non-methane hydrocarbons). Almost all of the latitudinal distributions of the non-methane hydrocarbons that have been published in the literature were obtained during the STRAT0Z III airborne campaign. This is the only published set of experiments that have measured C₂-C₅ alkanes, C₂-C₃ alkenes, and acetylene from 70°N to 60°S and from the surface up to 12 kilometers. Singh has published some surface latitudinal distributions from shipboard measurements and some vertical profiles at high northern latitudes for species such as ozone, peroxyacetylnitrate, and non-methane hydrocarbons.

Typically, hemispheric-scale measurements of non-methane hydrocarbon species are made in the northern hemisphere. Data tend to be relatively sparse or non-existent for the southern hemisphere. Measurements for benzene and toluene are exceptionally scarce and no data have been reported for hexane. Latitudinal distributions of surface concentrations are available for the simple hydrocarbons: C₂-C₅ alkanes, C₂-C₃ alkenes, and acetylene (e.g., Singh, Viezee, and Salas, 1988; Rudolph and Johnen, 1990). Unfortunately, there is not enough global data available. Measurements are available for ethane, propane, butane, pentane, ethylene, propylene, and acetylene. Very few measurements are available for hexane, aromatics, isoprene, and terpenes. There are almost no measurements available for NMHC oxidation intermediates. Due to the low levels of NMHCs encountered in the atmosphere (ppb to ppt range), good measurements generally are difficult to obtain. Finlayson-Pitts and Pitts (1986) offer an excellent overview of measurement techniques for NMHCs.

Overall, very few papers have been published that quantify global inventories of non-methane hydrocarbon emissions. Estimates of these emission rates tend to be based on the results of global modeling assessments. Emissions databases for carbon dioxide, carbon monoxide, methane, nitrogen oxides, and CFCs are in somewhat better shape. The Global Emission Inventories Activity of the International Global Atmospheric Chemistry Project is compiling a list of inventories recommended for use in modeling studies. In their first report (Graedel *et al.*, 1993), the authors compile a listing of inventories for many different compounds including non-methane hydrocarbons. Graedel *et al.* assign qualitative ratings to the emissions inventories based on their availability and estimates of their uncertainty level:

- The CFC inventory is the only good one.
- Inventories for CO₂, CO, CH₄, NO_x, SO₂, reduced sulfur, and radon are fair.
- Overall spatial resolution of the inventories is uniformly poor.
- Overall temporal resolution of the inventories is almost uniformly poor but is good to fair for CO₂, N₂O, and CFCs.

Furthermore, they discuss the typical uncertainties that arise in volatile organic compound inventories:

- Extrapolation of emission factors generated from a small number of mid-latitude regions.

- Significant uncertainties exist in the source categories. Industrial activities have been studied the most, but large uncertainties remain in the emission factors and speciation profiles. For biomass burning, activity rates, emission factors, and speciation profiles are less adequately known. In general, biogenic processes are not well understood.

According to Graedel *et al.*, the best that can be expected in the near future for global research is an inventory extrapolated from studies in countries that are members of the Organization for Economic Cooperation and Development along with additional research from other regions. Also, compatible estimation techniques must be used. Most of the hydrocarbon inventories cited in this project are regional, but there are some global data sets as well. Piccot, Watson, and Jones (1992) have developed a volatile organic compound emission inventory comprising anthropogenic sources. The latitudinal distribution is from 80°N to 60°S on a 10° × 10° grid. There are seven lumped species for anthropogenic NMHCs included in this inventory. The NMHC sources used by Piccot *et al.* are taken from the 1985 National Acid Precipitation and Assessment Program (NAPAP) emission inventory. Graedel *et al.* note that the NAPAP inventory (developed by the EPA's Air and Energy Engineering Research Laboratory) contains the largest number of species of any regional database. Hough (1991) has developed a comprehensive non-methane hydrocarbons emissions inventory for use in his two-dimensional modeling studies. He incorporates ten emission categories for each source gas. Also, each emission category is zonally averaged and varies with latitude. The emissions of each source gas have a unique seasonal variation function. Müller (1992) has developed an inventory of surface emissions and deposition velocities for trace gases. The source categories include industrial emissions, biomass burning, plant foliage, and other natural sources. The data is gridded on a 5° × 5° scale. A summary of these three emission inventories is provided in Table 2.2. None of the inventories that have been published include oceanic sources of the NMHCs. This is due to the uncertainty about the actual formation mechanisms. The world's oceans could be a significant source of NMHCs, particularly ethylene and propylene. This would be entirely dependent on the biological activity within each oceanic region. Therefore, spatial variability in the oceanic emissions can be expected (Rudolph and Johnen, 1990).

Table 2.2. Summary of non-methane hydrocarbon emission databases referenced in the scientific literature.

Reference	Resolution	Speciation	Sources
Hough (1991)	Equal divisions in the sine of latitude (24 zones)	N ₂ O, NO _x , H ₂ , CO, CH ₄ , normal C ₂ -C ₆ alkanes, ethylene, propylene, acetylene, benzene, toluene, isoprene, and terpenes	Manmade/industrial, ruminants, vegetation, terpenes from vegetation, soils and fauna, natural wetlands, paddy fields, biomass burning, oceans, and lightning
Piccot, Watson, and Jones (1992)	10° × 10°	Paraffins (branched alkanes, alcohols, esters, and ketones); Olefins (30 straight-chained and branched olefins); Aromatics (benzene, toluene, and xylene); Formaldehyde; Other aldehydes; Other aromatics; Marginally reactive compounds (chlorofluorocarbons)	Fuelwood utilization, savanna burning, gasoline, refuse disposal, chemical manufacturing, solvent use, and agricultural deforestation

Müller (1992)	5° × 5°	CO, NO _x , SO _x , CH ₄ , Paraffins, Aromatics, Isoprene, and Terpenes	Technological sources, biomass burning, biogenic sources, and oceans

The surface boundary conditions for the ambient version of the two-dimensional model consist of fixed concentration for carbon monoxide and fluxes for methane, nitrogen dioxide, and the 11 non-methane hydrocarbons. The hydrocarbon fluxes are specified for each latitude zone in Table 2.3. Methane emissions are distributed latitudinally according to the recommendations of Fung *et al.*, 1991. The methane flux used for these calculations is obtained by determining the steady state chemical loss rate from a previous ambient model run. At this point, we have adapted Hough's (1991) NMHC inventory for use in the LLNL two-dimensional model. However, we have not implemented seasonal variations in the source gas emissions. This can lead to discrepancies between the magnitudes of the calculated and observed species distributions. Another potential source of discrepancy in the current model is the current representation of advective and diffusive transport in the troposphere. This would adversely affect short-lived species such as the NMHCs. In the current model, the diffusion coefficients are constant across all latitudes and seasons in the troposphere. We currently use diffusive transport to represent fast vertical transport processes such as convection. If the diffusivities are too low, then species will undergo very slow vertical mixing. Fast vertical transport is often implicated in explaining unusually high levels of short-lived species in the middle and upper troposphere. We plan to investigate these issues in future studies with the model.

Table 2.3. Hydrocarbon emission inventory for the LLNL two-dimensional model.

Model Zone	Latitude Center	Meth- ane	Ethane	Pro- pane	Butane	Pen- tane	Hex- ane	Ethy- lene	Pro- pylene	Ace- tylene	Ben- zene	Tol- uene	Iso- prene
1	-80.1	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00
2	-70.9	0.00	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00
3	-52.3	0.00	0.05	0.07	0.00	0.00	0.00	0.11	0.09	0.00	0.00	0.00	0.00
4	-53.1	0.15	0.13	0.16	0.03	0.03	0.05	0.25	0.21	0.01	0.02	0.05	0.00
5	-42.5	4.08	0.31	0.35	0.19	0.18	0.27	0.56	0.49	0.05	0.10	0.26	0.72
6	-30.0	18.99	1.13	0.98	0.58	0.40	0.53	1.68	1.32	0.19	0.31	0.49	12.15
7	-17.5	24.67	3.67	3.26	1.73	1.10	1.16	5.07	4.32	0.32	0.49	0.44	75.06
8	-5.7	39.25	5.82	5.34	2.81	1.87	1.90	7.95	7.07	0.36	0.55	0.44	134.82
9	5.7	42.43	5.53	5.09	2.73	1.85	1.92	7.57	6.76	0.34	0.53	0.52	128.16
10	17.5	54.99	3.73	3.22	1.85	1.20	1.37	5.21	4.30	0.43	0.69	0.82	66.60
11	30.0	81.71	2.89	2.50	2.63	2.27	3.38	4.39	3.69	0.78	1.42	3.29	19.71
12	42.5	70.41	3.15	2.93	4.12	3.92	6.03	5.05	4.64	1.11	2.15	5.89	7.83
13	53.1	57.51	1.94	1.83	2.74	2.66	4.10	3.15	2.96	0.73	1.42	4.00	2.70
14	62.3	30.00	0.49	0.44	0.55	0.50	0.77	0.77	0.67	0.16	0.30	0.76	1.82
15	70.9	15.92	0.05	0.04	0.02	0.01	0.01	0.08	0.05	0.01	0.02	0.02	0.27
16	80.1	12.77	0.03	0.02	0.01	0.01	0.01	0.05	0.03	0.01	0.01	0.01	0.16
Totals													
(Tg/yr)		452.88	28.95	26.25	20.00	16.00	21.50	41.90	36.60	4.50	8.00	17.00	450.00

These issues are raised to inform the reader about potential sources of discrepancy between model results and measurement data. For this report, however, limited resources and computer time do not allow the more complete analysis and sensitivity studies to be accomplished. The purpose of this report specifically is to investigate the effects of methane and emissions of other gases on tropospheric ozone and climate.

3. Model-derived Current Atmosphere

3.1. Introduction

In this chapter, we will focus on comparison of results from the LLNL two-dimensional model in the troposphere with available databases towards attempting to determine the validity of the existing model for tropospheric chemistry studies. Previous studies (e.g., Wuebbles *et al.*, 1991; Miller *et al.*, 1992; Kinnison, 1989) have attempted to validate the model's treatment of stratospheric processes. The primary source of data for this comparison is the STRATOZ III experiment. This is the only published study that shows meridional cross-sections for a variety of important tropospheric species. Rudolph, Vierkorn-Rudolph, and Meixner (1987) mention that the data represent a snapshot and should not be considered a global or long-term average. They also provide a detailed mission outline. The aerial measurement campaign occurred during June 1984 in cooperation between several French and German research groups. The flights covered altitudes from the surface up to 12 km and a latitude range of about 70°N to 60°S. The southbound flight path began in Bretigny, France and proceeded via Scotland, Iceland, and southern Greenland to the North American east coast and down the South American west coast to Punta Arenas, Chile. The northbound track of the flight followed the east coast of South America, crossed the Atlantic to the west coast of Africa, returned to Europe and terminated at Bretigny, France. In general, the northbound and southbound flights exhibit some differences in the distributions of the shorter-lived species due to the different origins of the air masses encountered during each leg of the flight. This implies that there is a regional variation in species distributions that can not be represented in zonally averaged two-dimensional models. Thus, we seek to compare the model results with the general features of the species distributions. All of the model distributions are values for June 22 corresponding to the time period of the STRATOZ measurements. Another feature of the STRATOZ data for the shorter-lived species is the existence of substantial concentration gradients across latitude but not necessarily altitude. One interpretation is that very fast convection processes mix these species in the vertical to wipe out altitudinal gradients and very slow meridional transport result in latitudinal gradients. Unfortunately, the various researchers involved in the study do not discuss the transport in enough detail to allow us to reach a conclusion about this issue. Also, we will compare the model surface zone concentrations of methane and carbon monoxide with data from the National Oceanic and Atmospheric Administration's Climate Monitoring Diagnostics Laboratory. In addition, we will compare tropospheric hydroxyl distributions with those calculated by a three-dimensional model used by Spivakovsky *et al.* (1990).

3.2. Methane

3.2.1. Data

The data in Figure 3.1.a are from Marenco, Macaigne, and Prieur, 1989. In general, methane concentrations are higher in the Northern Hemisphere (NH) relative to the Southern Hemisphere (SH). Below 10 km, there is a latitudinal gradient across all meridians. Also, there are some vertical gradients from 0–1 km apparent that arise from localized emission sources. Possible sources include methane releases from petroleum fields in Mexico and southern North America as well as natural emissions from the Amazonian forest. A limited impact from Rio de Janeiro is also evident. From 5–10 km between 40–60°N, there are elevated methane mixing ratios corresponding to the industrialized areas of North America. Note that ozone concentrations are elevated in this area as well (see Figure 3.4.a).

(a)

(b)

Figure 3.1. Methane meridional distribution in mixing ratio units of ppmv. (a) STRATOZ III data observed during June 1984 (Marenco, Macaigne, and Prieur, 1989). Only the northbound flight is shown. (b) LLNL two-dimensional model ambient field during June 22 (boreal summer solstice).

3.2.2. Model

The calculated methane fields shown in Figure 3.1.b compare favorably with the STRATOZ III data. Mixing ratios in the NH are higher than in the SH as observed in the STRATOZ data as well as other data sets (see WMO, 1991 for an overview). The following table shows the annual global tropospheric average concentration of methane in the model:

Region	[CH ₄] (ppmv)
Global	1.59
Northern Hemisphere	1.61
Southern Hemisphere	1.57

Furthermore, the calculated mixing ratios at all altitudes are very close to the measured values: 1.56–1.71 ppmv near the surface, approximately 1.56–1.64 ppmv in the free troposphere, and below 1.6 ppmv in the upper troposphere and lower stratosphere. Since the model is zonally averaged, the effects due to localized sources observed in STRATOZ can not be represented in our distributions. We do show a latitudinal gradient below 12 km in the SH. This meridional gradient is more evident in the SH than NH. However, a latitudinal gradient from the equator to 50°N is found between 2–12 km.

The data do exhibit some longitudinal variability. This is probably due to regional sources and fast transport processes. The model cannot represent such variations. One reason is that the model is zonally averaged. Another reason has to do with the current transport formulation. No convective processes are included in the model. Such transport is modeled by diffusive processes. Since the diffusivities do not vary by latitude or season in the troposphere, there is currently no way to address such transport processes. The observed fields indicate that fast vertical mixing tends to occur in certain latitude bands and that horizontal mixing is much slower in the troposphere. Unfortunately, none of these studies discussed the transport phenomena encountered during the flights in great detail. In order to address these concerns, we would have to modify our diffusivities by reducing the K_{yy} coefficients (slower horizontal mixing) and increasing the K_{zz} coefficients (faster vertical mixing). Seasonal variations will also have to be considered.

3.2.3. Surface Concentrations

We wish to examine our methane surface concentrations by comparing them against data in order to ascertain whether our boundary conditions are correct. Figure 3.1.c shows the annual mean mixing ratios of methane for our model as well as from the Climate Monitoring and Diagnostics Laboratory (CMDL) sampling network. The measurements are taken from the CMDL annual report (CMDL, 1992). These are flask samples collected in the remote troposphere (marine boundary layer) from 1984–1991. The data clearly indicate the well-documented increasing trend in methane and the hemispheric difference in mixing ratios. Although the shape of our model's calculated distribution appears to be substantially in agreement with the data, the magnitudes of the concentrations are not the same. This is a result of our methane surface emission rate not being in balance with the atmospheric chemical loss rate. We discovered the problem after the runs for this report were completed. Test runs using an updated version of the two-dimensional model without the non-methane hydrocarbon chemistry did not exhibit this problem. We are in the process of adding the higher hydrocarbon chemistry to the updated model in order to correct the discrepancy.

Figure 3.1.c. Annual mean mixing ratios of methane in units of ppmv. The data for LLNL are ambient surface zone (0–1.5 km) results obtained with the two-dimensional model. The data labelled 1984–1990 are marine boundary layer measurements from the National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory (CMDL, 1991)

3.3. Carbon Monoxide

3.3.1. Data

The data in Figure 3.2.a are from Marenco, Macaigne, and Prieur, 1989. Marenco's data include samples taken in the boundary layer over polluted South American cities where combustion sources contribute to the CO levels observed. Carbon monoxide levels are higher in the NH relative to the SH. The data indicate a significant latitudinal gradient in middle to high northern latitudes from 1–11 km. This was caused by: polluted air masses that originated from continental areas; twelve days elapsed between flights over northern latitudes (June 4–6 & 18–24); the carbon monoxide distribution exhibited a longitudinal variation. Also, the data reveal a vertical gradient in the NH from 0–2 km indicating the presence of surface sources. From 5–10 km between 40–60°N, the elevated carbon monoxide levels correspond to industrial North American emissions. There are higher levels of ozone (see Figure 3.4.a) in this region. This implies a photochemical origin for the elevated ozone levels.

(a)

(b)

Figure 3.2. Carbon monoxide meridional distribution in mixing ratio units of ppbv. (a) STRATOZ III data observed during June 1984 (Marenco, Macaigne, and Prieur, 1989).

Only the northbound flight is shown. (b) LLNL two-dimensional model ambient field during June 22 (boreal summer solstice).

3.3.2. Model

Carbon monoxide in ambient atmosphere shows good agreement overall with the results obtained during the STRAT0Z III experiment. As shown in Figure 3.2.b, calculated CO mixing ratios are higher throughout all altitudes in the Northern Hemisphere than in the Southern Hemisphere, as shown in the STRAT0Z data. The following table shows the annual global tropospheric average concentration of carbon monoxide in the model:

Region	[CO] (ppbv)
Global	67.1
Northern Hemisphere	90.8
Southern Hemisphere	43.2

A vertical gradient exists from the surface up to 8 km in the NH. However, the latitudinal gradients observed in the data are not a feature of the calculated distribution. This may be due to zonal averaging. Below 12 km, the vertical gradients are much steeper in the NH than in the SH. This is probably due to higher hydroxyl abundances in the summertime (i.e., northern) hemisphere (see Figure 3.3.a).

3.3.3. Surface Concentrations

In this section, we examine our derived carbon monoxide surface concentrations in comparison with available data. Figure 3.2.c shows the annual mean mixing ratios of carbon monoxide for our model as well as from the Climate Monitoring and Diagnostics Laboratory (CMDL) sampling network. The measurements are taken from the CMDL annual report (CMDL, 1992). These are flask samples collected in the remote troposphere (marine boundary layer) during 1991. The data indicate a hemispheric difference in mixing ratios. Unfortunately, the dataset is very sparse relative to the methane measurements. Also, the station at 36°N (mixing ratio ~230 ppbv) is affected by regional anthropogenic trace gas sources. In the tropics, the shape and magnitude of our model's calculated distribution appears to be substantially in agreement with the limited data.

Figure 3.2.c. Annual mean mixing ratios of carbon monoxide in units of ppbv. The data for LLNL are ambient surface zone (0–1.5 km) results obtained with the LLNL two-dimensional model. The data for 1991 are marine boundary layer measurements from the National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory (CMDL, 1991).

3.4. Hydroxyl

Due to the difficulty of measuring hydroxyl radicals, there are no published measurements of meridional distributions with which to compare the model results. Therefore, we must use indirect methods as well as comparison to other models to determine whether the OH fields are reasonable. Our OH field for June 22 is shown in Figure 3.3.a. The strong horizontal gradients with no vertical gradient below 60°S are a result of the SH being in winter solstice (June 22). The calculated diurnally averaged surface concentrations are the correct order of magnitude—approximately 1×10^6 molecules per cubic centimeter—as indicated by various OH measurements (e.g., Hofzumahaus *et al.*, 1991). The following table shows the annual global surface average concentration of hydroxyl in the model:

Region	[OH] (molecules/cm ³)
Global	1.20×10^6
Northern Hemisphere	1.11×10^6
Southern Hemisphere	1.29×10^6

Figure 3.3.a. Hydroxyl meridional distribution in units of molecules/cm³. LLNL two-dimensional model ambient field during June 22 (boreal summer solstice).

The methyl chloroform lifetime in this ambient atmosphere is 5.5 years, which is well within the 5.7 (+0.7, -0.6) years deduced by Prinn *et al.*, 1992 based on measurements of CH₃CCl₃. Observations of CH₃CCl₃ are used to assess the globally and annually integrated OH concentration because reaction with OH is the dominant sink and methyl chloroform emissions are documented by industry. Furthermore, our global average tropospheric hydroxyl concentration is 8.29×10^5 molecules/cubic centimeter as compared to the value calculated by Prinn *et al.* of $(8.7 \pm 1.0) \times 10^5$ molecules/cubic centimeter. Prinn *et al.* also state that if the methyl chloroform oceanic loss rate is included in the calculation, their calculated hydroxyl concentration drops to $(8.1 \pm 0.9) \times 10^5$ molecules/cubic centimeter. This is in good agreement with our result. Spivakovsky *et al.* (1990) calculated the three-dimensional global distribution of hydroxyl over an annual cycle using a parameterization scheme. The zonally-averaged hydroxyl distributions from their study are shown in Figure 3.3.b. The hydroxyl concentrations are highest over the tropics and over midlatitudes in the summer hemisphere. Calculation of hydroxyl was not performed for the polar night regions, for the stratosphere, and for altitudes below the surface (e.g., Antarctica). The methyl chloroform lifetime for their model is 5.5 years. This is in agreement with our calculated lifetime. For comparison, ambient hydroxyl distributions for our model are depicted in Figure 3.3.c. Hydroxyl concentrations are highest over the tropics and over midlatitudes in the summer hemisphere. The range of concentrations is also the same. However, a significant difference is that our profiles indicate much greater vertical mixing in the troposphere than the model used by Spivakovsky *et al.* This points out the difference in dynamical formulations used by each model. Of course, other differences play a role as well:

- Two-dimensional versus three-dimensional representation of the troposphere
- Detailed chemical model versus parameterized hydroxyl scheme

The following table shows the annual global tropospheric average concentration of hydroxyl in the model:

Region	[OH] (molecules/cm ³)
Global	8.29×10^5
Northern Hemisphere	7.78×10^5
Southern Hemisphere	8.78×10^5

The average hydroxyl concentration in the SH is higher relative to the NH. This may occur because the concentration of key gases such as methane and carbon monoxide, which are important sinks for hydroxyl, is lower. This difference between the two hemispheres also has been reported by Brenninkmeijer *et al.*, 1992. They measured atmospheric ¹⁴CO and have inferred that OH abundances may be significantly higher in the SH than in the NH.

Figure 3.3.b. Plot of the zonally-averaged ambient hydroxyl distribution during January, April, July, and October from the three-dimensional model used by Spivakovsky *et al.* (1990). The concentration is in units of 10^5 molecules/cm³.

Figure 3.3.c. Plot of the ambient hydroxyl distribution during January, April, July, and October from the LLNL two-dimensional model. The concentration is in units of 10^5 molecules/cm³.

3.5. Ozone

3.5.1. Data

The data in Figure 3.4.a are from Marenco and Said, 1989. Ozone levels in the NH are higher than in the SH. Marenco and Said calculate a mean ozone concentration for each hemisphere as:

Hemisphere	Mixing Ratio (ppbv)
Northern	50-60
Southern	25-30

Figure 3.4. Ozone meridional distribution in mixing ratio units of ppbv. (a) STRATOZ III data observed during June 1984 (Marenco and Said, 1989). Only the southbound

flight is shown. (b) LLNL two-dimensional model ambient field during June 22 (boreal summer solstice).

Essentially, the average NH concentration is twice that in the SH. In the lower troposphere over the tropics, the decreased ozone mixing ratios up to the tropopause indicate a sink for this species. The sink is localized to the lower layers but is also perceptible up to the stratosphere, which corresponds to a region of very important vertical air ascents. In the NH, a latitudinal gradient is apparent. Elevated ozone concentrations occur over mid-latitudes (40–60°N) in the middle to upper troposphere (5–10 km). This region corresponds to highly industrialized regions of North America where elevated methane and carbon monoxide mixing ratios are found (see Figures 3.1.a and 3.2.a). This implies that the ozone may be produced by photochemistry, but a contribution via stratospheric injection can not be ruled out. In the SH, the ozone distribution is much more homogeneous and constant.

3.5.2. Model

Ozone in the ambient model run shows very good agreement overall with the STRATOZ measurements. Figure 3.4.b depicts a meridional plot of our calculated ozone mixing ratios. From the surface up to 12 km, the calculated mixing ratios are slightly higher in the NH relative to the SH just as the observations indicate. In addition, the calculated mixing ratios are roughly the same as the measurements in this altitude range. Ozone levels in the troposphere and lower stratosphere over the tropics are lower than in either hemisphere. Above 12 km, the calculated ozone mixing ratios exceed 200 ppbv, as the measurements also indicate. Over the middle and high latitudes of both hemispheres, the isolines are fairly homogeneously stratified. Mixing ratios at a given altitude remain fairly constant over these latitudes. Significant latitudinal gradients become evident as we approach the low latitudes and tropics from either hemisphere. The elevated concentrations observed near North America during STRATOZ III are not represented because of zonal averaging. The following table shows the annual global tropospheric average concentration of ozone in the model:

Region	[O ₃] (ppbv)
Global	67.2
Northern Hemisphere	73.7
Southern Hemisphere	60.8

Our average mixing ratios for each hemisphere are higher than the values calculated by Marengo and Said. This may be due to the fact that our model domain's tropopause heights (approximately 8 km over the poles and 15 km over the tropics) are higher than those determined by the authors. Their tropopause height during the experiment appears to be 10–12 km.

3.6. Nitrogen oxides

3.6.1. Data

The STRATOZ III data for the nitrogen oxides (NO + NO₂) are from Ehhalt and Drummond, 1988. The authors averaged all the data into a grid that measures 1 km altitude by 10° latitude. They filtered the data to remove excursions by using a special averaging procedure and excluded the high values measured in the boundary layer. The authors did this to prevent the propagation of the high boundary layer values into the layer between 1–2 km. Nitrogen oxides (NO_x) were calculated from the original nitric oxide distribution by using simultaneously measured ozone concentrations and calculated nitrogen dioxide photolysis rates. These photolysis rates were partially

verified experimentally because photon flux from below was monitored during the flights. The nitric oxide distribution does not provide a quantitative mapping of the sources because it is not a conserved quantity because it interconverts so quickly into nitrogen dioxide. Therefore, NO_x is a much better conserved tracer. The overall pattern of the NO_x distribution closely resembles that of nitric oxide.

As shown in Figure 3.5.a, NO_x in the SH is generally lower than in the NH. A trough of higher NO_x mixing ratios is apparent in the upper troposphere (> 7 km) from 60°N-20°S. This exceeds the concentrations in the middle troposphere and suggests large scale input of NO_x into the upper troposphere. Ehhalt and Drummond note the following about possible NO_x sources in the upper troposphere:

- Downward stratospheric flux appears to be minor in this experiment.
- Nitric oxide emissions from high-flying aircraft were minimal because the flights (for the most part) did not travel along commercial air routes.
- The major sources appear to be: fast upward transport of NO_x from the boundary layer by deep convection; continental sources; and lightning.

(a)

(b)

Figure 3.5. NO_x meridional distribution in mixing ratio units of pptv. (a) STRATOZ III data observed during June 1984 (Ehhalt and Drummond, 1988). This graph combines the distributions from both flights. The number in each grid cell corresponds to the average mixing ratio for that box. (b) LLNL two-dimensional model ambient field during June 22 (boreal summer solstice).

Lower concentrations are encountered in the middle troposphere (2–8 km). The latitudinal gradient above 2 km over middle and high southern latitudes is due to winter in the SH. Middle to high northern latitudes from 1–4 km have higher NO_x mixing ratios relative to 0–30°N. This is due to the influence of continental NO_x sources in industrialized regions of North America. The peak from 1–2 km over 20–40°S arises because the flight paths were over continental areas. Routes over the same latitude range in the NH were over ocean (southbound) and off the west African coast (northbound). These flights encountered air masses influenced by marine conditions.

3.6.2. Model

The model's NO_x distribution is in substantial agreement with the STRATOZ data published by Ehhalt and Drummond, 1988. Concentrations of NO_x in the Northern Hemisphere are higher relative to the Southern Hemisphere throughout the troposphere as shown in Figure 3.5.b. In the upper troposphere (≥ 10 km), a trough of elevated NO_x mixing ratios that exceeds those in the middle troposphere extends from 90°N to ~30°S. Nitrogen oxide concentrations in the middle troposphere (2–8 km) from 90°N–30°S range from 10–20 pptv, which is less than the levels found in the upper tropospheric trough. Since it is winter in the SH, a latitudinal gradient above 2 km from middle to high southern latitudes exists. From 1–4 km, NO_x mixing ratios are higher over 30°N–70°N relative to 0–30°N. This effect on the NO_x distributions results because we include industrial emissions in the NH and indicates that we are correctly modeling these sources. The NO_x peak below 2 km from 25–50°S suggests that we are also representing

SH emissions correctly. The following table shows the annual global tropospheric average concentration of nitrogen oxides in the model:

Region	[NO _x] (pptv)
Global	53.1
Northern Hemisphere	55.7
Southern Hemisphere	50.6

3.7. Ethane

3.7.1. Data

The ethane distribution data in Figure 3.6.a are from Rudolph, 1988. Over middle to high northern latitudes, ethane mixing ratios are approximately 1.5–2 ppbv below 10 km. During the northbound flights below 50°N, ethane concentrations are less than 1–1.5 ppbv at all altitudes. This is due to air masses originating from lower latitudes over the Atlantic Ocean. During southbound flights over this same region, ethane mixing ratios are about 1.5–2 ppbv as a result of air masses originating over North and Central America. Ethane concentrations in the SH are about a factor of 5 lower in general than in the NH. In the SH, there is a definite latitudinal gradient (decreasing) in ethane from the equator towards 90°S. Above 10 km over high latitudes in each hemisphere, there is a decrease in the mixing ratios (< 0.7 ppbv). There are a few isolated maxima found over the equator at a few kilometers altitude (northbound: 2–3 km; southbound: 1–2 km) ranging from ~1.5–2 ppbv. This indicates the presence of ethane sources at low latitudes, such as biomass burning. These elevated levels are much less pronounced than at middle to high northern latitudes where ethane mixing ratios remain rather uniform at ~1.5 ppbv.

(a)

(b)

Figure 3.6. Ethane meridional distribution in mixing ratio units of ppbv. (a) STRAT0Z III data observed during June 1984 (Rudolph, 1988). Both flights are shown. (b) LLNL two-dimensional model ambient field during June 22 (boreal summer solstice).

3.7.2. Model

The ethane distributions calculated by the model agree pretty well with the general features of the STRAT0Z data. As shown in Figure 3.6.b, the ethane concentrations in the NH are higher than in the SH at all altitudes. The difference in the mixing ratios is less than a factor of two. From middle to high northern latitudes, the ethane concentrations range from about 1–1.5 ppbv below 4 km. However, there is a steady decrease in the concentration with increasing altitude. We do not see fairly constant values below 10 km as in the STRAT0Z data. Over middle to high southern latitudes, ethane mixing ratios are about 0.5–0.8 ppbv below 4 km. There is a steady decrease with altitude, but the change is much slower than in the NH. The elevated levels of ethane between 30°S–30°N correspond to the area where the highest surface emissions in our model occur and are transported vertically very quickly by equatorial upwelling. Above 10 km in the upper troposphere, ethane levels are less than ~0.3 ppbv over middle to high latitudes and less than ~0.7 ppbv from 30°S–30°N. The highest surface concentrations are found in the tropics (1.4–2.0 ppbv) and middle northern latitudes (~1.4–1.5 ppbv). This occurs because our highest emission rates are in the tropics and the second largest in middle northern latitudes. Although we do not have a seasonal variation in the emissions, this may only be part of the discrepancy. Since STRAT0Z III covered a particular longitudinal region, we can not determine on a global basis whether the strongest sources are located in middle northern latitudes or the tropics. Further study is required. Certainly, the difference is essentially related to the zonal averaging involved in a two-dimensional model. The following table shows the annual global tropospheric average concentration of ethane in the model:

Region	[C ₂ H ₆] (ppbv)
Global	0.812
Northern Hemisphere	0.954
Southern Hemisphere	0.670

3.8. Propane

3.8.1. Data

The data in Figure 3.7.a are from Rudolph, 1988. The propane mixing ratios in the SH are about a factor of ten lower than in the NH. Propane mixing ratios decrease northward of 50°N. This is most evident in the southbound flights. Below 50°N, concentrations range from 0.3–0.5 ppbv for the southbound flights. The air masses encountered during these flights originated over North and Central America. For the northbound flights, propane mixing ratios range from 0.1–0.3 ppbv. In this case, the air masses originated in lower latitudes over the Atlantic Ocean. There is a definite latitudinal gradient (decreasing) in the SH going from the equator to the pole. Above 10 km over the high latitudes in each hemisphere, there is a decrease in propane levels to below 0.1 ppbv. Over the equator there is an isolated propane maximum ≥ 0.5 ppbv at 1–2 km during the southbound flights and at 3–6 km during the northbound flights. This indicates the existence of sources at low latitudes such as biomass burning. Below 2 km, the peak values of 0.3–0.5 ppbv are found from 20°S–30°N during southbound flights and (albeit weakly) over northern midlatitudes during northbound flights.

(a)

(b)

Figure 3.7. Propane meridional distribution in units of pptv. (a) STRAT0Z III data observed during June 1984 (Rudolph, 1988). Both flights are shown. (b) LLNL two-dimensional model ambient field during June 22 (boreal summer solstice).

3.8.2. Model

The propane distributions calculated by the model agree fairly well with the general characteristics of the STRAT0Z data. The model distribution of propane is shown in Figure 3.7.b. Over middle to high latitudes in either hemisphere the distribution does not indicate a strong latitudinal gradient. Instead, the isolines are horizontally stratified. This difference from the data is due to zonal averaging. The propane mixing ratios in the NH are higher than in the SH, but the difference is less than a factor of two. Peak values (> 0.2 ppbv) below 2 km found in the tropics are fairly symmetric around the equator. Slightly lower levels (~ 0.2 ppbv) are found in northern middle latitudes. The STRAT0Z data are not conclusive about where to expect peak values exactly, but the model does seem to agree with the measurements. For the reasons set forth earlier, the model can not represent the "isolated maxima" seen in STRAT0Z III. Above 10 km over high latitudes in each hemisphere, propane mixing ratios are less than 0.2 ppbv. Between 30°S – 30°N , propane levels are higher relative to either hemisphere. This occurs because the model's largest surface emissions are found here and the rapid vertical motion afforded by the tropical upwelling transports the emitted gas. The following table shows the annual global tropospheric average concentration of propane in the model:

Region	[C ₃ H ₈] (pptv)
Global	28.4
Northern Hemisphere	47.2
Southern Hemisphere	9.59

3.9. Acetylene

3.9.1. Data

The data in Figure 3.8.a are from Rudolph, 1988. The highest acetylene mixing ratios (~ 100 to ≥ 300 pptv) over middle to high northern latitudes from the surface to eleven km agrees with the geographic distribution of the chief source: car exhaust. During the southbound flights, substantially elevated acetylene levels (> 300 pptv) at low altitudes (< 2 km) from 10°S – 30°N were encountered. Also, acetylene mixing ratios decrease by nearly an order of magnitude ($300 \rightarrow 30$) toward higher southern latitudes below 4 km. South of 35°S , the acetylene levels range from 10–30 pptv. This coincides with a change in the origin of air masses from continental to marine regions. The northbound flights overflew the South American and west African coasts. During these legs of the flights with prevailing offshore winds, elevated acetylene concentrations were found below 2 km. Rudolph suggests that a possible source at these low latitudes may be biomass burning or perhaps car exhaust emanating from the more densely populated coastal areas of tropical Africa and South America. This is a great example of the existence of longitudinal variability in the STRAT0Z experiment and the inherent limitation of comparing zonally averaged distributions with these measurements. Above 4 km, there is a definite latitudinal gradient as concentrations drop an order of magnitude from the high latitudes of the NH to those of the SH.

a)

((b))

Figure 3.8. Acetylene meridional distribution in mixing ratio units of pptv. (a) STRAT0Z III data observed during June 1984 (Rudolph, 1988). Both flights are shown. (b) LLNL two-dimensional model ambient field during June 22 (boreal summer solstice).

3.9.2. Model

The acetylene distributions calculated by the model are in overall agreement with the general features of the STRAT0Z data. The model distribution of acetylene is shown in Figure 3.8.b. Over middle to high northern latitudes, acetylene mixing ratios range from 100–200 pptv from 0–4 km, 20–100 pptv from 4–10 km, and < 20 pptv above 10 km. Values greater than 100 pptv above 4 km are not encountered as in STRAT0Z III, but the upper troposphere measurements (< 30–50 pptv) do agree. From 10°S–30°N, acetylene mixing ratios range from 50–100 pptv below 2 km. The peak encountered in southbound flights is not indicated in the model distribution. This peak in the data must be attributed to continental air masses from South America blowing out to the Pacific Ocean. Above 30° in either hemisphere, acetylene decreases steadily with altitude and there is no significant latitudinal gradient. A latitudinal gradient is really evident only between 30°N–30°S. In this same region, there is a pocket of elevated acetylene levels above 9 km. The model distribution does not show an order-of-magnitude drop below 4 km from middle to high southern latitudes; mixing ratios fall about a factor of two from 50 pptv to 25 pptv. Recall that this feature was observed during the southbound flight. The discrepancy may be due to the lack of seasonal variation in the emission rates. The decrease in acetylene concentrations from the NH to the SH is not a full order of magnitude at all altitudes because of the homogeneous stratification of the isolines above 30° in either hemisphere. Depending on the altitude, the differences are factors of two, three, or ten. The following table shows the annual global tropospheric average concentration of acetylene in the model:

Region	[C ₂ H ₂] (pptv)
Global	48.9
Northern Hemisphere	80.1
Southern Hemisphere	17.7

3.10. Peroxyacetylnitrate

3.10.1. Data

The data in Figure 3.9.a are from Rudolph, Vierkorn-Rudolph, and Meixner, 1987. The authors state that the number of measurements are limited because of a temporary malfunction in the measurement apparatus. Since the peroxyacetylnitrate (PAN) lifetime in the middle and upper troposphere is fairly long, they expect that the data should show the most prominent features of its distribution. In the SH, PAN concentrations range from 7–10 pptv below 10 km. During southbound flights, the mixing ratios are greater than 10 pptv from 2–8 km over low southern latitudes. These elevated mixing ratios coincide with the areas where air masses are continentally influenced. In the NH, a substantial latitudinal gradient is observed. The authors note that PAN levels were considerably higher during flights along the east coast of North America relative to flights along the west African coast. This probably reflects the impact of North America's large industrial areas since the air masses originated there. The implication is that there should be longitudinal variations in PAN that can not be addressed by a two-dimensional model. Peak values are observed from 4–10 km over middle to high northern latitudes.

(a)

(b)

Figure 3.9. Peroxyacetylnitrate meridional distribution in mixing ratio units of pptv. (a) STRATOZ III data observed during June 1984 (Rudolph, Vierkorn-Rudolph, and Meixner, 1987). Only the southbound flight is shown. (b) LLNL two-dimensional model ambient field during June 22 (boreal summer solstice).

3.10.2. Model

The PAN distributions calculated by the model agree pretty well with the general features of the STRATOZ data. The model distribution of PAN is shown in Figure 3.9.b. Peroxyacetylnitrate mixing ratios are much higher in the NH relative to the SH. This is due to the greater abundance of PAN precursors in the NH. In the SH below 10 km the PAN mixing ratios range from 10–70 pptv. There is a substantial latitudinal gradient in the NH from 2–12 km. The peak values are observed over the middle to high northern latitudes from 1–12 km. Thus, the model is substantially in agreement with the main features of the data. However, the model does tend to calculate higher mixing ratios in the SH than indicated by the data. Recall that the NMHC emissions in the model do not possess a seasonal variation. Since the NMHCs are PAN precursors, this probably helps to account for the fact that PAN is somewhat higher than the observations in the SH because the emissions are lower in the winter. The following table shows the annual global tropospheric average concentration of peroxyacetylnitrate in the model:

Region	[PAN] (pptv)
Global	59.8
Northern Hemisphere	75.6
Southern Hemisphere	44.0

4. Perturbations

4.1. Effects of Increasing Methane Emissions

We have assembled four scenarios to investigate the effects of methane emission perturbations and artificially low surface NO_x concentrations on the ambient atmosphere:

Scenario	Description	Methane Emission (Teragrams/yr)
	Ambient	452.9
1	50% Increase	679.3
2	100% Increase	905.8
3	Low NO _x	452.9
4	Low NO _x & 50% Increase	679.3

The ambient atmosphere is listed in order to indicate the basis for the methane global surface flux in each scenario. For the low nitrogen oxides scenarios, we have fixed NO_x (NO+NO₂) mixing ratios at the surface to 20 parts per trillion by volume (pptv). We seek to understand how trace species distributions are affected under "clean" conditions. The photostationary state relation is used to calculate the mixing ratios of NO and NO₂:

$$\frac{[NO]}{[NO_2]} = \frac{j(NO_2)}{k_{NO}[O_3]} \quad (1)$$

We calculate the ratio on the right hand side of the equation in every latitude zone for each season, average the results, and subsequently obtain the surface mixing ratios for each species. Since the photostationary state relation is applied only at the surface, any error would be confined there. Both Chameides *et al.* (1990) and Ridley *et al.* (1992) mention that the photostationary state relation holds quite well in polluted atmospheres because O₃ and NO levels are very high. Furthermore, both groups state that peroxy radicals must be taken into consideration in clean air. The chemical mechanism used in the model includes peroxy radical chemistry. Since the LLNL two-dimensional model is diurnally- and zonally-averaged, it will provide an average representation of polluted and clean regions. In the real atmosphere, emissions of nitrogen oxides are spatially and temporally heterogeneous (e.g., NO_x concentrations differ by several orders of magnitude between continental and marine regions).

Our examination of these scenarios is directed especially toward analyzing the effects on tropospheric hydroxyl and ozone. An understanding of the overall chemistry provides us with a guide to validating (albeit qualitatively) and interpreting the results obtained for each scenario. Wuebbles and Tamareis (1993) discuss the role of methane in the atmosphere and how methane oxidation pathways help to regulate the tropospheric ozone and hydroxyl budget. They show that in regions characterized by high nitric oxide concentrations, the net methane oxidation reaction is:

We see that complete methane oxidation results in net production of 3.6–3.8 moles of ozone and 0.4–0.5 moles of hydroxyl in the polluted troposphere. For areas with low nitric oxide levels, they show that the net methane oxidation reaction is:

In this case, complete methane oxidation results in the net destruction of approximately 1.7–1.8 moles of ozone and 3.7–3.9 moles of odd hydrogen ($\text{OH} + \text{HO}_2$). Thus, we have a situation where the production or destruction of ozone and odd hydrogen depends on NO_x levels.

4.2. Scenarios 1 and 2: Increasing CH_4 Emissions

4.2.1. Methane

Scenario 1

The percent change of methane for all 4 seasons is shown in Figure 4.2.1.1. As seen in the figure, the percent increase ranges from 71%–73% in the troposphere and lower stratosphere. Over the middle and high latitudes, the percent increase in the SH troposphere is higher than in the NH below 12 km. Above 12 km, the situation reverses. The percent increases are slightly larger between 30°S – 30°N from 0–20 km. This is due to the Hadley circulation bringing material from the surface in each hemisphere towards the tropics. Then, the tropical upwelling quickly transports the material vertically. In Table 4.1.a for this scenario, we see that the average concentration is higher in the NH than in the SH. The global average concentration is 2.75 ppmv. The hemispheric difference in methane levels corresponds to the fact that hydroxyl concentrations are higher in the SH than in the NH (see Table 4.3.a). This is consistent with the fact that the chief chemical sink for methane is reaction with hydroxyl. In Table 4.1.b for this scenario, we see that the average percentage increase of methane concentration is slightly higher in the SH than in the NH. This is due to a net transport of material by transport processes from the NH to the SH, which helps to reduce hydroxyl levels further and causes the relatively larger net increase in methane. Globally, average methane levels increase by 73.1% in the troposphere.

Figure 4.2.1.1. Percentage change of methane during all four seasons (Dec22=winter solstice; Mar22=vernal equinox; Jun22=summer solstice; Sep22=autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 1 relative to the model-derived ambient atmosphere.

Table 4.1. Methane tropospheric annual average (a) mixing ratios and (b) percentage difference relative to model-derived ambient atmosphere.

(a)

Scenario	All CH ₄ mixing ratios in units of ppmv		
	Global	Northern Hemisphere	Southern Hemisphere
1	2.75	2.78	2.71
2	4.09	4.13	4.06
3	3.39	3.41	3.37
4	6.39	6.42	6.36

(b)

Scenario	Percent Difference Relative to Ambient		
	Global	Northern Hemisphere	Southern Hemisphere
1	73.1%	72.7%	73.0%
2	158%	156%	159%
3	113%	112%	115%
4	302%	299%	306%

Scenario 2

The percent change of methane for all 4 seasons is shown in Figure 4.2.1.2. As seen in the figure, the percent increase ranges from 164% in the lower stratosphere to 150%–160% in the lower troposphere. Over the middle and high latitudes, the percent increase in the SH troposphere is higher than in the NH below 12 km. In Table 4.1.a for this scenario, we see that the average concentration is higher in the NH than in the SH. The global average concentration is 4.09 ppmv. The hemispheric difference in methane levels corresponds to the fact that hydroxyl concentrations are higher in the SH than in the NH (see Table 4.3.a). This is consistent with the fact that the chief chemical sink for methane is reaction with hydroxyl. In Table 4.1.b for this scenario, we see that the average percentage increase of methane concentration is slightly higher in the SH than in the NH. This is due to a net transport of material by diffusive processes from the NH to the SH, which helps to reduce hydroxyl levels further and causes the relatively larger net increase in methane. Globally, average methane levels increase by 158% in the troposphere.

Figure 4.2.1.2 Percentage change of methane during all four seasons (Dec22=winter solstice; Mar22=vernal equinox; Jun22=summer solstice; Sep22=autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 2 relative to the model-derived ambient atmosphere.

4.2.2. Carbon Monoxide

Scenario 1

The percent change of carbon monoxide for all 4 seasons is shown in Figure 4.2.2.1. As shown in the figure, the percent increase of carbon monoxide ranges from 40% in the lower stratosphere to ~2% in the lower troposphere. In the middle to high latitudes of each hemisphere, we see that the percent increase in the SH troposphere is definitely higher than in the NH below 15 km. The increases are slightly higher between 30°S–30°N from 0–7.5 km. From 7.5–17.5 km, an interesting feature becomes apparent. The percent increase from 30°S to the equator is higher than that from the equator to 30°N. In Table 4.2.a for this scenario, we see that the average concentration in the NH is almost twice as large as that in the SH. The global average concentration is 74.7 ppbv. The hemispheric difference in carbon monoxide levels corresponds to the fact that its chemical precursor (methane) exhibits the same type of behavior. In Table 4.2.b for this scenario, we see that the average percentage increase of carbon monoxide concentration is higher in the SH than in the NH. This is related to the fact that methane exhibits similar characteristics in its hemispheric difference. Globally, average carbon monoxide levels increase by 11.4% in the troposphere.

Figure 4.2.2.1 Percentage change of carbon monoxide during all four seasons (Dec22=winter solstice; Mar22=vernal equinox; Jun22=summer solstice; Sep22=autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 1 relative to the model-derived ambient atmosphere.

Table 4.2. Carbon monoxide tropospheric annual average (a) mixing ratios and (b) percentage difference relative to model-derived ambient atmosphere.

(a)			
All CO mixing ratios in units of ppbv			
Scenario	Global	Northern Hemisphere	Southern Hemisphere
1	74.7	99.0	50.2
2	82.1	107.0	57.1
3	80.8	106.3	55.2
4	93.7	120.0	67.3
(b)			
Percent Difference Relative to Ambient			
Scenario	Global	Northern Hemisphere	Southern Hemisphere
1	11.4%	9.08%	16.1%
2	22.4%	17.9%	32.0%
3	20.5%	17.1%	27.6%
4	39.7%	32.2%	55.6%

Scenario 2

The percent change of carbon monoxide for all 4 seasons is shown in Figure 4.2.2.2. As shown in the figure, the percent increase of carbon monoxide ranges from 90% in the lower stratosphere to 10%–20% in the lower troposphere. In the middle to high latitudes of each hemisphere, we see that the percent increase in the SH troposphere is definitely higher than in the NH below 15 km. The increases are slightly higher between 30°S–30°N from 0–7.5 km. From 7.5–17.5 km, an interesting feature becomes apparent. The percent increase from 30°S to the equator is higher than that from the equator to 30°N. In Table 4.2.a for this scenario, we see that the average concentration in the NH is almost twice as large as that in the SH. The global average concentration is 82.1 ppbv. The hemispheric difference in carbon monoxide levels corresponds to the fact that its chemical precursor (methane) exhibits the same type of behavior. In Table 4.2.b for this scenario, we see that the average percentage increase of carbon monoxide concentration is higher in the SH than in the NH. This is related to the fact that methane exhibits similar characteristics in its hemispheric difference. Globally, average carbon monoxide levels drop by 22.4% in the troposphere.

Figure 4.2.2.2. Percentage change of carbon monoxide during all four seasons (Dec22=winter solstice; Mar22=vernal equinox; Jun22=summer solstice; Sep22=autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 2 relative to the model-derived ambient atmosphere

4.2.3. Hydroxyl

Scenario 1

The percent change of hydroxyl for all 4 seasons is shown in Figure 4.2.3.1. As shown in the figure, there is a net decrease in hydroxyl concentrations across all latitudes and below ~12.5 km. Above approximately 12.5 km, there is a net increase in hydroxyl concentrations. The difference is due to the fact that 12.5 km is very roughly the dividing line between the stratosphere and troposphere in our model. In the troposphere, we expect that hydroxyl will decrease because of the increase in methane levels. In the stratosphere, hydroxyl will increase because it is no longer controlled by methane oxidation. The largest percentage decreases occur between 2.5–7.5 km from middle to high southern latitudes. In Table 4.3.a for this scenario, we see that the average concentration is higher in the SH relative to the NH. This hemispheric difference is expected because the levels of trace gases oxidized by hydroxyl are generally higher in the NH than in the SH. The global average concentration is 7.14×10^5 molecules/cm³. We calculate a methyl chloroform lifetime for this scenario of 6.38 years, which is up by 15.4% from the ambient case. Globally, hydroxyl levels decrease by 13.9% in the troposphere. The percentage decrease is greater in the SH than in the NH. This is related to the fact that methane exhibits similar characteristics in its hemispheric difference.

Figure 4.2.3.1. Percentage change of hydroxyl during all four seasons (Dec22=winter solstice; Mar22=vernal equinox; Jun22=summer solstice; Sep22=autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 1 relative to the model-derived ambient atmosphere

Table 4.3. Hydroxyl tropospheric annual average (a) concentrations and
(b) percentage difference relative to model-derived ambient atmosphere.

(a)

Scenario	All OH concentrations in units of 10^5 molecules/cm ³		
	Global	Northern Hemisphere	Southern Hemisphere
1	7.14	6.79	7.46
2	6.23	5.98	6.46
3	5.15	4.76	5.53
4	3.97	3.73	4.21

(b)

Scenario	Percent Difference Relative to Ambient		
	Global	Northern Hemisphere	Southern Hemisphere
1	-13.9%	-12.7%	-15.0%
2	-24.9%	-23.1%	-26.4%
3	-37.9%	-38.8%	-37.0%
4	-52.1%	-52.1%	-52.0%

Scenario 2

The percent change of hydroxyl for all 4 seasons is shown in Figure 4.2.3.2. As shown in the figure, there is a net decrease in hydroxyl concentrations across all latitudes and below ~12.5 km. Above approximately 12.5 km, there is a net increase in hydroxyl concentrations. The difference is due to the fact that 12.5 km is very roughly the dividing line between the stratosphere and troposphere. In the troposphere, we expect that hydroxyl will decrease because of the increase in methane levels. In the stratosphere, hydroxyl will increase because it is no longer controlled by methane oxidation. The largest percentage decreases occur between 2.5–7.5 km from middle to high southern latitudes. In Table 4.3.a for this scenario, we see that the average concentration is somewhat higher in the SH relative to the NH. This hemispheric difference is expected because the levels of trace gases oxidized by hydroxyl are generally higher in the NH than in the SH. The global average concentration is 6.23×10^5 molecules/cm³. We calculate a methyl chloroform lifetime for this scenario of 7.21 years, which is up by 30.4% from the ambient case. Globally, hydroxyl levels decrease by 24.9% in the troposphere. The percentage decrease is greater in the SH than in the NH. This is related to the fact that methane exhibits similar characteristics in its hemispheric difference.

Figure 4.2.3.2. Percentage change of hydroxyl during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sept 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 2 relative to the model-derived ambient atmosphere.

4.2.4. Ozone

Scenario 1

The percent change of ozone for all 4 seasons is shown in Figure 4.2.4.1. As shown in the figure, ozone increases everywhere in the troposphere and lower stratosphere. The largest percent increases are found over the tropics in the lower and middle troposphere. In general, the percent increase in ozone mixing ratios is larger between 30°S–30°N relative to either hemisphere. In Table 4.4.a for this scenario, we see that the average concentration of ozone is higher in the NH than in the SH. This is reasonable because nitrogen oxide levels are also higher in the NH (see Table 4.5.a) and they are the photochemical source of ozone in the troposphere. The global average concentration of ozone is 73.1 ppbv. In Table 4.4.b for this scenario, we see that the percentage increase in the SH is higher than in the NH. This is related to the fact that methane exhibits similar characteristics in its hemispheric differences. Globally, average ozone levels increase by 8.77% in the troposphere.

Figure 4.2.4.1. Percentage change of ozone during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 1 relative to the model-derived ambient atmosphere.

Table 4.4. Ozone tropospheric annual average (a) mixing ratios and (b) percentage difference relative to model-derived ambient atmosphere.

(a)			
Scenario	All O ₃ mixing ratios in units of ppbv		
	Global	Northern Hemisphere	Southern Hemisphere
1	73.1	79.5	66.8
2	77.8	84.1	71.6
3	68.6	74.0	63.3
4	74.0	79.4	68.7
(b)			
Scenario	Percent Difference Relative to Ambient		
	Global	Northern Hemisphere	Southern Hemisphere
1	8.77%	7.93%	9.86%
2	15.8%	14.2%	17.8%
3	2.07%	0.501%	4.10%
4	10.1%	7.79%	13.0%

Scenario 2

The percent change of ozone for all 4 seasons is shown in Figure 4.2.4.2. As shown in the figure, ozone increases everywhere in the troposphere and lower stratosphere. The largest percent increases are found over the tropics in the

troposphere. In general, the percent increase in ozone mixing ratios is larger between 30°S–30°N relative to either hemisphere. In Table 4.4.a for this scenario, we see that the average concentration of ozone is higher in the NH than in the SH. This is reasonable because nitrogen oxide levels are also higher in the NH (see Table 4.5.a) and they are the photochemical source of ozone in the troposphere. The global average concentration of ozone is 77.8 ppbv. In Table 4.4.b for this scenario, we see that the percentage increase in the SH is higher than in the NH. This is related to the fact that methane exhibits similar characteristics in its hemispheric differences. Globally, average ozone levels increase by 15.8% in the troposphere.

Figure 4.2.4.2. Percentage change of ozone during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 2 relative to the model-derived ambient atmosphere.

4.2.5. Nitrogen Oxides

Scenario 1

The percent change of nitrogen oxides for all 4 seasons is shown in Figure 4.2.5.1. As shown in the figure, nitrogen oxides increase across all latitudes below ~7.5 km. A percentage increase may be found at extreme high latitudes of the NH during winter in the lower stratosphere. The reason that nitrogen oxides increase in the lower to middle troposphere (below 7.5 km) is due to photochemistry. The methane increase decreases hydroxyl levels. Since the chief photochemical sink for nitrogen oxides is the reaction of hydroxyl with nitrogen dioxide to form nitric acid, we expect nitrogen oxides to increase as hydroxyl decreases. Above the middle troposphere (≥ 7.5 km), hydroxyl concentrations are increasing and consequently are high enough to decrease nitrogen oxide levels. In Table 4.5.a for this scenario, average nitrogen oxide levels in the NH are higher than in the SH. The global tropospheric average concentration of nitrogen oxides is 50.7 pptv. In Table 4.5.b for this scenario, we see that the percentage decrease is larger in the SH than in the NH. This is related to the fact that hydroxyl exhibits the

same characteristics in its hemispheric difference. Globally, average nitrogen oxide levels decrease by 4.58% in the troposphere.

Figure 4.2.5.1. Percentage change of nitrogen oxides (NO_x) during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 1 relative to the model-derived ambient atmosphere.

Table 4.5. Nitrogen oxides (NO_x) tropospheric annual average (a) mixing ratios and (b) percentage difference relative to model-derived ambient atmosphere.

Scenario	All NO_x mixing ratios in units of pptv		
	Global	Northern Hemisphere	Southern Hemisphere
1	50.7	53.4	48.0
2	48.7	51.5	45.9
3	35.5	33.3	37.8
4	31.4	29.5	33.4

Scenario	Percent Difference Relative to Ambient		
	Global	Northern Hemisphere	Southern Hemisphere
1	-4.58%	-4.14%	-5.12%
2	-8.34%	-7.55%	-9.27%
3	-33.2%	-40.2%	-25.3%
4	-40.9%	-47.0%	-34.0%

Scenario 2

The percent change of nitrogen oxides for all 4 seasons is shown in Figure 4.2.5.2. As shown in the figure, nitrogen oxides increase across all latitudes below ~7.5 km. A percentage increase may be found at extreme high latitudes of the winter hemisphere in the lower stratosphere. The reason that nitrogen oxides increase in the lower to middle troposphere (below 7.5 km) is due to photochemistry. The methane increase decreases hydroxyl levels. Since the chief photochemical sink for nitrogen oxides is the reaction of hydroxyl with nitrogen dioxide to form nitric acid, we expect nitrogen oxides to increase as hydroxyl decreases. Above the middle troposphere (≥ 7.5 km), hydroxyl concentrations are increasing and consequently are high enough to decrease nitrogen oxide levels. In Table 4.5.a for this scenario, average nitrogen oxide levels in the NH are higher than in the SH. The global tropospheric average concentration of nitrogen oxides is 48.7 pptv. In Table 4.5.b for this scenario, we see that the percentage decrease is larger in the SH than in the NH. This is related to the fact that hydroxyl exhibits the same characteristics in its hemispheric difference. Globally, average nitrogen oxide levels decrease by 8.34% in the troposphere.

Figure 4.2.5.2. Percentage change of nitrogen oxides (NO_x) during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 2 relative to the model-derived ambient atmosphere.

4.2.6. Non-methane hydrocarbons

Scenario 1

The percentage changes of ethane, propane, and acetylene for all 4 seasons are shown in Figures 4.2.6.1, 4.2.6.2, and 4.2.6.3, respectively. As shown in each figure, levels of these three NMHCs increase ~20% in the lower troposphere and ~100% in the lower stratosphere. As the abundance of hydrocarbons increases, the competition for

hydroxyl oxidation rises. Below 15 km, the percentage increase is greater in the SH than in the NH. The global annual average tropospheric mixing ratios and percentage increases relative to ambient conditions for ethane, propane, and acetylene are listed in Tables 4.6–4.8 respectively. For each species, we see that the average concentration is higher in the NH than in the SH. This is a result of hydroxyl levels being higher in the SH than in the NH (see Table 4.3.a). The global average concentrations of ethane, propane, and acetylene are 0.991 ppbv, 113.8 pptv, and 55.9 pptv, respectively. The average percentage increase of each species is higher in the SH than in the NH. This is related to the fact that hydroxyl levels show a higher percentage decrease in the SH than in the NH. Globally, average levels of ethane, propane, and acetylene decrease in the troposphere by 22.0%, 17.0%, and 14.3%, respectively.

Figure 4.2.6.1. Percentage change of ethane during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 1 relative to the model-derived ambient atmosphere.

Figure 4.2.6.2. Percentage change of propane during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 1 relative to the model-derived ambient atmosphere.

Figure 4.2.6.3. Percentage change of acetylene during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 1 relative to the model-derived ambient atmosphere.

Table 4.6. Ethane tropospheric annual average (a) mixing ratios and (b) percentage difference relative to model-derived ambient atmosphere.

(a)			
All C ₂ H ₆ mixing ratios in units of ppbv			
Scenario	Global	Northern Hemisphere	Southern Hemisphere
1	0.991	1.14	0.846
2	1.18	1.32	1.03
3	1.89	2.10	1.68
4	2.55	2.75	2.35
(b)			
Percent Difference Relative to Ambient			
Scenario	Global	Northern Hemisphere	Southern Hemisphere
1	22.0%	19.5%	26.4%
2	45.3%	38.4%	53.8%
3	133%	120%	151%
4	214%	188%	251%

Table 4.7. Propane tropospheric annual average (a) mixing ratios and (b) percentage difference relative to model-derived ambient atmosphere.

(a)			
All C ₃ H ₈ mixing ratios in units of pptv			
Scenario	Global	Northern Hemisphere	Southern Hemisphere
1	114	149	78.6
2	131	169	94.3
3	242	311	172
4	319	391	246
(b)			
Percent Difference Relative to Ambient			
Scenario	Global	Northern Hemisphere	Southern Hemisphere
1	17.0%	14.2%	22.7%
2	35.1%	29.1%	47.4%
3	148%	138%	169%
4	228%	200%	284%

Table 4.8. Acetylene tropospheric annual average (a) mixing ratios and (b) percentage difference relative to model-derived ambient atmosphere.

(a)			
All C ₂ H ₂ mixing ratios in units of pptv			
Scenario	Global	Northern Hemisphere	Southern Hemisphere
1	55.9	89.5	22.3
2	63.3	99.3	27.3
3	114	174	52.9
4	144	210	77.3
(b)			
Percent Difference Relative to Ambient			
Scenario	Global	Northern Hemisphere	Southern Hemisphere
1	14.3%	11.8%	25.7%
2	29.5%	24.0%	53.9%
3	133%	118%	198%

Scenario 2

The percentage changes of ethane, propane, and acetylene for all 4 seasons are shown in Figures 4.2.6.4, 4.2.6.5, and 4.2.6.6, respectively. As shown in each figure, levels of ethane and acetylene increase ~30%–50% in the lower troposphere and >100% in the lower stratosphere. Propane mixing ratios rise >50% in the lower troposphere and >250% in the lower stratosphere. As the abundance of hydrocarbons increases, the competition for hydroxyl oxidation rises. Below 15 km, the percentage increase is greater in the SH than in the NH. The global annual average tropospheric mixing ratios and percentage increases relative to ambient conditions for ethane, propane, and acetylene are listed in Tables 4.6–4.8 respectively. For each species, we see that the average concentration is higher in the NH than in the SH. This is a result of hydroxyl levels being higher in the SH than in the NH (see Table 4.3.a). The global average concentrations of ethane, propane, and acetylene are 1.18 ppbv, 131.4 pptv, and 63.3 pptv, respectively. The average percentage increase of each species is higher in the SH than in the NH. This is related to the fact that hydroxyl levels show a higher percentage decrease in the SH than in the NH. Globally, average levels of ethane, propane, and acetylene decrease in the troposphere by 45.3%, 35.1%, and 29.5%, respectively.

Figure 4.2.6.4. Percentage change of ethane during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 2 relative to the model-derived ambient atmosphere.

Figure 4.2.6.5. Percentage change of propane during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 2 relative to the model-derived ambient atmosphere.

Figure 4.2.6.6. Percentage change of acetylene during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 2 relative to the model-derived ambient atmosphere.

4.2.7. Peroxyacetylnitrate

Scenario 1

The percent change of peroxyacetylnitrate (PAN) for all 4 seasons is shown in Figure 4.2.7.1. As shown in the figure, PAN decreases below 2.5 km from the equator to the midlatitudes of both hemispheres. This occurs because the formation rate of peroxyacetyl (PA) radical decreases which results from a drop in the reaction rates of its hydrocarbon precursors since hydroxyl levels decrease. At higher latitudes and throughout the other parts of the troposphere and lower stratosphere, PAN concentrations increase. This occurs because the hydrocarbon precursors of PA radical are transported higher and subsequently react with hydroxyl. In Table 4.9.a for this scenario, we see that the average concentration of PAN is higher in the NH than in the SH. This is related to the fact that the hydrocarbon precursors are more abundant in the NH. The global average concentration is 64.5 pptv. In Table 4.9.b for this scenario, we see that the average percentage increase of PAN concentration is higher in the SH than in the NH. This is related to the fact that the precursor hydrocarbons show similar characteristics in their hemispheric differences. Higher nitrogen availability in the NH may also be a factor. Globally, average PAN levels increase by 7.85% in the troposphere.

Figure 4.2.7.1. Percentage change of peroxyacetylnitrate during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 1 relative to the model-derived ambient atmosphere.

Table 4.9. Peroxyacetylnitrate (PAN) tropospheric annual average (a) mixing ratios and (b) percentage difference relative to model-derived ambient atmosphere.

Scenario	All PAN mixing ratios in units of pptv		
	Global	Northern Hemisphere	Southern Hemisphere
1	64.5	80.2	48.8

2	68.5	84.0	52.9
3	85.9	98.8	73.0
4	96.8	110	84.1

(b)

Scenario	Percent Difference Relative to Ambient		
	Global	Northern Hemisphere	Southern Hemisphere
1	7.85%	6.03%	11.0%
2	14.5%	11.1%	20.4%
3	43.6%	30.6%	66.1%
4	61.9%	44.9%	91.3%

Scenario 2

The percent change of peroxyacetylnitrate (PAN) for all 4 seasons is shown in Figure 4.2.7.2. As shown in the figure, PAN decreases below 2.5 km from the equator to the midlatitudes of both hemispheres. This occurs because the formation rate of peroxyacetyl (PA) radical decreases which results from a drop in the reaction rates of its hydrocarbon precursors since hydroxyl levels decrease. At higher latitudes and throughout the other parts of the troposphere and lower stratosphere, PAN concentrations increase. This occurs because the hydrocarbon precursors of PA radical are transported higher and subsequently react with hydroxyl. In Table 4.9.a for this scenario, we see that the average concentration of PAN is higher in the NH than in the SH. This is related to the fact that the hydrocarbon precursors are more abundant in the NH. The global average concentration is 68.5 pptv. In Table 4.9.b for this scenario, we see that the average percentage increase of PAN concentration is higher in the SH than in the NH. This is related to the fact that the precursor hydrocarbons show similar characteristics in their hemispheric differences. Globally, average PAN levels increase by 14.5% in the troposphere.

Figure 4.2.7.2. Percentage change of peroxyacetylnitrate during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox)

autumnal equinox; seasons are identified with respect to Northern Hemisphere for Scenario 2 relative to the model-derived ambient atmosphere.

4.3. Discussion of Increasing CH₄ Scenarios

The behavior of the methane response in scenarios 1 and 2 is nonlinear. For an increase of 50% and 100% the global tropospheric average concentration of methane rises 73.1% and 158% respectively. The reason for these increases can be deduced from Figure 4.3.1 where the total atmospheric mass of methane (i.e., burden) is plotted as a function of surface flux. Both variables are normalized with respect to the appropriate ambient values. Increasing levels of methane feed back directly via the oxidation mechanism to decrease hydroxyl concentrations in the troposphere because over 90% of the methane is oxidized in this region. As hydroxyl decreases, methane increases (solid line) resulting in a positive feedback. If there were no feedback (dashed line), the increase would be linear.

Figure 4.3.1. Feedback of methane on hydroxyl. If there were no feedback, we would expect a linear increase in the total atmospheric mass (i.e. burden) of methane with respect to surface flux. However, due to the feedback, we see that the amount of methane in the atmosphere increases nonlinearly. The variables are normalized with respect to the appropriate ambient values.

There is another feedback that affects hydroxyl as well. As ozone levels increase due to methane oxidation (cf. Figures 4.2.4.1,2), the stratospheric ozone column increases thereby reducing the ultraviolet actinic flux into the troposphere. This will then reduce the photolysis rate constant for $O_3 \rightarrow O(^1D)$. Both of these effects are shown in Figure 4.3.2. Even though the photolysis rate constant decreases, the abundance of ozone in the troposphere increases. The net effect is that the $O_3 \rightarrow O(^1D)$ photolysis rate rises producing higher levels of $O(^1D)$ which results in increased production of hydroxyl due to the $O(^1D) + H_2O$ reaction as shown in Figure 4.3.3. Thus, the destruction of hydroxyl due to $CH_4 + OH$ is counteracted by its production due to $O(^1D) + H_2O$.

Figure 4.3.2 Percentage change of O_3 photolysis rate constant $j(O_3 \rightarrow O(^1D))$ during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 2 relative to the model-derived ambient atmosphere.

Figure 4.3.3. Percentage change of OH production rate ($O(^1D) + H_2O \rightarrow 2OH$) during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer

solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 2 relative to the model-derived ambient atmosphere.

This effect emphasizes the importance of including troposphere-stratosphere feedbacks in atmospheric chemical-radiative-transport modeling. The percentage changes in the tropospheric average concentrations of ozone and hydroxyl for a doubling in methane flux (same as Scenario 2) are tabulated in Table 4.10 for 4 atmospheric models. The predicted changes differ between the models; the discrepancies are greater for hydroxyl than for ozone. A key difference between the LLNL model and the others is its inclusion of the entire stratosphere (domain height: 60km); this includes the region of peak ozone abundances. The other models have domain heights between 15–24 kilometers and use an upper boundary condition that fixes the stratospheric ozone column. As a result, the other models will not reflect properly the changes in stratospheric ozone column that result from perturbations such as an increase in methane emissions. Therefore, the troposphere-stratosphere feedbacks will not be represented adequately. Consequently, the other models' hydroxyl changes will be less sensitive to source gas emission perturbations than the LLNL two-dimensional model.

Table 4.10. Percentage difference in tropospheric average concentrations of OH and O₃ relative to model-derived ambient atmosphere for a doubling of methane emissions. Results from 4 atmospheric models are tabulated.

Species	Percentage difference due to 2 × CH ₄ flux			
	NASA/GSFC ⁵	Harwell ⁶	Oslo ⁷	LLNL ⁸
O ₃	15.2%	11.3%	10.4%	15.8%
OH	-17.7%	-10.2%	-16.9%	-24.9%

⁵NASA Goddard Space Flight Center multi-region one-dimensional model.

⁶Harwell Laboratory two-dimensional model.

⁷University of Oslo two-dimensional model.

⁸Lawrence Livermore National Laboratory two-dimensional model.

4.4. Scenario 3: Low NO_x

4.4.1. Methane

The percent change of methane for all 4 seasons is shown in Figure 4.4.1.1. As seen in the figure, the percent increase ranges 114% in the lower stratosphere and ~110%–116% in the lower troposphere. Over all latitudes, the percent increase in the SH troposphere is higher than in the NH below 12 km. Above 12 km, changes are pretty similar. In Table 4.1.a for this scenario, we see that the average concentration is almost the same in each hemisphere. The global average concentration is 3.39 ppmv. In Table 4.1.b for this scenario, we see that the average percentage increase of methane concentration is slightly higher in the SH than in the NH. This is due to a net transport of material by diffusive processes from the NH to the SH, which helps to reduce hydroxyl levels further and causes the slight, relatively larger net increase in methane. Globally, average methane levels increase by 113% in the troposphere.

Figure 4.4.1.1. Percentage change of methane during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 3 relative to the model-derived ambient atmosphere.

4.4.2. Carbon Monoxide

The percent change of carbon monoxide for all 4 seasons is shown in Figure 4.4.2.1. As shown in the figure, the percent increase of carbon monoxide ranges from >60% in the lower stratosphere to ~10% in the lower troposphere. In the lower troposphere, the percentage increase is fairly constant across all latitudes. From 7.5–17.5 km, an interesting feature becomes apparent. The percent increase from 30°S to the equator is higher than that from the equator to 30°N. In Table 4.2.a for this scenario, we see that the average concentration in the NH is almost twice as large as that in the SH. The global average concentration is 80.8 ppbv. In Table 4.2.b for this scenario, we see that the average percentage increase of carbon monoxide concentration is higher in the SH than in the NH. This is related to the fact that methane exhibits similar characteristics in its hemispheric difference. Globally, average carbon monoxide levels increase by 20.5% in the troposphere.

Figure 4.4.2.1. Percentage change of carbon monoxide during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 3 relative to the model-derived ambient atmosphere.

4.4.3. Hydroxyl

The percent change of hydroxyl for all 4 seasons is shown in Figure 4.4.3.1. As shown in the figure, there is a net decrease in hydroxyl concentrations across all latitudes and below ~12.5 km. Above approximately 12.5 km, there is a net increase in hydroxyl concentrations. The difference is due to the fact that 12.5 km is very roughly the dividing line between the stratosphere and troposphere. In the troposphere, we expect that hydroxyl will decrease because of the increase in methane levels. In the stratosphere, odd hydrogen will increase because it is controlled by methane oxidation. As odd hydrogen increases, the sinks for NO_x will also increase (e.g. $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$ and $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$). Thus, the NO_x destination of O_3 (via the $\text{NO} + \text{O}_3$ reaction) will decrease. This will also raise O_3 levels. The largest percentage decreases occur near the surface over middle latitudes. In Table 4.3.a for this scenario, we see that the average concentration is higher in the SH relative to the NH. This hemispheric difference is expected because the levels of trace gases oxidized by hydroxyl are generally higher in the NH than in the SH. The global average concentration is 5.15×10^5 molecules/cm³. We calculate a methyl chloroform lifetime for this scenario of 11.0 years, which is up by 98.1% from the ambient case. Globally, hydroxyl levels decrease by 37.9% in the troposphere. The percentage decrease is slightly greater in the NH relative to the SH.

Figure 4.4.3.1. Percentage change of hydroxyl during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 3 relative to the model-derived ambient atmosphere.

4.4.4. Ozone

The percent change of ozone for all 4 seasons is shown in Figure 4.4.4.1. As shown in the figure, ozone increases above 5 km in the troposphere and lower stratosphere. This is a result of a decrease in the NO_x destruction reactions as discussed in section 4.4.3. The largest percent increases are found over the tropics in the lower stratosphere and upper troposphere. In Table 4.4.a for this scenario, we see that the average concentration of ozone is higher in the NH than in the SH. The global average concentration of ozone is 68.6 ppbv. In Table 4.4.b for this scenario, we see that the percentage increase in the SH is higher than in the NH. Globally, average ozone levels increase by 2.07% in the troposphere.

Figure 4.4.4.1. Percentage change of ozone during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 3 relative to the model-derived ambient atmosphere.

4.4.5. Nitrogen Oxides

The percent change of nitrogen oxides for all 4 seasons is shown in Figure 4.4.5.1. As shown in the figure, nitrogen oxides decrease substantially throughout the troposphere and lower stratosphere. A percentage increase may be found at extreme high latitudes of the winter hemisphere in the lower stratosphere. In Table 4.5.a for this scenario, average nitrogen oxide levels in the SH are somewhat higher than in the NH. The global tropospheric average concentration of nitrogen oxides is 35.5 pptv. In Table 4.5.b for this scenario, we see that the percentage decrease is larger in the NH than in the SH. Globally, average nitrogen oxide levels decrease by 33.2% in the troposphere.

Figure 4.4.5.1. Percentage change of nitrogen oxides (NO_x) during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 3 relative to the model-derived ambient atmosphere.

4.4.6. Non-methane hydrocarbons

The percentage changes of ethane, propane, and acetylene for all 4 seasons are shown in Figures 4.4.6.1, 4.4.6.2, and 4.4.6.3, respectively. As shown in each figure, levels of these three NMHCs increase throughout the lower stratosphere and troposphere due to the hydroxyl decrease in the troposphere which allows more of the hydrocarbons to be transported to higher altitudes. The global annual average tropospheric mixing ratios and percentage increases relative to ambient conditions for ethane, propane, and acetylene are listed in Tables 4.6–4.8 respectively. For each species, we see that the average concentration is higher in the NH than in the SH. This is a result of hydroxyl levels being higher in the SH than in the NH (see Table 4.3.a). The global average concentrations of ethane, propane, and acetylene are 2.10ppbv, 311 pptv, and 174 pptv, respectively. The average percentage increase of each species is higher in the SH than in the NH. Globally, average levels of ethane, propane, and acetylene decrease in the troposphere by 133%, 148%, and 133%, respectively.

Figure 4.4.6.1 Percentage change of ethane during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere for Scenario 3 relative to the model-derived ambient atmosphere.

Figure 4.4.6.2. Percentage change of propane during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 3 relative to the model-derived ambient atmosphere.

Figure 4.4.6.3. Percentage change of acetylene during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 3 relative to the model-derived ambient atmosphere.

4.4.7. Peroxyacetylnitrate

The percent change of peroxyacetylnitrate (PAN) for all 4 seasons is shown in Figure 4.4.7.1. As shown in the figure, PAN decreases in the lower troposphere from 90°N to 60°S. This occurs because the formation rate of PAN decreases drastically which results from the low nitrogen oxide levels near the surface. Throughout the other parts of the troposphere and lower stratosphere, PAN concentrations increase. This occurs because the hydrocarbon precursors of PA radical are transported higher and subsequently react with hydroxyl. In Table 4.9.a for this scenario, we see that the average concentration of PAN is higher in the NH than in the SH. This is related to the fact that the hydrocarbon precursors are more abundant in the NH. The global average concentration is 85.9 pptv. In Table 4.9.b for this scenario, we see that the average percentage increase of PAN concentration is higher in the SH than in the NH. This is related to the fact that the precursor hydrocarbons show similar characteristics in their hemispheric differences. Globally, average PAN levels increase by 43.6% in the troposphere.

Figure 4.4.7.1 Percentage change of peroxyacetylnitrate during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 3 relative to the model-derived ambient atmosphere.

4.5. Scenario 4: Low NO_x and 50% CH_4 Increase

4.5.1. Methane

The percent change of methane for all 4 seasons is shown in Figure 4.5.1.1. As seen in the figure, the percent increase is roughly 300% in the troposphere and lower stratosphere. Over the middle and high latitudes, the percent increase in the SH troposphere is higher than in the NH below 12 km. Above 12 km, the situation reverses. In Table 4.1.a for this scenario, we see that the average concentration is slightly higher in the NH than in the SH. The global average concentration is 6.39 ppmv. The hemispheric difference in methane levels corresponds to the fact that hydroxyl concentrations are higher in the SH than in the NH (see Table 4.3.a). This is consistent with the fact that the chief chemical sink for methane is reaction with hydroxyl. In Table 4.1.b for this scenario, we see that the average percentage increase of methane concentration is slightly higher in the SH than in the NH. This is due to a net transport of material by diffusive processes from the NH to the SH, which helps to reduce hydroxyl levels further and causes the relatively larger net increase in methane. Globally, average methane levels increase by 302% in the troposphere.

Figure 4.5.1.1. Percentage change of methane during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 4 relative to the model-derived ambient atmosphere.

4.5.2. Carbon Monoxide

The percent change of carbon monoxide for all 4 seasons is shown in Figure 4.5.2.1. As shown in the figure, the percent increase of carbon monoxide is ~150% in the lower stratosphere and ranges from 10%–50% in the lower troposphere. In Table 4.2.a for this scenario, we see that the average concentration in the NH is almost twice as large as that in the SH. The global average concentration is 93.7 ppbv. The hemispheric difference in carbon monoxide levels corresponds to the fact that its chemical precursor (methane) exhibits the same type of behavior. In Table 4.2.b for this scenario, we see that the average percentage increase of carbon monoxide concentration is higher in the SH than in the NH. This is related to the fact that methane exhibits similar characteristics in its hemispheric difference. Globally, average carbon monoxide levels increase by 39.7% in the troposphere.

Figure 4.5.2.1. Percentage change of carbon monoxide during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 4 relative to the model-derived ambient atmosphere.

4.5.3. Hydroxyl

The percent change of hydroxyl for all 4 seasons is shown in Figure 4.5.3.1. As shown in the figure, there is a net decrease in hydroxyl concentrations across all latitudes and below ~12.5 km. Above approximately 12.5 km, there is a net increase in hydroxyl concentrations. The difference is due to the fact that 12.5 km is very roughly the dividing line between the stratosphere and troposphere. In the troposphere, we expect that hydroxyl will decrease because of the increase in methane levels. In the stratosphere, odd hydrogen will increase because it is controlled by methane oxidation. (See section 4.4.3 for discussion. In Table 4.3.a for this scenario, we see that the average concentration is higher in the SH relative to the NH. This hemispheric difference is expected because the levels of trace gases oxidized by hydroxyl are generally higher in the NH than in the SH. The global average concentration is 3.97×10^5 molecules/cm³. We calculate a methyl chloroform lifetime for this scenario of 13.6 years, which is up by 146% from the ambient case. Globally, hydroxyl levels decrease by 52.1% in the troposphere. The percentage decrease is the same in both hemispheres.

Figure 4.5.3.1. Percentage change of hydroxyl during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 4 relative to the model- derived ambient atmosphere.

4.5.4. Ozone

The percent change of ozone for all 4 seasons is shown in Figure 4.5.4.1. As shown in the figure, ozone increases above ~2.5 km across all latitudes. (See section 4.4.4 for explanation.) Ozone decreases below ~2.5 km because nitrogen oxide levels decrease near the surface and nitrogen dioxide photolysis is the chemical source of ozone. In Table 4.4.a for this scenario, we see that the average concentration of ozone is higher in the NH than in the SH. The global average concentration of ozone is 74.0 ppbv. In Table 4.4.b for this scenario, we see that the percentage increase in the SH is higher than in the NH. This is related to the fact that methane exhibits similar characteristics in its hemispheric differences. Globally, average ozone levels increase by 10.1% in the troposphere.

Figure 4.5.4.1. Percentage change of ozone during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 4 relative to the model-derived ambient atmosphere.

4.5.5. Nitrogen Oxides

The percent change of nitrogen oxides for all 4 seasons is shown in Figure 4.5.5.1. As shown in the figure, nitrogen oxides decrease throughout most of the lower stratosphere and troposphere. In Table 4.5.a for this scenario, average nitrogen oxide levels in the SH are slightly higher than in the NH. The global tropospheric average concentration of nitrogen oxides is 31.4 pptv. In Table 4.5.b for this scenario, we see that the percentage decrease is larger in the NH than in the SH. Globally, average nitrogen oxide levels decrease by 40.9% in the troposphere.

Figure 4.5.5.1. Percentage change of nitrogen oxides (NO_x) during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 4 relative to the model-derived ambient atmosphere.

4.5.6. Non-methane hydrocarbons

The percentage changes of ethane, propane, and acetylene for all 4 seasons are shown in Figures 4.5.6.1, 4.5.6.2, and 4.5.6.3, respectively. As shown in each figure, levels of these three NMHCs increase throughout the troposphere and lower stratosphere due to the hydroxyl decrease in the troposphere which allows more of the hydrocarbons to be transported to higher altitudes. The global annual average tropospheric mixing ratios and percentage increases relative to ambient conditions for ethane, propane, and acetylene are listed in Tables 4.6–4.8 respectively. For each species, we see that the average concentration is higher in the NH than in the SH. This is a result of hydroxyl levels being higher in the SH than in the NH (see Table 4.3.a). The global average concentrations of ethane, propane, and acetylene are 2.55 ppbv, 319 pptv, and 144 pptv, respectively. The average percentage increase of each species is higher in the SH than in the NH. Globally, average levels of ethane, propane, and acetylene decrease in the troposphere by 214%, 228%, and 194%, respectively.

Figure 4.5.6.1. Percentage change of ethane during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 4 relative to the model-derived ambient atmosphere.

Figure 4.5.6.2. Percentage change of propane during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 4 relative to the model-derived ambient atmosphere.

Figure 4.5.6.3. Percentage change of acetylene during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 4 relative to the model-derived ambient atmosphere.

4.5.7. Peroxyacetylnitrate

The percent change of peroxyacetylnitrate (PAN) for all 4 seasons is shown in Figure 4.5.7.1. As shown in the figure, PAN decreases below 2.5 km from 90°N to 60°S. This occurs because the formation rate of PAN decreases drastically which results from the low nitrogen oxide levels near the surface. Throughout the other parts of the troposphere and lower stratosphere, PAN concentrations increase. This occurs because the hydrocarbon precursors of PA radical are transported higher and subsequently react with hydroxyl. In Table 4.9.a for this scenario, we see that the average concentration of PAN is higher in the NH than in the SH. This is related to the fact that the hydrocarbon precursors are more abundant in the NH. The global average concentration is 96.8 pptv. In Table 4.9.b for this scenario, we see that the average percentage increase of PAN concentration is higher in the SH than in the NH. This is related to the fact that the precursor hydrocarbons show similar characteristics in their hemispheric differences. Globally, average PAN levels increase by 61.9% in the troposphere.

Figure 4.5.7.1. Percentage change of peroxyacetylnitrate during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 4 relative to the model-derived ambient atmosphere.

4.6. Discussion of Low NO_x Scenarios

Since NO_x has decreased at the surface in scenarios 3 and 4, we will examine the perturbations of O₃ and OH in the troposphere. Qualitatively, the subsequent analysis will hold for both cases. NO_x chemistry is coupled to O₃ formation in the troposphere and thereby to OH production. Thus, a decrease in NO_x levels will result in a decrease of these two oxidants. Ozone decreases below 5 km and increases above 5 km as depicted in Figure 4.4.4.1. This is a result of nitrogen dioxide photolysis ($\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$) decreasing substantially below 5 km as shown in Figure 4.6.1. Due to this decline in the oxygen atom production rate, ozone production ($\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$) also falls below 5 km as depicted in Figure 4.6.2.

Figure 4.6.1 Percentage change of NO_2 photolysis rate ($\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$) during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 3 relative to the model-derived ambient atmosphere.

Figure 4.6.2. Percentage change of O_3 production ($O+O_2+M \rightarrow O_3+M$) during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 3 relative to the model-derived ambient atmosphere.

As shown in Figure 4.4.3.1, OH decreases throughout the troposphere. This is a result of several effects. First, ozone near the surface has decreased. Therefore the amount of ozone available for photolysis ($O_3 + h\nu \rightarrow O(^1D) + O_2$) will decrease. Second, ozone in the stratosphere has increased which will decrease the actinic flux into the troposphere as shown in the plot of the photolysis rate constant $J(O_3 \rightarrow O(^1D))$ in Figure 4.6.3. These two effects will act to decrease dramatically the $O(^1D)$ production rate in the lower troposphere thereby causing a drop in the OH production rate from the reaction $O(^1D) + H_2O \rightarrow 2 OH$. This is depicted in Figure 4.6.4. The OH production rate decreases substantially below 5 km and increases above that altitude. The reason for the increase above 5 km is linked to the rise in O_3 levels in this region (see Figure 4.4.4.1).

Figure 4.6.3. Percentage change of O_3 photolysis rate constant $j(O_3 \rightarrow O(^1D))$ during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 3 relative to the model-derived ambient atmosphere.

Figure 4.6.4. Percentage change of production rate ($O(^1D)+H_2O \rightarrow 2OH$) during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario 3 relative to the model-derived ambient atmosphere.

The reason that the hydrocarbons increase throughout the atmosphere (e.g., Figure 4.4.1.1) is due to the decrease in OH levels in the troposphere. For example, over 90% of methane oxidation occurs in the troposphere and especially in the layers closest to the surface. Thus, hydrocarbons will be transported higher up into the atmosphere before substantial removal via OH oxidation begins. A case in point is the reaction of $CO+OH$ shown in Figure 4.6.5. The oxidation rate decreases below 7.5 km and begins to increase again above that altitude. The increase is a result of the levels of CO becoming sufficiently high to compete successfully with other hydrocarbons for OH radicals. Hydrocarbon oxidation also will increase ozone levels in the stratosphere. This will decrease the actinic flux of ultraviolet radiation into the troposphere and act as a feedback that reinforces the decrease in OH production.

Figure 4.6.5. Percentage change of CO oxidation rate ($\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$) during all four seasons (Dec 22 = winter solstice; Mar 22 = vernal equinox; Jun 22 = summer solstice; Sep 22 = autumnal equinox; seasons are identified with respect to Northern Hemisphere) for Scenario X relative to the model-derived ambient atmosphere.

5. Determination of Global Warming Potentials

The Global Warming Potential concept (IPCC, 1990) was developed at the request of policymakers as a relative measure of the potential effects on climate from various greenhouse gases, in much the same way as the Ozone Depletion Potential concept (Wuebbles, 1981) is used in policy analyses of the relative effects of CFCs and other compounds on stratospheric ozone destruction. We have recognized for some time that there are a number of uncertainties and limitations associated with the GWPs as defined in the IPCC reports. For example, the carbon cycle model used in examining the behavior of CO₂ did not consider a balanced carbon budget. In this study, we examine some of the major uncertainties associated with the derivation of GWPs. Included are calculations of the sensitivity of GWPs to various assumptions associated with modeling the carbon cycle. We also examine the effect of assumptions regarding the background atmosphere on the derived GWPs. Finally, we examine the sensitivity of derived GWPs to recognized uncertainties in the atmospheric lifetimes of non-CO₂ greenhouse gases.

GWPs depend upon the change in concentration of a trace gas with time arising from the impulse of gas. Behavior of an impulse of most trace gases is dependent on the atmospheric lifetime of the gas; atmospheric lifetime reflects the removal rate for a given gas by chemical reactions and physical processes. However, the normal assumption of a constant atmospheric lifetime is not a sufficient description of the response of the atmosphere to an impulse of CO₂. A more complicated function is required due to the interaction of atmospheric CO₂ with the oceans and biosphere. The CO₂ impulse response function can be expected to change with future CO₂ emission changes due to its dependence on concentration.

The background atmosphere upon which to base GWPs has been taken as the atmosphere which existed just before an impulse. Radiative forcing is always calculated with respect to the time-independent atmospheric concentrations just before the impulse. The concentration of many gases, CO₂ in particular, is expected to increase with time (IPCC, 1990, 1992) due to current and future emissions of those gases.

Any scenario of the time dependence of carbon dioxide concentration in the atmosphere should be consistent with the observed past and present concentration of CO₂; carbon-cycle models which meet this condition given reasonable past emissions are known as "balanced" models. Accurate calculation of the current concentration of CO₂ is one condition needed to insure that the response of the atmosphere to CO₂ with time is modeled correctly. However, previously published GWP studies (IPCC, 1990, 1992; WMO, 1991) obtain GWPs based on CO₂ response functions from models which do not correctly calculate the current CO₂ concentration based on a reasonable emission history ("unbalanced" models). To estimate the GWP values and the past and future CO₂ concentrations, a balanced carbon cycle model is required. One of the purposes of the present study is to assess the effects of balancing the carbon budget on GWP values.

This report also presents the effects of various carbon dioxide emission scenarios upon the GWP values calculated. The dependence of the CO₂ radiative forcing upon increased concentration in the future is also considered in the disequilibrium GWP defined below. Finally, the effect of uncertainties in the WMO (1991) atmospheric lifetimes on GWPs is determined. Since the time of the original preparations for this report, we have continued to refine these analyses; unfortunately there is insufficient time within the constraints of EPA's timetable for us to include all of the changes into this report; however, a journal article is being prepared containing all of the updated studies.

5.1. Global Warming Potentials

In this study, GWPs are evaluated using the radiative forcing expressions of IPCC (1990; see their Tables 2.2 and 2.4) over time from the time of an impulse to the user-selected GWP time horizon. The Global Warming Potential of a greenhouse gas is the time-integrated commitment to climate forcing from the instantaneous release of an incremental amount (e.g., one kilogram) of a trace gas expressed relative to the climate forcing of an incremental amount of CO₂. This is equivalent to solving the equation:

$$GWP(i) = \frac{\int_0^T g[t_1 c_i(t)] dt}{\int_0^T g[t_1 c_{CO_2}(t)] dt}$$

In this equation, the GWP for species *i* is derived over an integration time *T* following initial emission. the variable *c(t)* is the atmospheric concentration of *i* or CO₂ at time *t* after emission and *g* is the radiative forcing.

The IPCC-derived GWPs assume that the background atmosphere is in equilibrium (that background concentrations are constant over the GWP integration period). In our calculations, the equilibrium GWP takes the background concentration for a trace gas as that present in the atmosphere just before the impulse, while the disequilibrium GWP bases radiative forcing upon the time-dependent concentration of the trace gas in the absence of an impulse for a given scenario of future CO₂ emission. Atmospheric disequilibrium affects the integrated radiative forcings for trace gases with linear radiative forcing functions in concentration (CFCs, HCFCs, halons) in direct proportion to the concentration change produced by the impulse with no dependence upon the initial trace gas concentration. Disequilibrium in CO₂, CH₄, and N₂O does affect integrated radiative forcings due to the dependence of that quantity on trace gas concentration in the absence of the impulse. Such nonlinear radiative forcing functions arise when the central peak of absorption in infrared transitions is saturated and further increases in absorption with concentration can occur only in the wings of the transition. The current study addresses only the effect of disequilibrium in CO₂, and other gases are treated as if they were at equilibrium at the concentrations given in the IPCC (1990) standard atmosphere with atmospheric lifetimes according to IPCC (1992). These lifetimes are reproduced in Table 5.1. The disequilibrium effect due to time-dependent changes in background concentration of methane will depend on chemical interactions that have not been considered here (future studies will address these effects).

The definition of direct GWP (IPCC, 1990) requires integration of radiative forcing (or tropospheric temperature change) resulting from a one-kilogram release of trace gas and of CO₂. The small change in atmospheric concentration resulting from such a release is difficult for most computers, so that a larger release of trace gas is preferable, such as 1 gigaton of carbon (1 GtC, equal to 3.7 × 10¹² kg of CO₂). Radiative forcing scales linearly for many gases at reasonable concentrations; only for CO₂, CH₄, and N₂O does nonlinearity occur. In most of our cases, the mass released is set at 1000 kg for all gases except CO₂. The CO₂ release is also set at 1000 kg when the program is given an impulse response function, including the triple-exponential decay function for CO₂ given by Derwent (1990) and used by IPCC, but is determined from the initial difference in concentrations between presence and absence of impulse when the program is supplied with that information from the balanced carbon cycle model. Radiative forcing is scaled by the mass of CO₂ released when needed. While the radiative forcing of CO₂ is sufficiently linear with respect to mass released for amounts up to 1 GtC, reducing the mass released below 1000 kg exacts a severe penalty in computation time and eventually in precision due to roundoff error. Table 5.2 presents

GWPs calculated by our method for the IPCC (1992) conditions; these are not significantly different from those reported by the IPCC.

Table 5.1. IPCC (1992) atmospheric lifetimes for greenhouse gases

Gas	Lifetime/yr.
CH ₄	10.5
N ₂ O	132.0
CFC-11	55.0
CFC-12	116.0
CFC-113	110.0
CFC-114	220.0
CFC-115	550.0
HCFC-22	15.8
HCFC-123	1.75
HCFC-124	7.1
HFC-125	40.5
HFC-134a	15.6
HCFC-141b	11.4
HCFC-142b	22.6
HFC-143a	64.2
HFC-152a	1.8
CCl ₄	47.0
CH ₃ CCl ₃	6.1
CF ₃ Br	77.0

Table 5.2. Equilibrium GWPs for the IPCC (1992) impulse response function and atmospheric lifetimes

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	34.3	18.9	11.2	6.9	3.8
N ₂ O	254	269	266	239	165
CFC-11	4420	4100	3370	2400	1360
CFC-12	7010	7330	7090	6180	4100
HCFC-22	4090	2580	1580	968	535
CFC-113	4490	4670	4480	3850	2510
CFC-114	5960	6600	6950	6960	5780
CFC-115	5390	6210	6970	7820	8460
HCFC-123	331	157	92.1	56.4	31.2
HCFC-124	1540	776	455	279	154
HFC-125	5150	4430	3350	2230	1240
HFC-134a	3080	1940	1180	725	401
HCFC-141b	1810	1020	608	372	206
HCFC-142b	3930	2820	1830	1140	628
HFC-143a	4670	4470	3820	2830	1640
HFC-152a	524	248	145	89.0	49.1
CCl ₄	1770	1580	1250	854	478
CH ₃ CCl ₃	351	173	101	62.0	34.2
CF ₃ Br	5530	5460	4880	3000	2270

5.2. Balanced Carbon Cycle Model

We have used a coupled climate carbon-cycle model of Jain and Bach (1991) to calculate the decay rate for CO₂. This model contains a box-diffusion carbon cycle model consisting of three reservoirs, namely the atmosphere, the mixed ocean layer (ca. 75 m) and the deep ocean (ca. 3925 m). The model equations which describe the rate of change of carbon in each box are those taken from Oeschger *et al.* (1975). The model ocean is treated as a diffusion medium with constant vertical eddy diffusivity. The model also takes into account the interaction with the biosphere. The biospheric emissions are calculated by a multi-box globally-aggregated terrestrial biosphere submodel developed by Harvey (1989). Carbon dioxide fertilization effects are modeled by allowing the rate of photosynthesis N to increase via the β factor, whereby

$$N = N_0 \left(1 + \beta \ln \left(\frac{C(t)}{C(0)} \right) \right) \quad (1)$$

where C is the CO₂ concentration. Finally, the one-dimensional upwelling-diffusion model of Harvey and Schneider (1985) is used to model the surface temperature changes.

To balance the carbon cycle means to remove any inconsistencies between model output and observations. When a balanced model is run from pre-industrial times to the current date using the observed emissions (industrial and land use), it will give the correct history of CO₂ concentration changes. As a further condition of agreement, the model is constrained to have a 1980s mean flux of CO₂ into the ocean of 1 - 3 GtC/yr (IPCC, 1990).

The CO₂ variations can be made to fit observations by assuming the larger ocean flux, accounting for CO₂ fertilization feedback, and/or assuming the existence of additional CO₂ sinks. In the present study we fit CO₂ estimations with observations by the first two methods. The ocean flux can be controlled by the transport parameters (eg. eddy diffusivity) to give a faster rate of CO₂ uptake and the fertilization effect by factor β . Table 5.3 shows the combination values of β and 1980-mean ocean flux ($F(1980s)$) which give close to the observed 1990 concentration. Also given in Table 5.3 are the cumulative fluxes up to 1990 and 1980s fluxes ($B(1980s)$) due to land use changes and from temperature- and CO₂ biospheric feedbacks. Fossil fuel and land use emissions from 1860 to 1990 are specified as described in Jain and Bach (1991). The estimated CO₂ emissions due to land use changes (without CO₂ fertilization effect) for the 1980s and for the period of 1860-1990 were 1.8 GtC/yr and 117 GtC as compared to the IPCC estimates of 0.6-2.6 GtC/yr and 83-163 GtC, respectively.

Table 5.3. Atmospheric CO₂ concentration in 1990 for various combinations of β factor and mean-1980 ocean flux, $F(1980s)$. Also given are cumulative fluxes (1860-1990) and mean-1980 fluxes due to land use changes and CO₂ feedback on the terrestrial biosphere

β	F(1980s) 1860-1990 GtC/yr	Land use		Feedback		Concentration ppm
		1980s GtC	1860-1990 GtC/yr	1980s GtC	1990 GtC/yr	
0.0	3.0	117	1.8	1	0.0	375.4
0.2	3.0	117	1.8	-36	-0.8	353.8
0.4	2.3	117	1.8	-68	-1.4	354.0
0.6	1.5	117	1.8	-106	-2.2	353.9
0.8	1.0	117	1.8	-130	-2.8	353.9

Previous studies have found $\beta = 0.2-0.6$ necessary to simulate the observed atmospheric CO_2 concentration. A β value of 0.4 is currently considered as the most likely estimate (Bacastow and Keeling, 1973; Goudrian and Ketner, 1984; Harvey, 1989). For a β range of 0.2 (0.4) 0.6, the model estimated F(1980s) and B(1980s) ranges between 3.0 (2.3) 1.5 GtC/yr and -0.8 (-1.4) -2.2 GtC/yr , respectively (bracketed values are the best estimates). Our estimated F(1980s) fluxes fall within the IPCC-recommended range of 1.0-3.0 GtC/yr . According to recent estimates, the present day contribution of the CO_2 fertilization effect is of the order of - 0.7 (-1.4) -2.2 GtC/yr (Kohlmaier *et al.*, 1987). Our estimates are in good agreement with these values.

For F(1980s) of 1 GtC/yr , a lower limit of oceanic uptake of CO_2 , $\beta=0.8$ is required, which is an unreasonably high value. Gates (1985) summarizes empirical data from a variety of plant species indicating a β value of 0.5-0.7 at 340 ppm CO_2 , decreasing to 0.3-0.5 at 680 ppm. Further evidence against a β this large is that the 1980s-biospheric feedback flux is -2.8 GtC (Table 5.3), which is well above the upper limit of recent estimates of CO_2 fertilization effects (Kohlmaier *et al.*, 1987). A β of 0.6 is therefore used here as an upper limit in simulating the past and future CO_2 variations.

In Figure 5.1, the CO_2 measurements series of Mauna Loa, Hawaii, which are considered as representative of the global mean (Keeling *et al.*, 1989), are compared with the results of the carbon cycle model. Figure 5.1 shows that the carbon cycle model including the biospheric feedback reproduces satisfactorily the observed atmospheric CO_2 concentration. Excluding the effects of the biosphere results in a significant overestimation. The pre-industrial CO_2 concentration appears to have ranged between 280 and 285 ppm (Gammon, 1985; Oeschger and Stauffer, 1986). In the present study, we take 281 ppm as the starting concentration. In 1990, modeled atmospheric CO_2 concentration for the balanced case was 353.9 ppm compared to the observed concentration of 353.9 ppm (IPCC, 1990), as shown in Table 5.4.

Figure 5.1. Model-computed CO_2 concentration (with and without feedback), 1860–1990, and observed CO_2 concentration, 1959–1990.

Table 5.4. Atmospheric concentration of CO₂ in parts per million (volume) with respect to time for the emission scenarios

(A) Constant-emission scenarios:

F(1980s)= ^a	2.3	3.0	1.5	3.0
β	0.4	0.0	0.6	0.2
year				
1991	356.9	357.3	357.7	357.8
2000	372.1	378.6	373.5	373.0
2010	387.3	399.9	389.6	388.1
2040	428.8	456.0	435.1	427.7
2090	491.8	534.7	509.4	485.0
2190	605.9	663.2	657.6	582.3
2290	708.6	770.6	804.0	665.6
2390	802.5	865.1	946.5	740.0
2490	890.5	950.7	1084.3	808.7

(B) IPCC Emission Scenarios:^b

F(1980s) = 2.3 GtC/yr., $\beta = 0.4$

	Scenario					
year	A	B	C	D	E	F
1991	356.0	356.0	355.9	355.7	356.0	356.0
2000	370.7	370.4	368.3	367.3	372.2	371.5
2010	389.9	388.3	382.9	380.5	395.1	392.9
2040	462.8	457.8	425.8	423.5	493.0	483.3
2090	611.3	596.9	460.1	493.5	753.9	681.6
2190	944.2	907.5	502.4	643.6	1391.7	1136.5
2290	1220.8	1166.2	546.9	772.5	1906.0	1509.9
2390	1464.7	1394.8	589.3	888.8	2351.7	1836.4
2490	1685.2	1601.6	630.6	995.4	2750.2	2130.1

^aUnits for ocean absorption rates F are GtC/yr.

^bEmission rates past 2100 remain constant at the 2100 value from the scenario.

The balanced model concentrations in the presence and absence of a 1 GtC pulse of CO₂ in 1990 are used to evaluate the impulse response function for calculation of equilibrium GWPs. Figure 5.2 shows the impulse response function for four constant-emission scenarios. All experiments begin with present day (end of 1990) conditions (i.e., with the disequilibrium state) and the background atmosphere receives constant CO₂ emission, i.e., industrial and land use emissions are kept constant at the 1990s level of 7.4 GtC/yr.

Figure 5.2. Model response of atmospheric CO₂ to a pulse input of 1 GtC for various experiments. For the best case, $\beta = 0.4$ and $F(1980s)$ is 2.3 GtC/year. For $F(1980s)$ of 3.0 and 1.5 GtC/yr curves, β values are 0.2 and 0.6. The IPCC curve is based on the Siegenthaler and Oeschger carbon cycle model and was used in the IPCC studies.

The effect of including a fertilization feedback can be assessed by comparing the best case ($\beta = 0.4$) and no-feedback case ($\beta = 0.0$), the latter of which closely matches the impulse response function of the IPCC. Figure 5.2 shows that for the best case, the decay of the CO₂ is much more rapid than in the no-feedback case. The fertilization feedback withdraws more CO₂ from the atmosphere, producing an enhanced short-term decay which converges toward the no-feedback case at longer times. From the high $F(1980s) = 3.0$ GtC/yr and low $F(1980s) = 1.5$ GtC/yr curves we can also examine the time-varying budget for a range of ocean uptake efficiencies. These two curves clearly show that the response of the 3 GtC/yr curve is much more rapid than the 1.5 GtC/yr curve. Also shown in Figure 5.2 is the impulse response curve which was used in the IPCC studies and is based on the Siegenthaler and Oeschger carbon cycle model. It is important to note that there are various differences between present and IPCC estimations namely, the carbon cycle model is different (balanced versus unbalanced model), the background atmosphere is different (constant emission versus constant concentration), and the initial state of the carbon cycle model is different (1990 disequilibrium versus a hypothetical equilibrium state).

Equilibrium GWPs for the constant-emission impulse response functions are given in Table 5.5. The difference between these GWPs and the IPCC GWPs (Table 5.2) is in the integrated radiative forcing of CO₂ arising from the balanced carbon cycle model compared with that from the IPCC unbalanced model. Percentage differences are listed in Table 5.6; since this effect only changes the integrated radiative forcing of CO₂, the difference does not depend on the identity of the trace gas (note that the GWP for CO₂ is always unity by definition; the factors shown apply to other trace gases). The rapid CO₂ decay in the "best" case ($\beta = 0.4$, $F = 2.3$ GtC/yr) compared with the IPCC unbalanced model causes a systematic enhancement in GWPs at short time horizons T : 9 percent

for $T = 20$ yr which increases to 16 percent at $T = 100$ yr. As time proceeds, however, the two impulse response functions converge, and the balanced carbon cycle response function is larger than the IPCC function for times exceeding 200 yr (Figure 5.2). The enhancement in GWPs decreases for T greater than 100 yr, and is only 3 percent at $T = 500$ yr.

Table 5.5. Equilibrium GWPs for CO₂ constant-emission scenarios with the balanced carbon cycle model

(A) Best Case: $F(1980s) = 2.3$ GtC/yr, $\beta = 0.4$

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	37.2	21.8	13.0	7.6	3.9
N ₂ O	275	309	308	267	170
CFC-11	4800	4720	3910	2680	1400
CFC-12	7600	8430	8230	6890	4220
HCFC-22	4430	2970	1830	1080	551
CFC-113	4870	5370	5190	4290	2590
CFC-114	6460	7590	8060	7760	5950
CFC-115	5850	7140	8080	8730	8720
HCFC-123	360	181	107	62.9	32.1
HCFC-124	1670	892	528	311	159
HFC-125	5580	5100	3890	2490	1280
HFC-134a	3340	2230	1370	809	413
HCFC-141b	1960	1180	705	415	212
HCFC-142b	4260	3240	2130	1270	646
HFC-143a	5060	5140	4430	3160	1690
HFC-152a	568	285	169	99.2	50.6
CCl ₄	1910	1820	1440	952	493
CH ₃ CCl ₃	380	198	117	69.1	35.3
CF ₃ Br	6000	6280	5660	4240	2330

(B) No Feedback: $F(1980s) = 3.0 \text{ GtC/yr.}$, $\beta = 0.0$

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	32.8	17.8	10.5	6.3	3.4
N ₂ O	242	254	249	220	148
CFC-11	4230	3870	3160	2210	1220
CFC-12	6690	6910	6640	5690	3670
HCFC-22	3910	2430	1480	892	478
CFC-113	4290	4400	4190	3540	2250
CFC-114	5690	6220	6510	6410	5170
CFC-115	5150	5850	6520	7210	7570
HCFC-123	317	148	86.2	51.9	27.9
HCFC-124	1470	731	426	257	138
HFC-125	4920	4180	3140	2050	1110
HFC-134a	2940	1830	1110	668	358
HCFC-141b	1730	965	569	343	184
HCFC-142b	3750	2660	1720	1050	561
HFC-143a	4460	4210	3580	2610	1460
HFC-152a	500	234	136	82.0	44.0
CCl ₄	1690	1490	1170	786	428
CH ₃ CCl ₃	335	163	94.8	57.1	30.6
CF ₃ Br	5280	5150	4570	3500	2030

(C) $F(1980s) = 1.5 \text{ GtC/yr.}$, $\beta = 0.6$

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	37.6	21.3	12.2	6.7	3.0
N ₂ O	278	302	289	234	133
CFC-11	4850	4610	3660	2350	1100
CFC-12	7680	8240	7710	6040	3300
HCFC-22	4480	2900	1710	946	431
CFC-113	4920	5250	4860	3760	2020
CFC-114	6530	7410	7550	6800	4650
CFC-115	5910	6980	7570	7650	6810
HCFC-123	363	176	100	55.1	25.1
HCFC-124	1690	871	495	273	124
HFC-125	5640	4980	3640	2180	998
HFC-134a	3380	2180	1280	709	323
HCFC-141b	1980	1150	660	364	166
HCFC-142b	4300	3160	1990	1110	505
HFC-143a	5110	5020	4150	2770	1320
HFC-152a	573	278	158	87.0	39.6
CCl ₄	1930	1770	1350	835	385
CH ₃ CCl ₃	384	194	110	60.6	27.6
CF ₃ Br	6060	6140	5300	3720	1820

(D) $F(1980s) = 3.0 \text{ GtC/yr}$, $\beta = 0.2$

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	37.6	21.9	13.4	8.2	4.4
N ₂ O	278	312	317	285	193
CFC-11	4850	4750	4030	2860	1590
CFC-12	7680	8500	8470	7370	4770
HCFC-22	4480	2990	1880	1150	625
CFC-113	4920	5410	5350	4590	2920
CFC-114	6530	7650	8300	8300	6720
CFC-115	5910	7200	8320	9330	9860
HCFC-123	364	182	110	67.3	36.3
HCFC-124	1690	899	544	333	179
HFC-125	5640	5140	4010	2660	1440
HFC-134a	3380	2250	1410	865	467
HCFC-141b	1980	1190	726	444	240
HCFC-142b	4300	3260	2190	1350	731
HFC-143a	5120	5180	4560	3380	1910
HFC-152a	574	287	174	106	57.2
CCl ₄	1930	1830	1490	1020	557
CH ₃ CCl ₃	384	200	121	73.9	39.9
CF ₃ Br	6060	6330	5830	4540	2640

As seen in Table 5.6, the particular combination of biological feedback β and ocean uptake rate F produce a considerable effect on GWPs defined for a balanced carbon cycle. The GWPs for the $\beta = 0.0$ case are smaller than the IPCC GWPs for all time horizons T . The range of the derived GWPs within reasonable uncertainty limits in β and F are now described. For $\beta = 0.6$, the enhancement at $T = 20$ yr is 10 percent due to the fast initial decay of CO₂. However, in order to balance this scenario, the smaller ocean uptake $F = 1.5 \text{ GtC/yr}$ is required. The impulse response function exhibits a considerably slower decay than the IPCC function for times beyond 50 yr, and the two functions cross over before $T = 100$ yr (Figure 5.2). The GWP enhancement of 8 percent at $T = 100$ yr thus becomes -3 percent at $T = 200$ yr, then -20 percent at $T = 500$ yr. The balanced scenario with $\beta = 0.2$ and $F = 3.0 \text{ GtC/yr}$ has a long-term decay that is somewhat greater than that of the best case $\beta = 0.4$ (Figure 5.2). Accordingly, the GWPs are greater for this case than the IPCC GWPs for all time horizons studied, varying from 10 percent at $T = 20$ yr to 19 percent at $T = 100$ and 200 yr, then 16 percent at $T = 500$ yr. An examination of all of the cases for the balanced carbon cycle indicate that the GWPs are least uncertain at $T = 20$ yr and become more uncertain with increasing T , up to the range of -20 to +16 percent at $T = 500$ yr.

Table 5.6. Percent change in GWPs for the balanced carbon cycle compared with IPCC (1992) calculations

F(1980s) (GtC yr ⁻¹)		Emission Case	Percent Difference in GWPs at Time Horizon (yr)				
β			20	50	100	200	500
2.3	0.4	constant	8.6	11.0	15.9	11.2	3.0
3.0	0.0	constant	-4.4	-9.0	-6.4	-8.2	-10.6
1.5	0.6	constant	9.7	8.4	8.6	-2.6	-19.5
3.0	0.2	constant	9.7	11.8	19.3	18.9	16.4

5.3. Effect of Emission Scenarios on Atmospheric CO₂ Response and GWPs

When the emission rate of CO₂ into the atmosphere varies in the future, two atmospheric effects can contribute to the GWPs. First, the response to a pulse input in 1990 is expected to depend not only on the past emissions but also on future emissions. Secondly, the radiative forcing due to CO₂ varies nonlinearly with CO₂ concentration, so that the CO₂ integrated radiative forcing (and therefore GWP) should vary nonlinearly with the CO₂ concentration resulting from a given emission scenario. In this section, we examine the response of derived GWPs to the first effect. In order to estimate the effect of changes in the future background atmosphere, we consider six new IPCC CO₂ -emission scenarios (IPCC, 1992). The balanced carbon cycle is used to calculate concentrations of CO₂ in the presence and absence of a 1 GtC pulse of CO₂ using the best values of fertilization parameter $\beta = 0.4$ and 1980s ocean flux $F = 2.3$ GtC/yr. The CO₂ concentrations give impulse response functions for these scenarios, from which equilibrium GWPs are found and compared with those of the best constant-emission case (Table 5.5A). Figures 5.3 (a) and (b) show the emissions and concentrations for the six scenarios from 1990 to 2100. To estimate the impulse response curves to 500 yr, emissions in these scenarios are assumed to remain constant after 2100. Figure 5.4 shows that the IPCC (1992) impulse response functions found vary somewhat with emission scenarios in the balanced carbon cycle model, so that GWP should change from that of the constant-emission best case, but that the difference among the IPCC emission scenarios should not be large.

The equilibrium GWPs for the IPCC (1992) scenarios are given in Table 5.7. Percentage differences in GWP between three of the IPCC scenarios and those of the constant-emission best case are shown in Table 5.8. The chosen IPCC emission scenarios represent the intermediate case (Scenario A), the lower extreme of emission (Scenario C, which is nearly similar to the constant-emission case), and the upper extreme (Scenario E). At a time horizon from 20 yr to 50 yr, the differences among the GWPs for the emission scenarios are insignificant at less than one percent. The slight enhancement in the nearly constant-emission Scenario C GWPs remains insignificant at time horizons up to 500 yr. For Scenarios A and E, however, slight increases in the impulse response functions compared to Scenario C occur (Figure 5.4) past time horizons of 50 yr, and a significant decrease in GWPs begins at 100 yr. The change increases in magnitude to a 5 percent decrease for Scenario A and 7 percent for Scenario E at 500 yr. Overall, in comparison to the magnitude of other uncertainties, the effect of emission on derived GWPs through the impulse response function is not significant.

Table 5.7. Equilibrium atmosphere GWPs for the IPCC (1992) CO₂ emission scenarios(A) F(1980s) = 2.3 GtC/yr, $\beta = 0.4$, IPCC Scenario A

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	37.2	21.8	12.9	7.4	3.7
N ₂ O	275	309	305	259	162
CFC-11	4800	4710	3880	2600	1330
CFC-12	7600	8430	8150	6700	4010
HCFC-22	4440	2970	1810	1050	524
CFC-113	4870	5370	5140	4170	2460
CFC-114	6470	7580	7990	7540	5650
CFC-115	5850	7140	8000	8480	8290
CFC-123	360	181	106	61.1	30.5
CFC-124	1670	892	523	302	151
HFC-125	5580	5090	3850	2420	1210
HFC-134a	3340	2230	1360	786	392
CFC-141b	1970	1180	698	404	201
CFC-142b	4260	3240	2110	1230	614
HFC-143a	5070	5130	4390	3070	1600
HFC-152a	568	285	167	96.4	48.1
CCl ₄	1910	1810	1430	925	468
CH ₃ CCl ₃	381	198	116	67.2	33.5
CF ₃ Br	6000	6280	5600	4120	2220

(B) F(1980s) = 2.3 GtC/yr, $\beta = 0.4$, IPCC Scenario B

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	37.2	21.8	12.9	7.5	3.7
N ₂ O	275	309	306	260	162
CFC-11	4800	4720	3880	2610	1340
CFC-12	7600	8430	8160	6720	4020
HCFC-22	4440	2970	1820	1050	525
CFC-113	4870	5370	5150	4180	2460
CFC-114	6470	7590	8000	7560	5670
CFC-115	5850	7140	8020	8500	8310
HCFC-123	360	181	106	61.3	30.6
HCFC-124	1670	892	524	303	151
HFC-125	5580	5100	3860	2420	1220
HFC-134a	3340	2230	1360	788	393
HCFC-141b	1970	1180	699	405	202
HCFC-142b	4260	3240	2110	1230	616
HFC-143a	5070	5140	4400	3080	1610
HFC-152a	568	285	167	96.7	48.2
CCl ₄	1920	1820	1430	928	469
CH ₃ CCl ₃	381	198	116	67.3	33.6
CF ₃ Br	6000	6280	5610	4130	2220

(C) $F(1980s) = 2.3 \text{ GtC/yr}$, $\beta = 0.4$, IPCC Scenario C

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	37.2	21.8	13.0	7.7	3.9
N ₂ O	275	310	309	269	171
CFC-11	4800	4730	3920	2700	1410
CFC-12	7600	8450	8250	6950	4240
HCFC-22	4440	2980	1840	1090	554
CFC-113	4870	5380	5210	4330	2600
CFC-114	6470	7610	8090	7820	5980
CFC-115	5850	7160	8100	8800	8760
HCFC-123	360	181	107	63.4	32.3
HCFC-124	1670	894	530	313	160
HFC-125	5580	5110	3900	2510	1280
HFC-134a	3340	2230	1380	815	415
HCFC-141b	1970	1180	707	419	213
HCFC-142b	4260	3250	2130	1280	650
HFC-143a	5070	5150	4450	3190	1700
HFC-152a	568	286	169	100	50.9
CCl ₄	1920	1820	1450	960	495
CH ₃ CCl ₃	381	199	118	69.7	35.4
CF ₃ Br	6000	6300	5680	4280	2350

(D) $F(1980s) = 2.3 \text{ GtC/yr}$, $\beta = 0.4$, IPCC Scenario D

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	37.3	21.8	13.0	7.6	3.8
N ₂ O	275	310	309	266	166
CFC-11	4800	4730	3920	2670	1370
CFC-12	7610	8460	8250	6870	4120
HCFC-22	4440	2980	1840	1080	537
CFC-113	4880	5390	5210	4280	2520
CFC-114	6470	7610	8090	7730	5800
CFC-115	5850	7170	8100	8690	8510
HCFC-123	360	181	107	62.7	31.3
HCFC-124	1670	895	530	310	155
HFC-125	5590	5110	3900	2480	1250
HFC-134a	3350	2240	1380	806	403
HCFC-141b	1970	1180	707	414	207
HCFC-142b	4260	3250	2130	1260	631
HFC-143a	5070	5150	4450	3150	1650
HFC-152a	568	286	169	98.9	49.4
CCl ₄	1920	1820	1450	948	481
CH ₃ CCl ₃	381	199	118	68.9	34.4
CF ₃ Br	6000	6310	5680	4230	2280

(E) $F(1980s) = 2.3 \text{ GtC/yr}$, $\beta = 0.4$, IPCC Scenario E

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	37.2	21.7	12.8	7.3	3.6
N ₂ O	275	309	303	254	159
CFC-11	4800	4700	3840	2550	1310
CFC-12	7600	8410	8080	6570	3940
HCFC-22	4440	2960	1800	1030	514
CFC-113	4870	5360	5100	4090	2410
CFC-114	6460	7570	7920	7400	5550
CFC-115	5850	7120	7930	8320	8140
HCFC-123	360	180	105	60.0	30.0
HCFC-124	1670	890	519	297	148
HFC-125	5580	5080	3820	2370	1190
HFC-134a	3340	2220	1350	771	385
HCFC-141b	1960	1170	692	396	198
HCFC-142b	4260	3230	2090	1210	603
HFC-143a	5060	5120	4350	3010	1570
HFC-152a	568	284	166	94.6	47.3
CCl ₄	1920	1810	1420	908	460
CH ₃ CCl ₃	381	198	115	65.9	32.9
CF ₃ Br	6000	6270	5560	4050	2180

(F) $F(1980s) = 2.3 \text{ GtC/yr}$, $\beta = 0.4$, IPCC Scenario F

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	37.2	21.7	12.8	7.4	3.7
N ₂ O	275	309	304	257	161
CFC-11	4800	4710	3860	2580	1320
CFC-12	7600	8420	8110	6630	3980
HCFC-22	4440	2960	1800	1040	519
CFC-113	4870	5360	5120	4130	2440
CFC-114	6470	7570	7940	7470	5600
CFC-115	5850	7130	7960	8390	8210
HCFC-123	360	180	105	60.5	30.2
HCFC-124	1670	890	520	299	150
HFC-125	5580	5090	3830	2390	1200
HFC-134a	3340	2220	1350	778	389
HCFC-141b	1970	1180	695	400	200
HCFC-142b	4260	3230	2090	1220	609
HFC-143a	5070	5130	4370	3040	1590
HFC-152a	568	284	166	95.5	47.7
CCl ₄	1920	1810	1420	916	464
CH ₃ CCl ₃	381	198	116	66.5	33.2
CF ₃ Br	6000	6270	5580	4080	2200

Table 5.8. Differences in equilibrium GWPs (percent) between IPCC (1992) emission scenarios and the constant-emission reference case

F(1980s) (GtC yr ⁻¹)	Emission		Percent Difference in GWPs at Time Horizon (yr)				
	β	Scenario	20	50	100	200	500
2.3	0.4	A	0.06	-0.05	-0.92	-2.82	-4.95
2.3	0.4	C	0.07	0.24	0.33	0.80	0.52
2.3	0.4	E	0.04	-0.27	-1.78	-4.63	-6.65

5.4. Disequilibrium versus Equilibrium GWPs

The second atmospheric effect with potential to affect GWPs results from changes in CO₂ concentration, which will be different among various emission scenarios. CO₂ concentration increases with time, at least to 2100, for all current scenarios of emissions that have been developed by IPCC (Figure 5.3 (b)). The change in radiative forcing associated with a small impulse of CO₂ is inversely proportional to the concentration of CO₂ (IPCC, 1990). Where atmospheric CO₂ concentrations increase with time, integrated CO₂ radiative forcing should be smaller for the disequilibrium than for equilibrium, and resulting GWPs for gases other than CO₂ should be larger. Table 5.9 lists the GWP values resulting for disequilibrium CO₂ concentrations following the constant-emission reference scenario and the six IPCC emission scenarios. Percentage enhancements for GWP are given in Table 5.10 for the reference scenario and the three representative IPCC scenarios A, C, and E. Since the disequilibrium enhancement is produced through the denominator CO₂ concentration c_0 in the expression for radiative forcing (IPCC, 1990; see Table 2.2),

$$\Delta F_{CO_2} = 6.3 \ln \left(\frac{c(t)}{c_0} \right) \quad (2)$$

no significant effect of gas identity upon GWP enhancement is expected. All emission scenarios produce increases in disequilibrium GWPs compared with equilibrium in CO₂. The percentage enhancement for disequilibrium is lowest at shorter time horizons; at a time horizon of 20 yr., the enhancement ranges from 6 to 7 percent. Since the differences in CO₂ concentration among the scenarios become more apparent at longer times, the disequilibrium enhancement depends more strongly upon the emission scenario chosen. At a time horizon of 500 yr, the difference in disequilibrium enhancement thus ranges from 38 percent for IPCC Scenario C to 166 percent for IPCC Scenario E. Figure 5.3 and Table 5.4 both show that IPCC Scenario E gives the largest CO₂ concentration and Scenario C the smallest among all of the emission scenarios studied in the year 2100.

Figure 5.3. Emission (a) and concentration (b) of CO₂ for various IPCC scenarios from 1990–2100.

Figure 5.4. Response of atmospheric CO₂ to a pulse of 1 GtC for various IPCC scenarios. For all scenarios, $\beta = 0.4$ and $F(1980s) = 2.3$ GtC/yr is assumed.

Table 5.9. Disequilibrium GWPs for CO₂ emission scenarios with the balanced carbon cycle model

(A) Best F, $\beta = 0.4$, constant emission

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	39.7	24.1	15.3	10.0	6.2
N ₂ O	293	342	362	347	272
CFC-11	5120	5210	4600	3490	2240
CFC-12	8110	9320	9670	8980	6740
HCFC-22	4730	3280	2150	1410	879
CFC-113	5200	5940	6110	5590	4120
CFC-114	6900	8380	9480	10100	9490
CFC-115	6240	7890	9500	11400	13900
HCFC-123	384	200	126	82.0	51.2
HCFC-124	1790	986	621	405	253
HFC-125	5960	5630	4570	3240	2040
HFC-134a	3570	2460	1610	1050	658
HCFC-141b	2100	1300	829	541	338
HCFC-142b	4540	3580	2500	1650	1030
HFC-143a	5400	5680	5210	4120	2690
HFC-152a	606	315	198	129	80.8
CCl ₄	2040	2010	1700	1240	786
CH ₃ CCl ₃	406	219	138	90.1	56.3

CF ₃ Br	6400	6940	6650	5530	3720
(B) F(1980s) = 2.3 GtC/yr, $\beta = 0.4$, IPCC Scenario A					
Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	39.7	24.4	16.1	11.3	8.0
N ₂ O	293	347	382	395	348
CFC-11	5110	5300	4850	3970	2860
CFC-12	8100	9470	10200	10200	8610
HCFC-22	4730	3330	2270	1600	1120
CFC-113	5190	6030	6440	6360	5280
CFC-114	6890	8520	9990	11500	12100
CFC-115	6230	8020	10000	12900	17800
HCFC-123	383	203	132	93.2	65.5
HCFC-124	1780	1000	655	461	324
HFC-125	5950	5720	4820	3680	2610
HFC-134a	3560	2500	1700	1200	842
HCFC-141b	2090	1320	874	615	432
HCFC-142b	4540	3640	2630	1880	1320
HFC-143a	5390	5770	5490	4680	3440
HFC-152a	605	320	209	147	103
CCl ₄	2040	2040	1790	1410	1000
CH ₃ CCl ₃	405	223	146	102	71.9
CF ₃ Br	6390	7060	7010	6280	4760

(C) F(1980s) = 2.3 GtC/yr, $\beta = 0.4$, IPCC Scenario B

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	39.6	24.4	16.0	11.2	7.8
N ₂ O	293	346	379	390	340
CFC-11	5110	5280	4820	3910	2800
CFC-12	8090	9440	10100	10100	8420
HCFC-22	4720	3320	2250	1580	1100
CFC-113	5190	6010	6390	6270	5160
CFC-114	6880	8490	9920	11300	11900
CFC-115	6224	7990	9940	12800	17400
HCFC-123	383	202	131	91.9	64.0
HCFC-124	1780	998	650	454	316
HFC-125	5940	5700	4790	3630	2550
HFC-134a	3560	2490	1690	1180	823
HCFC-141b	2090	1320	868	607	423
HCFC-142b	4530	3620	2620	1850	1290
HFC-143a	5390	5750	5450	4620	3360
HFC-152a	604	319	207	145	101
CCl ₄	2040	2030	1780	1390	983
CH ₃ CCl ₃	405	222	144	101	70.3
CF ₃ Br	6380	7030	6960	6200	4660

(D) F(1980s) = 2.3 GtC/yr, $\beta = 0.4$, IPCC Scenario C

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	39.4	23.9	15.1	9.5	5.4
N ₂ O	291	340	360	330	237
CFC-11	5080	5180	4540	3320	1950
CFC-12	8050	9260	9550	8540	5870
HCFC-22	4700	3260	2120	1340	766
CFC-113	5160	5900	6020	5320	3590
CFC-114	6840	8330	9350	9620	8270
CFC-115	6190	7840	9370	10800	12100
HCFC-123	381	198	124	77.9	44.6
HCFC-124	1770	980	613	385	221
HFC-125	5910	5600	4510	3080	1780
HFC-134a	3540	2450	1590	1000	574
HCFC-141b	2080	1290	818	515	294
HCFC-142b	4510	3560	2470	1570	898
HFC-143a	5360	5640	5140	3920	2340
HFC-152a	601	313	196	123	70.4
CCl ₄	2030	1990	1680	1180	685
CH ₃ CCl ₃	403	218	136	85.7	49.0
CF ₃ Br	6350	6900	6560	5260	3240

(E) F(1980s) = 2.3 GtC/yr, $\beta = 0.4$, IPCC Scenario D

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	39.3	23.8	15.1	10.0	6.3
N ₂ O	290	338	359	348	277
CFC-11	5070	5160	4560	3500	2280
CFC-12	8030	9230	9600	9000	6860
HCFC-22	4680	3250	2130	1410	895
CFC-113	5140	5880	6060	5600	4200
CFC-114	6820	8300	9400	10100	9660
CFC-115	6170	7810	9420	11400	14200
HCFC-123	380	198	125	82.1	52.1
HCFC-124	1770	976	616	406	258
HFC-125	5900	5580	4540	3250	2070
HFC-134a	3530	2440	1600	1060	670
HCFC-141b	2070	1290	822	542	344
HCFC-142b	4500	3540	2480	1650	1050
HFC-143a	5350	5620	5170	4130	2740
HFC-152a	600	312	197	130	82.2
CCl ₄	2020	1990	1680	1240	800
CH ₃ CCl ₃	402	217	137	90.3	57.3
CF ₃ Br	6330	6870	6600	5540	3790

(F) $F(1980s) = 2.3 \text{ GtC/yr}$, $\beta = 0.4$, IPCC Scenario E

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	39.8	24.8	16.9	12.6	9.7
N ₂ O	294	353	401	441	422
CFC-11	5130	5380	5080	4430	3480
CFC-12	8130	9620	10700	11400	10500
HCFC-22	4740	3390	2380	1790	1370
CFC-113	5210	6130	6750	7100	6410
CFC-114	6910	8660	10500	12800	14700
CFC-115	6260	8150	10500	14400	21600
HCFC-123	385	206	139	104	79.5
HCFC-124	1790	1020	686	514	393
HFC-125	5970	5820	5060	4110	3170
HFC-134a	3580	2540	1780	1340	1020
HCFC-141b	2100	1340	916	687	525
HCFC-142b	4550	3700	2760	2090	1600
HFC-143a	5420	5860	5760	5220	4180
HFC-152a	607	325	219	164	126
CCl ₄	2050	2070	1880	1570	1220
CH ₃ CCl ₃	407	226	153	114	87.4
CF ₃ Br	6420	7170	7350	7010	5790

(G) $F(1980s) = 2.3 \text{ GtC/yr}$, $\beta = 0.4$, IPCC Scenario F

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	39.8	24.7	16.6	12.0	8.8
N ₂ O	294	351	393	419	383
CFC-11	5120	5350	4990	4210	3160
CFC-12	8120	9580	10500	10800	9490
HCFC-22	4740	3370	2330	1700	1240
CFC-113	5200	6100	6620	6740	5810
CFC-114	6900	8610	10300	12200	13400
CFC-115	6240	8110	10300	13700	19600
HCFC-123	384	205	136	98.8	72.1
HCFC-124	1790	1010	673	488	357
HFC-125	5960	5790	4960	3900	2870
HFC-134a	3570	2530	1750	1270	928
HCFC-141b	2100	1340	899	652	476
HCFC-142b	4540	3680	2710	1990	1450
HFC-143a	5410	5830	5650	4960	3790
HFC-152a	606	324	215	156	114
CCl ₄	2040	2060	1840	1500	1110
CH ₃ CCl ₃	406	225	150	109	79.3
CF ₃ Br	6400	7140	7210	6660	5250

Table 5.10. Differences in disequilibrium GWPs (percent) from equilibrium GWPs for several model and emission scenarios

F(1980s) (GtC yr ⁻¹)	Emission		Percent Difference in GWPs at Time Horizon (yr)				
	β	Case	20.0	50.0	100.0	200.0	500.0
2.3	0.4	constant	6.7	10.5	17.6	30.3	59.5
2.3	0.4	IPCC A	6.5	12.4	25.1	52.4	114.7
2.3	0.4	IPCC C	5.8	9.6	15.7	22.9	38.3
2.3	0.4	IPCC E	7.0	14.4	32.3	73.4	165.5

5.5. Combined GWP Effects of CO₂ Radiative Forcing Terms

We now consider the combined changes in GWPs from the balanced carbon cycle and with atmospheric disequilibrium relative to the IPCC (1992) treatment. First, we obtain a reference value for the total effect from the best case carbon cycle with constant CO₂ emissions. Then, we estimate lower and upper limits to these changes based upon the uncertainty limits of the biological feedback parameter β and the IPCC (1992) emission scenarios C and E, which represent extrema for this study as shown in Figure 5.3 and Table 5.4.

Table 5.11 shows the percentage difference between the disequilibrium GWPs for the best case balanced carbon cycle model with constant post-1990 CO₂ emissions of Table 5.9A and the IPCC (1992) equilibrium GWPs of Table 5.2 as the "reference value" of the changes introduced. The lower limit is estimated from the sum of effects for the F = 1.5 GtC/yr balanced carbon cycle (Table 5.6), the change in the equilibrium GWPs for IPCC emission scenario C (Table 5.8), and the disequilibrium change of the IPCC (1992) emission scenario C (Table 5.10). The upper limit is estimated for the F = 3.0 GtC/yr balanced carbon cycle, the impulse response effect of IPCC emission scenario E, and the disequilibrium effect of scenario E. Both the systematic change from the IPCC (1992) values and the range of possible effects on GWPs increase considerably as the time horizon for integration increases. The total increase in GWPs is 16 percent with less than one percent range at a time horizon of 20 yr, but a time horizon of 500 yr gives a 64 percent increase with a possible range from 19 to 175 percent. This demonstrates that the dominant effect in the total systematic increase is the effect of using a disequilibrium atmosphere; in turn, the disequilibrium effect is strongly dependent upon the CO₂ emission scenario.

Table 5.11. Total percentage change in GWPs from IPCC (1992) due to balanced carbon cycle model and use of disequilibrium atmospheres in CO₂ integrated radiative forcing calculations

Time Horizon (yr)	Lower Limit	Reference Value	Upper Limit
20	15.6	15.7	16.7
50	18.2	27.1	25.9
100	24.6	36.4	49.8
200	21.1	45.4	87.7
500	19.3	64.3	175.4

5.6. Uncertainties in Atmospheric Lifetimes

Evaluation of the uncertainties associated with the atmospheric lifetimes of non-CO₂ greenhouse gases are subject to limitations in the measurements of emissions, loss processes, and atmospheric concentrations of the gases. There are no definitive

evaluations of the range of lifetimes that would include all known measurement uncertainties. However, the combination of data from existing measurement programs with results from atmospheric models does provide a measure of the reasonable range of uncertainties in atmospheric lifetimes. The WMO (1991) international scientific assessment provides estimated uncertainty limits on most of the relevant greenhouse gases. The WMO recommended lifetime values and their error bounds are shown in Table 5.12.

Table 5.12. WMO (1991) trace gas atmospheric lifetimes with uncertainties

Species	Lifetime (years)		
	Shorter	Intermediate	Longer
CH ₄	8.40	10.5	12.6
N ₂ O	110.0	132.0	168.0
CFC-11	42.0	55.0	66.0
CFC-12	95.0	116.0	130.0
CFC-113	75.0	110.0	144.0
CFC-114	197.0	220.0	264.0
CFC-115	400.0	550.0	800.0
HCFC-22	12.0	15.8	19.6
HCFC-123	1.31	1.71	2.11
HCFC-124	5.33	6.9	8.47
HFC-125	31.6	40.7	49.8
HFC-134a	11.3	15.7	20.1
HCFC-141b	9.1	10.8	12.5
HCFC-142b	17.9	22.4	26.9
HFC-143a	57.6	64.6	71.6
HFC-152a	1.27	1.80	2.33
CCl ₄	30.0	47.0	58.0
CH ₃ CCl ₃	4.97	6.1	7.23
CF ₃ Br	69.0	77.0	88.0

This uncertainty range was used in evaluating GWPs for the standard IPCC approach of a disequilibrium background atmosphere and the balanced carbon cycle best case (F(1980s) = 2.3 GtC/yr, $\beta = 0.4$) with a constant CO₂ emission scenario. These results are shown in Table 5.13, and the percentage changes in both lifetimes and GWPs at the error limits versus the recommended lifetime values are given in Table 5.14. Uncertainty effects are by far most pronounced in short-lived gases. GWPs of the shortest-lived gases HCFC-123 and HFC-152a change essentially by the same percentage as does the lifetime, independent of the time horizon of evaluation. For most gases, the GWP change starts small in magnitude, but approaches equality with the lifetime change as T approaches 500 yr. However, for the two longest-lived gases CFC-114 and CFC-115, the GWP reaches a value significantly less than the lifetime change even after $T = 500$ yr.

Table 5.13. Equilibrium GWPs for the WMO (1991) atmospheric lifetimes

(A) Shorter Lifetime

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	31.7	17.0	10.6	7.1	4.7
N ₂ O	271	290	295	278	218

CFC-11	4550	4080	3310	2430	1630
CFC-12	7460	7850	7760	7040	5290
HCFC-22	3800	2250	1420	957	635
CFC-113	4670	4740	4460	3790	2700
CFC-114	6430	7280	8040	8660	8300
CFC-115	5800	6830	7990	9560	11500
HCFC-123	269	131	81.7	54.9	36.4
HCFC-124	1300	652	405	272	181
HFC-125	5240	4330	3250	2280	1510
HFC-134a	2780	1620	1020	684	453
HCFC-141b	1680	921	575	387	260
HCFC-142b	3860	2630	1730	1170	777
HFC-143a	4980	4800	4240	3350	2300
HFC-152a	400	195	122	81.7	54.2
CCl ₄	1710	1400	1030	719	477
CH ₃ CCl ₃	316	157	97.7	65.7	43.6
CF ₃ Br	5910	5910	5450	4530	3180

(B) Intermediate lifetime

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	37.2	21.2	13.3	8.9	5.9
N ₂ O	275	301	315	311	258
CFC-11	4790	4580	4000	3130	2130
CFC-12	7600	8200	8410	8040	6400
HCFC-22	4430	2890	1870	1260	836
CFC-113	4870	5220	5310	5010	3920
CFC-114	6460	7380	8240	9060	9020
CFC-115	5840	6940	8260	10200	13200
HCFC-123	351	172	107	71.7	47.6
HCFC-124	1630	843	524	353	234
HFC-125	5590	4970	3990	2920	1950
HFC-134a	3350	2180	1410	950	630
HCFC-141b	1900	1090	683	459	304
HCFC-142b	4240	3130	2150	1470	972
HFC-143a	5070	5000	4550	3710	2570
HFC-152a	567	277	172	116	76.8
CCl ₄	1910	1770	1480	1110	747
CH ₃ CCl ₃	380	193	120	80.7	53.5
CF ₃ Br	6000	6110	5780	4950	3540

(C) Longer lifetime

Gas	GWP at time horizon (years)				
	20	50	100	200	500
CO ₂	1.0	1.0	1.0	1.0	1.0
CH ₄	41.7	25.1	15.9	10.7	7.1
N ₂ O	279	313	339	353	319
CFC-11	4930	4890	4470	3670	2550
CFC-12	7660	8380	8750	8620	7120
HCFC-22	4900	3450	2310	1560	1040

CFC-113	4970	5490	5830	5870	5030
CFC-114	6510	7510	8540	9670	10300
CFC-115	5880	7040	8490	10700	15000
HCFC-123	434	212	132	88.5	58.7
HCFC-124	1920	1030	644	433	287
HFC-125	5820	5440	4630	3530	2380
HFC-134a	3760	2670	1800	1220	807
HCFC-141b	2080	1250	790	531	352
HCFC-142b	4520	3550	2550	1760	1170
HFC-143a	5140	5170	4820	4040	2850
HFC-152a	734	359	223	150	99.4
CCl ₄	1990	1920	1700	1350	922
CH ₃ CCl ₃	439	228	142	95.6	63.4
CF ₃ Br	6090	6340	6170	5480	4040

The sensitivity of relative GWP uncertainty to relative uncertainty in t may be analyzed by analytic integration of the equations of IPCC (1990) for gases with linear radiative forcing functions:

$$\Delta F = k\Delta c \quad (3)$$

This analysis does not apply to the gases CH₄ and N₂O, the radiative forcing functions of which are not linear and are coupled to one another. Integrated radiative forcing ΔW for the trace gas, the numerator of the GWP expression, is the above equation integrated over time t to the time horizon T :

$$\Delta W = \int_0^T k\Delta c(t)dt \quad (4)$$

The atmospheric lifetime provides t for the exponential impulse response function:

$$\Delta c(t) = \Delta c_0 \exp\left(-\frac{t}{\tau}\right) \quad (5)$$

in which Δc_0 represents the initial change of atmospheric concentration upon the occurrence of the pulse of trace gas. The integral in Equation 4 becomes:

$$\Delta W = k\Delta c_0 \tau \left(1 - \exp\left(-\frac{T}{\tau}\right)\right) \quad (6)$$

which is the GWP times the radiative forcing integral for CO₂ over T yr. From the definition of GWP, the relative change in GWP is

$$f_G = \frac{(\Delta W_2 - \Delta W_1)}{\Delta W_1} \quad (7)$$

Let two lifetimes t and t' be defined such that $t' = t(1 + \delta)$; then, δ is the relative change in lifetime. Equation 7 becomes:

$$f_G = \frac{\tau(1+\delta) \left(1 - \exp\left(-\frac{T}{\tau(1+\delta)}\right) \right)}{\tau \left(1 - \exp\left(-\frac{T}{\tau}\right) \right)} - 1 \quad (8)$$

The derivative of this function with respect to δ at $\delta = 0$ is the fraction of relative change in GWP per relative change in lifetime for lifetime t :

$$\left. \frac{df_G}{d\delta} \right|_{\delta=0} = 1 - \frac{\frac{T}{\tau} \exp\left(-\frac{T}{\tau}\right)}{1 - \exp\left(-\frac{T}{\tau}\right)} \quad (9)$$

This function is plotted against time horizon T for atmospheric lifetimes of 10, 100, and 1000 yr. in Figure 5.5. The behavior of those curves is very similar to the behavior of the percentage differences for various gases in Table 5.14: a short lifetime gives an immediate rise to a linear GWP dependence on t , GWPs for the 100 yr lifetime remains relatively insensitive to t changes for two lifetimes, and the GWP of an atmospheric species with $t = 1000$ yr would remain insensitive to t even at a time horizon of 500 yr.

Figure 5.5. Scaled derivative of the integrated radiative forcing with respect to atmospheric lifetime plotted against time horizon for several values of lifetime.

Table 5.14. Differences (percent) in WMO (1991) lifetime uncertainty limits and GWPs from values for intermediate lifetime

(A) Shorter Lifetime

Gas	Percent Difference in GWP for time horizon (yr)					
	t (yr)	20.0	50.0	100.0	200.0	500.0
CH ₄	-20.0	-14.8	-19.8	-20.3	-20.2	-20.3
N ₂ O	-16.7	-1.5	-3.5	-6.3	-10.5	-15.6
CFC-11	-23.6	-5.1	-11.0	-17.3	-22.2	-23.6
CFC-12	-18.1	-1.8	-4.3	-7.7	-12.5	-17.4
HCFC-22	-24.1	-14.2	-21.9	-23.9	-24.1	-24.1
CFC-113	-31.8	-4.0	-9.2	-15.9	-24.3	-31.2
CFC-114	-10.5	-0.5	-1.3	-2.4	-4.4	-8.1
CFC-115	-27.3	-0.7	-1.7	-3.2	-6.1	-13.1
HCFC-123	-23.4	-23.4	-23.4	-23.4	-23.4	-23.5
HCFC-124	-22.8	-20.2	-22.7	-22.8	-22.8	-22.8
HFC-125	-22.4	-6.2	-12.8	-18.7	-21.9	-22.4
HFC-134a	-28.0	-17.1	-25.8	-27.9	-28.0	-28.0
HCFC-141b	-15.7	-11.2	-15.3	-15.7	-15.7	-15.7
HCFC-142b	-20.1	-8.9	-16.0	-19.5	-20.1	-20.1
HFC-143a	-10.8	-1.8	-4.0	-6.7	-9.5	-10.8
HFC-152a	-29.4	-29.5	-29.5	-29.4	-29.4	-29.4
CCl ₄	-36.2	-10.4	-20.9	-30.1	-35.3	-36.2
CH ₃ CCl ₃	-18.5	-16.9	-18.5	-18.5	-18.6	-18.5
CF ₃ Br	-10.4	-1.4	-3.3	-5.7	-8.5	-10.3

(B) Longer Lifetime

Gas	Percent Difference in GWP for time horizon (yr)					
	t (yr)	20.0	50.0	100.0	200.0	500.0
CH ₄	20.0	12.1	18.4	19.5	20.2	20.3
N ₂ O	27.3	1.6	3.9	7.5	13.5	23.6
CFC-11	20.0	2.9	6.8	11.8	17.3	20.0
CFC-12	12.1	0.9	2.2	4.1	7.1	11.2
HCFC-22	24.1	10.5	19.4	23.5	24.0	24.0
CFC-113	30.9	2.1	5.1	9.8	17.3	28.2
CFC-114	20.0	0.7	1.8	3.6	6.8	13.7
CFC-115	45.5	0.6	1.4	2.8	5.5	13.2
HCFC-123	23.4	23.4	23.4	23.5	23.4	23.3
HCFC-124	22.8	17.7	22.5	22.8	22.8	22.8
HFC-125	22.4	4.2	9.6	15.9	21.0	22.4
HFC-134a	28.0	12.0	22.5	27.4	28.0	28.0
HCFC-141b	15.7	9.6	14.7	15.7	15.7	15.7
HCFC-142b	20.1	6.7	13.6	18.5	20.0	20.1
HFC-143a	10.8	1.5	3.4	5.9	9.0	10.8
HFC-152a	29.4	29.4	29.4	29.4	29.4	29.4
CCl ₄	23.4	3.9	8.9	15.1	21.2	23.4
CH ₃ CCl ₃	18.5	15.4	18.4	18.5	18.5	18.5
CF ₃ Br	14.3	1.6	3.7	6.7	10.8	14.1

6. Determining Indirect GWPs

One of the goals for this project is the determination of indirect Global Warming Potentials that better represent the effects of ozone and other radiatively important constituents on climate than those previously derived by the Intergovernmental Panel on Climate Change (IPCC, 1990). In some cases, we believe that it is possible to at minimum determine an uncertainty range for some of the indirect GWPs, such as for the effects of methane on ozone. In other cases, existing two- and three-dimensional models may not be able to even determine a meaningful uncertainty range; for example, the effects of NO_x emissions at the Earth's surface will be difficult because of the uncertainties associated with not knowing the background concentrations of NO_x throughout the troposphere. There are many uncertainties and some conceptual difficulties that need to be overcome before indirect GWPs can be used effectively in policy studies. Because of this incomplete understanding, the Intergovernmental Panel on Climate Change, in its recent 1992 report, recommends that none of the previously derived indirect GWPs be used. They suggest that several of the indirect GWPs in the 1990 report are likely to be in substantial error (the first report used what is now considered to be a poorly validated model from the U.K.). We agree wholeheartedly with the IPCC (1992) conclusions (in fact, one of the authors of this report, DJW, was a co-author of both the IPCC 1990 and 1992 reports). At the same time, we believe that there are substantial improvements that *can* be made in both the definition of and values derived for indirect GWPs.

One of the difficulties associated with indirect GWPs determined for effects on tropospheric ozone and hydroxyl is related to the localized nature of the emissions and resulting concentrations of nitrogen oxides, carbon monoxide, and some hydrocarbons in the troposphere. These gases have relatively short atmospheric lifetimes and do not get well mixed in the troposphere (in contrast, for example, to methane, nitrous oxide, carbon dioxide, and some of the other radiatively important constituents). However, we believe that indirect GWPs can still be derived for these species *if* the indirect GWPs are carefully defined in terms of the location of the emissions and in terms of the limitations of the model being used to derive them. For example, with a zonally-averaged model, indirect GWPs can be derived as a function of latitude and season of the emissions (or, in the case of aircraft emissions, as a function of the altitude and latitude, as well as season, of their emissions). With a three-dimensional model, indirect GWPs can be derived as a function of latitude, longitude, and season. While such definitions make policy analyses more strenuous, such definitions are absolutely necessary for species that are too short-lived to be well mixed in the troposphere.

Even with the above refinement on the definition of indirect GWPs, there will still be concerns about the derived GWPs. The uncertainties still existing in tropospheric chemistry processes will leave important ambiguities about the derived indirect GWPs. The inhomogeneity in NO_x , CO, some of the NMHCs, and in OH, along with the uncertainties about the extent of this inhomogeneity, will still leave some question about the validity of developing indirect GWPs for these gases. Such concerns about inhomogeneity are particularly relevant when considering the indirect GWPs derived from a zonally-averaged, two-dimensional model. However, policy makers need to have estimates of the indirect climatic effects resulting from emissions of such gases, at least to within the limits of our knowledge of the uncertainties.

Therefore, while we recognize the limitations associated with derivation of indirect GWPs, we also recognize the importance of getting better estimates of indirect GWPs for policy analyses. We believe it to be incorrect to totally ignore these needs; we believe that it is important to provide what knowledge we do have and our understanding of the uncertainties. Eventually, indirect GWPs will need to be derived with comprehensive three-dimensional models that can fully account for the chemistry and physics of the

global atmosphere (as well as the transition from local to global scales). However, existing three-dimensional models are too expensive and have too many limitations to tackle the derivation of indirect GWPs. Even with a state-of-the-art two-dimensional model, we do not expect to be able to derive indirect GWPs under all the conditions that need to be considered. We will need to develop priorities for the determination of indirect GWPs in order to meet the needs of policy analyses over the next few years.

The absolute priorities (at least as far as determining which gases to focus our analyses) for deriving indirect GWPs will need to be based on the needs of policy makers. However, without a priori knowledge of those priorities, we will attempt to establish our own priorities for determination of indirect GWPs:

- First priority will be given to determine the indirect GWPs (due to effects on ozone, hydroxyl, and stratospheric water vapor) for methane. Methane is not only one of the more important greenhouse gases, but is also sufficiently long-lived that it is well mixed in the troposphere. Determining indirect GWPs should be more straightforward for methane than some of the other gases of interest.
- Second priority will be given to determining the indirect GWPs for emissions of NO_x (from ground and aircraft sources), CO, and NMHCs. There are many more concerns about the localized nature of the effects from emissions of these gases; however, these gases are of interest to EPA and other agencies, and their indirect GWPs resulting from effects on tropospheric ozone were estimated in IPCC (1990). We will initially determine GWPs for limited latitudinal areas, concentrating on the effects from midlatitudes in the Northern Hemisphere. We are concerned that uncertainties about tropospheric NO_x , in particular, are so large that analysis of indirect GWPs for NO_x , especially with a 2-D model, may not be very meaningful. However, if we could demonstrate, in an absolute limit, that effects of NO_x emissions were relatively unimportant (not that this is necessarily the case without having done the analysis), then this conclusion in of itself would be valuable to policymakers. We will proceed in our analyses with caution.
- Third priority will be given to the indirect GWPs on stratospheric ozone, such as those from CFCs and their replacements.

The process of deriving new estimates of indirect GWPs needs to proceed with care. However, with a major new international assessment of climate change being planned by IPCC for 1995, it will be important to continue developing and refining the indirect GWPs and providing interim results for such assessments as they occur. It may be possible within the next few years to begin to use the new three-dimensional modeling capability (now being developed for use on massively parallel computers) to test the adequacy of the tropospheric effects on ozone and hydroxyl that will have been done with the two-dimensional model.

6.1. Methane Effect on Tropospheric and Stratospheric Ozone

In order to obtain an initial estimate of the indirect GWP due to the effect of methane on tropospheric and stratospheric ozone, the two-dimensional model is used to determine the changes in ozone over a thirty-year period following a pulse increase in the emissions of methane. Because of its long lifetime in the troposphere, the assumed latitude and season of the pulse emissions for methane, unlike some other gases, will not significantly impact the derived changes in ozone. For this study, therefore, we have assumed that the pulse of additional emissions is distributed with latitude in the same proportion as they are for the current atmosphere; the additional emissions were put

into the model on January 1. The background atmosphere corresponds to the current atmosphere.

This first evaluation is intended primarily to demonstrate the capability for deriving the changes in ozone and the resulting radiative forcing effects that are then used to derive an estimate for the indirect GWP. Therefore, because of its much faster computational running time, we used a version of the model with updated kinetics but lacking the non-methane hydrocarbon chemistry. We expect some minor effects on the resulting derived indirect GWPs (calculations with increased atmospheric methane show only minor differences on the ozone response for the two versions of the model). We are currently in the process of setting up the model with NMHC chemistry in order to repeat the analysis; this should be completed by the end of June, 1993.

Part of the difficulty in calculating the indirect climate forcing is that the impulse emissions need to be large enough that the chemical model determines a change in ozone significant enough to provide a meaningful change in radiative forcing, yet the emissions need to be small enough that the nonlinear effects on atmospheric chemistry are minimized. In this study, we used a pulse emission of methane corresponding to 25% of current methane emissions. Because we have not done these calculations before, we were concerned that a smaller pulse would not provide a change in ozone sufficiently large for the radiative forcing calculations. We will consider a smaller pulse in future studies.

Figure 6.1 shows the integrated change in the mass of methane calculated in the model as a function of time before and after the pulse emission. Figure 6.2 gives the globally and annually averaged change in total ozone column calculated before and after the methane pulse, while Figure 6.3 shows the calculated change with time in the annually-averaged tropospheric ozone column. Total global ozone takes six years before reaching the maximum effect, while the troposphere, as expected, responds much more quickly.

Figure 6.1 Total mass of methane (in units of teragrams) in the model atmosphere as a function of time before and after a pulse emission of methane corresponding to 25% of current total emissions. Feedbacks in the lifetime of methane result in about a 36% peak increase in total atmospheric methane.

Figure 6.2 Change in global annual average total ozone column before and after the pulse emission of methane.

Figure 6.3 Increase in annually-averaged tropospheric ozone column before and after the pulse emission of methane.

Our new infrared radiative transfer model, based on the correlated-k approach, was used in determining the radiative forcing due to the changes in ozone calculated with the 2-D model. The correlated-k approach is closely based on line-by-line calculations and is quite accurate. However, this is a new model. In order to validate the model, we compared the calculated change in radiative forcing for a doubling in methane and a fifteen percent increase in ozone at all altitudes for a McClatchey (a well-established background atmosphere under cloudless conditions that has been reported in a number of past reports from the Air Force Geophysical Laboratory) midlatitude atmosphere. The changes in radiative forcing calculated for these test cases were within a few percent of the values published by Ramanathan with the same background atmosphere (see Ramanathan *et al.*, 1985), well within the uncertainty range of the radiative transfer calculations of either model.

The most accurate means for determining the global climatic forcing from changes in the ozone distribution would be to derive the changes in radiative forcing as a function of latitude and then to determine a global average radiative forcing. However, the number of calculations required are computationally and labor intensive. Thus, for this first evaluation, we decided to use an approach more akin to that used in IPCC (1990). For the indirect GWPs calculated in the IPCC report, the radiative forcing equation for changes in ozone based on Lacis *et al.* (1990) was used based on the latitudinal and annual average ozone changes calculated in the Harwell 2-D model of the troposphere. In this study, we determined the latitudinal and annual averaged changes in ozone from the LLNL model of the troposphere and stratosphere, and, using a latitudinally-averaged background atmosphere based on the 2-D model, calculated the changes in radiative forcing with the LLNL radiative transfer model.

The derived radiative forcings were then used in our Global Warming Potential code. For CO₂, we used the impulse response function based on the balanced carbon cycle calculations described in Chapter 5 and the disequilibrium constant CO₂ emissions scenario for deriving GWPs. The calculated direct and indirect GWPs are shown in Table 6.1.

Table 6.1. Derived direct and indirect GWPs for methane. The only indirect GWP shown is the effect of methane emissions on tropospheric and stratospheric ozone.

GWPs Integration Period (yrs)	This study		IPCC (1990, 1992), WMO (1991)	
	Direct CH ₄	Indirect O ₃ (CH ₄)	Direct CH ₄	Indirect O ₃ (CH ₄)
20	37.7	23.1 (12-34)	35	24
50	21.7	16.6 (8-24)	19	
100	12.9	10.4 (5-15)	11	8
200	7.5	6.1 (3-9)	7	
500	3.8	3.1 (1.5-4.5)	4	3

The indirect GWPs for ozone effects from methane derived from this study are quite comparable to those derived in IPCC (1990). They are somewhat (roughly 10%) larger than what would be derived had we used the CO₂ impulse response function from the IPCC reports. However, it is also important to consider the uncertainties in the calculations of the indirect GWPs that may result both from the using a 2-D model in the analysis of tropospheric (and stratospheric) chemistry effects and from uncertainties in the chemistry itself. As the discussion below suggests, we are not able to well define the limits on the uncertainties at this time; however, we provide a range on the values derived in Table 6.1 as a representation of overall uncertainties. The derived central value should not be taken too seriously given the magnitude of the overall uncertainties.

There are two primary uncertainties that affect the impact of increasing methane on ozone. The first is the uncertainty associated with the lifetime of methane. This uncertainty depends primarily on the uncertainty in the amount of hydroxyl in the troposphere. Various analyses have determined that the atmospheric lifetime for methane is about 10-12 years, with our model deriving a lifetime of about 11 years. This implies an uncertainty of about 10% in the lifetime. The second uncertainty is in the production of ozone per oxidation of methane. This uncertainty depends on the reaction of $\text{CH}_3\text{O}_2 + \text{NO}$ to produce NO_2 which then photolyzes (in the troposphere) and produces ozone. The primary uncertainty in the rate of ozone formation will then largely depend on the amount of NO_x in the troposphere (we argue that the well recognized nonlinear relationship between NO_x and ozone is unimportant to the effect of methane oxidation to produce ozone, as the production of ozone depends only on the NO conversion reaction given above). Unfortunately, tropospheric NO_x concentrations are poorly characterized globally. The two-dimensional model gives a range in the tropospheric concentrations of NO_x of 1.8 to 416 pptv. By comparison, the MLOPEX study over the Pacific Ocean found a range of 2.4 to 358 pptv (Carroll *et al.*, 1992). Measurements over polluted areas can be much larger, giving NO_x values as large as 1ppbv or more. Therefore, the model appears to represent the expected values in the clean troposphere reasonably well, but may greatly underestimate the values in polluted areas. The impact of these polluted areas on the derived effects of methane will not be known until we are able to better characterize the global amounts of NO_x . Most of the uncertainty in the model representation of NO_x should be in underestimating the effects of polluted areas, but this will also depend on how well the model represents the variability of NO_x in less polluted areas of the troposphere. At this time, we believe that we can safely assume that the total uncertainty is no more than a factor of two.

Within their range of uncertainties, the indirect GWPs for methane effects on ozone are of the same general magnitude as the direct effects, implying that this indirect forcing on climate is quite important and should be considered in policy analyses. These results indicate that it will be important to reduce the level of uncertainties associated with these effects.

7. Findings

7.1. Discussion

The further development of the two-dimensional model as described in this report is an important element of meeting the needs of EPA. The two-dimensional model is much more computationally efficient than any existing three-dimensional model. Many more perturbation analyses and sensitivity studies can be done with the two-dimensional model. Although the two-dimensional model, because it is zonally averaged, will never be the perfect tool for studies of tropospheric chemistry, it is still reasonably representative of tropospheric processes and can provide useful insight into the effects of human-related emissions on ozone and hydroxyl. The improvements being made are critical to ensuring that advanced capabilities are being used in studies of tropospheric processes including the determination of human influences on ozone and on the oxidizing capacity of the atmosphere.

The improvements being made to the two-dimensional model also are aiding our conceptualization and development of a new next-generation three-dimensional model of the troposphere and stratosphere. Many of the capabilities being developed for the two-dimensional model will eventually be transferred to the new three-dimensional model. In the future, intercomparisons between the two- and three-dimensional models will be carried out at LLNL as they become available. An example of an initial study would be to zonally average the seasonal results of the three-dimensional model and compare them to the two-dimensional model output.

7.2. Ambient Atmosphere Validation

Overall, the ambient atmosphere compares very well with the STRAT0Z III data. Although further validation needs to be performed, this initial comparison is very encouraging because it indicates that the LLNL two-dimensional model is capable of reproducing the overall structure of tropospheric distributions of important trace gases. Additional sources we will consult for further validation of the current model include: other atmospheric models; published vertical profiles at a specific locations for the various trace gases; and latitudinal distributions of surface concentrations. These additional validation studies will enable us to make further enhancements to the model:

- Variation of surface emissions and concentrations according to a seasonal or monthly basis.
- Adjustments to the surface emissions that will ensure our calculated surface concentrations agree with published results.
- Refinements to the diffusivities (K_{yy} and K_{zz}) in the troposphere to add latitudinal and perhaps even seasonal variations.

7.3. Evaluation of Perturbation Scenarios

For Scenario 1, we can summarize the results of increasing the surface flux of methane by 50%. Methane concentrations increased by approximately 57% in the troposphere. Carbon monoxide concentrations also increased throughout the troposphere as a result of enhanced photochemical production due to methane oxidation. Hydroxyl concentrations decreased by nearly 10% in the troposphere and increased in the lower stratosphere. Ozone mixing ratios increased in the troposphere and lower stratosphere due to enhanced photochemical production resulting from methane oxidation in the presence of sufficient nitrogen oxides. The nitrogen oxides increased below 7.5 km across all latitudes because hydroxyl levels fell and thus the

chief photochemical loss rate (nitric acid formation) decreased. The three major non-methane hydrocarbons (ethane, propane, and acetylene) all increased in the troposphere because of the decrease in hydroxyl levels. Peroxyacetylnitrate (PAN) levels decreased near the surface because its hydrocarbon precursors were not being oxidized as quickly due to the decrease in hydroxyl levels. However, throughout the free troposphere and lower stratosphere PAN levels increased because the hydrocarbon precursors were transported higher and were subsequently oxidized.

For Scenario 2, the surface flux of methane increased by 100%. Methane concentrations increased by almost 96% in the troposphere. Carbon monoxide mixing ratios increased throughout the troposphere as a result of enhanced photochemical production. Hydroxyl concentrations fell almost 15% in the troposphere and increased in the lower stratosphere. Ozone mixing ratios increased in the troposphere and lower stratosphere due to methane oxidation in the presence of sufficient nitrogen oxides. The nitrogen oxides increased below 7.5 km across all latitudes because hydroxyl levels were perturbed downward and thus the chief photochemical loss rate (nitric acid formation) decreased. The three major non-methane hydrocarbons cited above all increased in the troposphere because of the decrease in hydroxyl levels. Peroxyacetylnitrate levels decreased near the surface and rose throughout the free troposphere and lower stratosphere due to the same photochemical mechanisms described for Scenario 1.

Analysis of our model results for these perturbation scenarios and the comparison of our results with those from specialized troposphere models (that extend only a few kilometers into the stratosphere) suggest that it is extremely important to include the full stratosphere in any studies examining perturbations from changing emissions of methane and other gases. The feedbacks between the troposphere and stratosphere require further study, but the initial results indicate that these feedbacks are extremely important to determining effects on tropospheric ozone and hydroxyl resulting from changes in surface emissions of methane, etc. This is a major finding in our studies and will be pursued further in our research.

7.4. Global Warming Potentials

Global Warming Potentials are significantly affected through the use of a balanced carbon cycle model compared with the unbalanced carbon cycle used by IPCC through changes in the CO₂ impulse response function. If a constant emission of CO₂ past 1990 is assumed for a balanced carbon cycle, the resulting GWPs are systematically 9 percent higher than the IPCC GWPs at a time horizon of 20 yr, 16 percent higher at a time horizon of 100 yr, and 3 percent higher at a time horizon of 500 yr. Current uncertainty in the fertilization feedback parameter allows for a significant range of GWP effects in this enhancement for long time horizons. Emission scenarios for CO₂ do not significantly affect GWPs in the equilibrium atmosphere assumption employed by the IPCC because the emission scenarios have only a small effect on the impulse response function for CO₂. However, for the parameters examined in this study, the change in CO₂ concentration due to atmospheric disequilibrium produces the single most dominant effect on derived GWPs through the nonlinearity of the CO₂ radiative forcing function. This effect increases with longer time horizons, increasing GWPs from 38 percent for IPCC (1992) emission scenario C to 166 percent for IPCC (1992) scenario E at a 500 yr time horizon. Atmospheric lifetime uncertainties indicated in WMO (1991) also give rise to uncertainties in GWPs nearly identical in magnitude to the lifetime uncertainties for gases with lifetimes less than 100 years. Longer-lived gases give GWP uncertainties of lesser magnitude than the lifetime uncertainty for time horizons less than twice the lifetime. Combined effects of a constant-emission, disequilibrium atmosphere and a balanced carbon cycle suggest that IPCC GWP values must be considered systematically low, by roughly 36 percent at the 100 yr time horizon. For the

cases examined, the disequilibrium atmosphere and balanced carbon cycle produced a range of 25 to 50 percent larger values for the 100 year time horizon than the values derived with the IPCC approach; the uncertainties in atmospheric lifetimes would increase the overall range, but are species dependent.

Because, as we have shown, CO₂ and the carbon cycle plays such an important role in determination of GWPs, we are putting additional effort into validating and evaluating the carbon cycle model we have used in the studies presented here. A forthcoming paper will provide a more detailed description of the model; studies are also underway to further enhance the treatment of ocean and biospheric processes affecting the carbon cycle.

7.5. Indirect GWPs

We have evaluated an indirect GWP for the effects of methane on ozone in the troposphere and stratosphere (unlike the earlier IPCC analysis, our model accounts for the effects on stratospheric chemistry as well as tropospheric chemistry). The derived indirect GWP for a 100 year integration period is 10.4 with an uncertainty range of about 5 to 15. The derived indirect GWPs due to methane effects on ozone are comparable to those derived in the IPCC(1990) report. The indirect GWPs are of similar magnitude to the direct GWPs for methane, implying that the indirect climatic forcing resulting from methane-induced changes in ozone concentrations needs to be considered in climate studies and policy analyses considering the effects of methane on climate. Indirect global warming from methane increases directly with nitrogen oxides; thus, these GWPs may be systematically low in polluted areas. Other indirect effects from methane, such as the radiative effects from induced increases in stratospheric water vapor (IPCC, 1990, 1992) and its dissociation to CO₂ also need to be considered.

8. Future Work

8.1. Introduction

Emphasis in the planned research outlined below is aimed at better determining the Global Warming Potentials (GWPs) of anthropogenically influenced gases, with particular emphasis at determining the indirect GWPs resulting from effects on ozone and other greenhouse gases. We are focusing our studies on further development of the treatment of tropospheric processes in the two-dimensional model and towards making initial evaluations of indirect GWPs on tropospheric ozone. As a necessary step in extending the state-of-the-art capabilities for such analyses, there are a series of research studies oriented at further improving and then applying the LLNL zonally-averaged two-dimensional chemical-radiative-transport model of the troposphere and stratosphere to these issues. We are also developing a new state-of-the-art three-dimensional chemical-transport model of the global atmosphere that should become an important tool for global change studies (we recognize that such capabilities provide the only way that many of the important issues of tropospheric chemistry and global change can ever be fully addressed). Outlined below are several research studies we believe necessary to fully addressing the important questions for determining the effects of human activities on global climatic forcing.

8.2. Modeling of tropospheric processes

8.2.1. Chemical mechanism

As discussed earlier, a tropospheric chemistry scheme with a reasonably comprehensive treatment of non-methane hydrocarbons and associated species has now been implemented into the 2-D model. We are currently attempting to validate this chemistry scheme and the resultant distributions of trace constituents against available observational data. The amount of atmospheric measurements in the troposphere are very limited, however, making it difficult to validate such global models. Nonetheless, several steps are planned for further refining and improving the treatment of tropospheric chemistry over the coming year. First, comparisons will be made with appropriate smog chamber datasets. We are also evaluating the laboratory kinetics literature for further changes that should be made to the mechanism. As better schemes become available (e.g., with better treatments of isoprene or aromatics reactivity), we will attempt to incorporate these into the model. Some of the specific plans are to improve chemistry in the following ways:

- Atherton and Penner (1990) have studied the problem of the missing component of NO_y that was first measured by Fahey *et al.* (1986). Both studies suggest that organic nitrates form the remainder of this missing NO_y . We would like to add the formation and degradation reactions for organic nitrates in future versions of the mechanism.
- The aromatic chemistry currently in the model is highly parameterized. The oxidation of aromatics produces roughly half ring-retaining compounds and half ring-opening species on a stoichiometric basis. In our current mechanism, benzene and toluene only produce ring-opening products. The number of products from the initial oxidation of benzene and toluene is indeed enormous (Calvert and Madronich, 1987; Grosjean, 1991). This complexity cannot be reflected easily in an Eulerian two-dimensional model. Therefore, we will seek to identify simplified mechanisms that can reasonably simulate the impact of aromatic species on ozone, nitrogen oxides, and hydroxyl, and odd nitrogen (i.e., the contribution of organic nitrates produced by aromatics).

8.2.2. Cloud processes

Two-dimensional models of the global atmosphere tend to have very simplistic treatments of cloud processes in the troposphere. We are attempting to incorporate a climatology for clouds into the model that properly considers the latitudinal and seasonal variations in cloud amount as a function of cloud type. This should provide a much more realistic treatment of clouds and their effects on photodissociation rates and other radiative transfer properties. The next phase of this development will be the use of new satellite datasets in refining the cloud database.

8.2.3. Heterogeneous chemistry

Heterogeneous chemistry reactions on clouds and particles may be quite important to determining changes in ozone and other important atmospheric constituents. We have now added such processes into our treatment of stratospheric chemistry; such reactions seem to play a major role in explaining the observed decrease in lower stratospheric ozone over the last decade. We next need to examine the potential importance of these processes on tropospheric chemistry. Unfortunately, there is little available laboratory data to base such mechanisms on; however, we can perform sensitivity analyses to test the potential importance of possible heterogeneous reaction mechanisms. As a beginning point, we intend to evaluate the potential importance of heterogeneous reaction involving nitrogen oxides that are be important in the stratosphere.

8.2.4. Radiative transfer

Accurate determination of climatic forcing requires that we have radiative transfer models for the solar and infrared wavelengths that are as accurate as possible. We are finishing development of a new state-of-the art infrared submodel, primarily under funding from DOE. Additional gases will need to be added to the model for determining GWPs related to NMHCs, etc. We also are incorporating a better treatment of the spherical Earth effect on high zenith angle photodissociation into the model. We hope to perform detailed comparisons of our radiative transfer model with other state-of-the-art models towards further refining our capabilities.

8.2.5. Tropospheric transport

The treatment of tropospheric dynamics and constituent transport in the two-dimensional model should be further evaluated and refined. We need to consider the effect of and proper derivation of eddy transport and mixing; this tends to be treated in an oversimplified manner in ours and other 2-D models. We have been working on this and have made several improvements already; however, we are looking at making the model treatment of atmospheric dynamics more self determining and less dependent on simple parameterizations of transport processes.

8.2.6. Convective cloud processes

Convective processes are thought to be an important means for transporting boundary layer gases to the free troposphere. We need to consider how these processes can best be treated in global two-dimensional (and three-dimensional) models. We plan on coordinating research in this area with the findings of other researchers (such as those supported by EPA) to determine appropriate ways of including convective processes in the model. We are looking at the Arakawa-Schubert scheme and will evaluating this scheme in a 1-D model over this summer and looking at possible inclusion of this scheme into the 2-D model.

8.2.7. Spatial scales

Many important tropospheric gases are emitted into the atmosphere under conditions where there is important chemistry occurring before the constituents can be transported to the global scale. We need to properly represent these local and regional scales in our modeling of global processes. We plan to use the knowledge gained by modelers of urban and regional scale chemistry to ensure that we properly treat the emissions of NO_x , NMHCs, and other constituents in the global scale model.

8.2.8 Model validation

This is a key element of the next year's studies. We will extend the comparison with the measurement database as much as possible. In addition, we plan on making more detailed comparisons with other models; in particular, Joyce Penner's group is now completing the capability to perform limited calculations with NMHC chemistry in the three-dimensional lagrangian-based GRANTOUR model of the troposphere. We plan on making comparison with this model over the coming year.

8.3. Interactions between Chemistry and Climate

There are several special issues that need to be considered in the future evaluation of direct and indirect GWPs. Eventually, indirect GWPs due to chemical interactions need to consider both tropospheric and stratospheric effects, but primary focus for current studies will be on effects from CH_4 , NMHCs, NO_x , and CO (within the limitations of uncertainties as discussed earlier).

8.3.1. Impacts on ozone

The two dimensional model is being used in a series of sensitivity studies to examine the effects of emissions from CH_4 , NMHCs, NO_x , and CO on tropospheric ozone and other important tropospheric constituents (e.g., OH, PAN, etc.). An important finding in initial studies is that it makes an extremely large difference to such perturbation as to whether the model account for interactions between the troposphere and stratosphere (this result suggests that specialized models of the troposphere may not be of any use in analyses of the effects of changing emissions of methane, etc. on tropospheric ozone and hydroxyl). We will extend these studies to further examine the importance of feedbacks between the troposphere and stratosphere. Also of interest are the effects of NO_x and other emissions from current aircraft on tropospheric and lower stratospheric ozone. We will begin analysis of these effects during the coming year, assuming that we have sufficient support for these studies.

8.3.2. Global Warming Potentials

We have developed a model that determines the direct GWPs for the major constituents. We have made initial studies in examining uncertainties associated with the carbon cycle calculations and other aspects of the GWP formulation. We will extend these studies, as well as consider evaluations of GWPs for additional chemicals. Based on limited results from the two-dimensional model, we are attempting to evaluate a meaningful range for the indirect GWPs on tropospheric ozone and other constituents from methane, and are considering what can be done in a meaningful way for other emissions within the confines of a two-dimensional model.

8.3.3. Aerosol effects

There is a growing concern about the effects of sulfuric aerosols and other particles in the troposphere in affecting climate. We would like to evaluate these effects and potential interactions with tropospheric chemistry in the model if sufficient support is available.

8.4. Three-dimensional global chemical-transport model development

We are developing a next-generation, state-of-the-art three-dimensional chemical-transport model of the global atmosphere. This model is being designed to be used in both stand alone studies of tropospheric and stratospheric chemistry, and in studies where it will be fully coupled with a climate model. The model is to be designed from the beginning for use on a massively parallel computer, where its great need for computational resources will be met by the machines now being developed. This model is essential to future studies to fully couple chemistry and climate processes towards understanding tropospheric chemistry issues as they relate to the predictability of climate change. The initial development is being started with support from the DOE CHAMMP program; however, this support is inadequate to the needs for having a core team of researchers working on the development of this highly complex model. As a likely user of the capabilities of this model, we would like to get support from EPA to enhance the model development. Much more so than many other laboratories, such development (and just as importantly, the proper application) of a three-dimensional model of the troposphere and stratosphere is a natural progression in extending our experience and expertise in the development and use of models for studies of the global atmosphere.

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