AIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

Indirect Global Warming Effects Of Ozone and Stratospheric Water Vapor Induced By Surface Methane Emission

D.J. Wuebbles

A.S. Grossman

J.S. Tamarais

K.O. Patten

A. Jain

K.E. Grant

July 1994

Abstract

Methane has indirect effects on climate due to chemical interactions as well as direct radiative forcing effects as a greenhouse gas. We have calculated the indirect, time-varying tropospheric radiative forcing and GWP of O₃ and stratospheric H₂O due to an impulse of CH₄. This impulse, applied to the lowest layer of the atmosphere, is the increase of the atmospheric mass of CH₄ resulting from a 25 percent steady state increase in the current emissions as a function of latitude. The direct CH₄ radiative forcing and GWP are also calculated. The LLNL 2-D radiative-chemistry-transport model is used to evaluate the resulting changes in the O₃, H₂O and CH₄ atmospheric profiles as a function of time. A correlated k-distribution radiative transfer model is used to calculate the radiative forcing at the tropopause of the globally-averaged atmosphere profiles. The O₃ indirect GWPs vary from ~27 after a 20 yr integration to ~4 after 500 years, agreeing with the previous estimates to within about 10 percent. The H₂O indirect GWPs vary from ~2 after a 20 yr integration to ~0.3 after 500 years, and are in close agreement with other estimates. The CH₄ GWPs vary from ~53 at 20 yrs to ~7 at 500 yrs. The 20 year CH₄ GWP is ~20% larger than previous estimates of the direct CH₄ GWP due to a CH₄ response time (~17 yrs) that is much longer than the overall lifetime (10 yrs). The increased CH₄ response time results from changes in the OH abundances caused by the CH₄ impulse. The CH₄ radiative forcing results are consistent with IPCC values. Estimates are made of latitude effects in the radiative forcing calculations, and UV effects on the O₃ radiative forcing calculations (10%).

MASTER

rp

I. Introduction

The current concerns about global warming and ozone depletion have necessitated detailed studies of the potential greenhouse effects of various trace gases that have been introduced into the atmosphere. The mechanism usually used for comparison of the greenhouse potential of trace gases is the global warming potential or GWP as defined by IPCC (1990). The GWP is the ratio of the radiative flux change at the tropopause caused by the introduction of a unit mass impulse of a trace gas into the atmosphere to the radiative flux change at the tropopause caused by the introduction of a unit mass impulse of CO₂. An essential part of the GWP determination is the calculation of the radiative forcing, which is defined as the radiative flux change at the tropopause produced by a unit change in the number of molecules of a particular gas with all other abundances held constant. Usually the amount of abundance change used in a radiative forcing calculation is chosen such that the change is just enough to produce a numerically significant flux change value at the tropopause. Parameterized experiments for radiative forcing have been published, for example, in IPCC (1990, 1992), and by Ramanathan et al. (1987). A model for determining GWPs has been developed by Wuebbles et al. (1992). This model approximates GWP's with an accuracy of a few percent and has been published by Wuebbles and Grossman (1992) for CF₄, and Grossman and Wuebbles (1993) for SF₆. In addition to the direct GWP and radiative forcing discussed above, there is the indirect GWP and radiative forcing. The indirect effects are caused when the atmospheric chemical processes produce a change in the abundance of species 2 after the introduction of an impulse of species 1. A GWP and radiative forcing effect results from the indirect abundance changes of species 2 as well as the direct GWP and forcing effect of the change in abundance of species 1. Indirect GWP effects of ozone and stratospheric water vapor have been discussed in IPCC (1990, 1992). IPCC (1990) gives an indirect ozone GWP, due to methane introduction, of 24 at a time of 20 years. IPCC (1992) gives an indirect water GWP of between 5 and 30 percent of the direct methane GWP. IPCC (1992) recommended that the indirect GWP's should be withdrawn due to incomplete understanding of the atmospheric chemical processes which cause the ozone changes. Yet, according to IPCC (1990), the indirect ozone forcing due to methane introduction could represent one of the main contributions to indirect GWP effects.

The main purpose of this paper is to reexamine the indirect effect on O₃ and stratospheric H₂O due to a tropospheric impulse of CH₄ and to determine the resulting GWPs. The LLNL 2-D radiative-chemistry-transport model is used to generate a set of annually and globally averaged model atmospheres which contain the perturbed O₃, H₂O, and CH₄ abundances as a function of time. A correlated k-distribution model for the atmospheric transmission is used to calculate the tropospheric radiative forcing for CH₄, O₃, H₂O, and CO₂. These forcing values are then used to calculate the direct GWP for CH₄, and the indirect GWP for O₃ and H₂O. Estimates are made for the UV contributions to the indirect O₃ radiative forcing values and latitude effects on the radiative forcing calculations for O₃, H₂O, and CH₄. Lastly, we make suggestions for future, more advanced, indirect O₃ and H₂O, GWP calculations.

II. Model Atmospheres

A. Model Structure

The version of the LLNL zonally-averaged two-dimensional chemical-radiative-transport model (Kinnison et al., 1994, Patten et al., 1994, Wuebbles et al., 1991) used for these calculations determines the atmospheric distributions of 44 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 the surface pressure is 1013 mb. The vertical resolution is 1.5 km in the troposphere and 3 km in the stratosphere.

B. Model Transport

In the dynamics portion of the two-dimensional code, the circulation field is obtained following the approach of Garcia and Solomon (1983). Since this approach is only partially implemented in the model at the present time, we use climatological temperature and mean zonal wind fields. Both the temperature and mean zonal wind field vary continuously over the annual cycle. The temperature field is based on the reference model of Barnett and Corney (1985), while the mean zonal wind is based on data from 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. The net heating rate is calculated knowing the temperature and chemical species 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 solving the zonal mean momentum equation.

The transport of chemical species is accomplished through both 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 season, but are different between the troposphere and stratosphere. The value of K_{zz} in the troposphere is $4 \text{ m}^2 \text{ sec}^{-1}$, while K_{zz} in the stratosphere has values of $0.1 \text{ m}^2 \text{ sec}^{-1}$ in the lower stratosphere increasing to $0.25 \text{ m}^2 \text{ sec}^{-1}$ near the middle stratosphere and returning to $0.1 \text{ m}^2 \text{ sec}^{-1}$ at the stratopause. Values of K_{yy} in the stratosphere are calculated using a similar method 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 $1 \times 10^5 \text{ m}^2 \text{ sec}^{-1}$. The values of K_{yy} in the troposphere are assigned a value of $2 \times 10^6 \text{ m}^2 \text{ sec}^{-1}$. The tropopause is determined from the latitude

dependent annual mean 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.

C. Solar Radiative Transfer Model

To capture the spectral detail needed for photodissociation calculations, the 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 (Joseph et al. 1976), 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 (1967) 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.

D. Infrared Radiative Transfer Model

The infrared model 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 CO₂, O₃, and H₂O. 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.

E. Model Chemistry

The mechanism we are currently using in the LLNL two-dimensional model has the following characteristics:

- A total of 44 species are allowed to vary with time in the troposphere and stratosphere. Four additional species (O, O(¹D), N, H) are treated as steady-state.

- There are 103 thermal (two- and three-body) reactions and 48 photolytic reactions in the mechanism.
- A complete representation of known stratospheric chemical processes.

The mechanism is listed in its entirety in Table 1. The reactions are classified by type: two-body, three-body, and photolytic. The kinetic parameters for two-body reactions are included as well.

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 44 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 48. 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., (1992). The rate constant for $CH_4 + OH$ calculated 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. (1992) 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 hydropause. Above the hydropause, 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 in this version of the model. Polar stratospheric aerosol surface has not been included. 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.

F. *Emission and Boundary Conditions*

In our modeling of current and possible future atmospheres, we need to represent the surface (and atmospheric emissions) and/or surface concentrations of a number of constituents that affect tropospheric and stratospheric chemistry. 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 determining the atmospheric concentrations and emission rates of a variety of trace species (e.g. nitrogen oxides, carbon monoxide, and hydrocarbons) 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.

The surface boundary conditions for the ambient version of the two-dimensional model consist of fixed concentration for nitrous oxide, molecular hydrogen, hydrochloric acid, and the halogenated organics and fluxes for methane, nitrogen dioxide, and carbon monoxide. The emission rates are specified for each latitude zone in Table 2.

Methane emissions are distributed latitudinally according to the recommendations of Fung et al., (1991). Carbon monoxide emissions are distributed latitudinally according to the emission categories defined by Hough (1991). The methane and carbon monoxide emission rates used for these calculations are obtained by determining the steady state chemical loss rate from a previous ambient model run. However, seasonal variations in the source gas emissions are not included in the results presented here. This can lead to discrepancies between the magnitudes of the calculated and observed species distributions. Another potential source of discrepancy is the representation of advective and diffusive transport in the troposphere. This would adversely affect short-lived species such as nitrogen oxides. 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.

G. *Ambient Atmosphere*

The 2-dimensional model-derived ambient atmosphere used for these calculations is based on 1990 emissions of the source gases. The two-dimensional (i.e. latitude, altitude) distributions of the radiatively important trace gases—water vapor, carbon dioxide, ozone, nitrous oxide, and methane—are averaged over the annual cycle and from pole to pole. The resulting globally- and annually-averaged altitude profiles for water vapor, ozone, and methane are depicted in Figure 1. Carbon dioxide is constant at 350 ppmv throughout the model atmosphere. Nitrous oxide decreases monotonically from 308 ppbv near the surface to 1.2 ppbv at 59 km. The pressure-temperature profile for the model atmosphere is shown in Figure 2. The tropopause in the globally-averaged atmosphere, is specified as the altitude at which the temperature gradient in the troposphere decreases to 2K/km. As indicated in Figure 2, this occurs at 166 mb (~13.2 km).

H. *Time Dependent Atmosphere Calculations*

The two-dimensional model is used to determine the changes in ozone following the pulse increase in the abundance of methane. Due to its long lifetime in the troposphere, the assumed latitude and season of the methane pulse should not impact significantly the derived changes in ozone. Therefore, the pulse is distributed latitudinally at the start of the run as a percentage increase of the ambient methane concentrations. The pulse needs to be sufficiently large for the chemical model to determine an ozone change providing a significant change in radiative forcing, yet sufficiently small for the nonlinear effects on atmospheric chemistry to be minimal. Based on the analysis of ozone radiative forcing in Lacis et al. (1990), we estimate that a sufficiently large change in tropospheric average ozone concentration should be approximately 4%. This corresponds to a 25% increase of current methane emissions in our model. For the calculations in this paper we estimate the equilibrium change in the total atmospheric mass of methane for a 25% emission increase based on model results for several increased flux scenarios. The difference between the perturbed and ambient burdens, 1702.9 teragrams, is added to the surface layer in the model. We then run the model for thirty years using ambient CH₄ emission fluxes and initial concentrations for the other species.

Figure 3 shows the integrated change in the mass of methane calculated in the model as a function of time before and after the initial pulse as well as the ambient value of the methane mass. The methane pulse decays approximately, exponentially in time with a lifetime of the order of 17 years. The decay function with time indicates that significant nonlinear feedbacks with hydroxyl have occurred. The methane depletion rate is proportional to both the concentration of methane as well as the concentration of hydroxyl. Since the hydroxyl lifetime is of the order of five minutes, it can be assumed that the hydroxyl concentration is in equilibrium. The equilibrium hydroxyl concentration is an inverse function of the methane concentration,

$$d[CH_4]/dt = -k_1[CH_4]/(k_2 + k_3[CH_4]) + S_0 \quad (1)$$

where S_0 is the background methane flux input into the atmosphere, and $[CH_4]$ is the concentration of methane. The value of $[CH_4]$ is the sum of the background atmosphere methane plus the extra methane due to the pulse. Eventually the methane added in the pulse will decay back to the background atmosphere methane abundance. Equation 1 implies that the methane pulse decay will be a complex function of the instantaneous methane abundance, but it will closely approximate an exponential decay with a lifetime of the order of 17 years. While the instantaneous methane lifetime in the ambient atmosphere is 10–12 years, the conjecture made in IPCC (1990) that a methane pulse will decay exponentially with a 10 year lifetime will not be the case for real methane pulses. Other analyses (Fisher, 1993, Prather, 1993) have determined that an equivalent lifetime of the order of 17 years appropriately describes the lifetime of a methane pulse in the atmosphere. We emphasize the point here that we do not use an exponential decay function in this paper, we use a direct integration of the actual radiative forcing which contains the actual value of the methane abundance at any particular time. Since the IPCC (1990) GWP numbers were based on an exponential methane decay function with a 10 year lifetime, we expect differences in the GWP values. This will be discussed in Section V. below.

Figure 4 depicts the annually-averaged change, with time, of the total ozone column calculated after the methane pulse. Figure 5 shows the calculated change with time of the annually-averaged tropospheric ozone column. Ambient values of the total and tropospheric values of the ozone column are shown in Figures 4 and 5. Total global ozone takes about six years before reaching the maximum effect while the troposphere responds within two years. The change in the ozone column abundance is a result of methane oxidation. In tropospheric regions characterized by high nitric oxide concentrations, the net methane oxidation reaction is (cf. Wuebbles and Tamara, 1993):

We see that complete methane oxidation results in net production of ozone. The difference in response times between the troposphere and stratosphere is due to transport, particularly across the tropopause. Since the pulse is emitted in the surface zone, dynamical processes will transport the methane upwards. Typically, it takes a long-lived gas emitted at the surface about four years to mix into the stratosphere. Furthermore, we observe that the tropospheric ozone column peaks two years after the pulse. Thus if the time constant for chemistry (two years) is added to that for transport (four years), we estimate that it should take six years for the stratospheric ozone column to peak.

Figure 6 shows the time variation of the increase in the annually and globally averaged stratospheric water vapor burden (kg). The peak value of the H_2O change occurs at a time of 10–11 years after the methane pulse. According to Lelieveld et al. (1993) the H_2O levels in the lower stratosphere are largely dependent on transport of CH_4 and O_3 from the troposphere. Since the stratospheric ozone peaks approximately 6 years

after the methane we expect the stratospheric water vapor to take at least this amount of time and possibly more to reach its peak value.

It is also important to consider the uncertainties in these calculations that may result both from the using a two-dimensional model in the analysis of tropospheric (and stratospheric) chemistry effects and from uncertainties in the chemistry itself. We are not able to define precisely the limits on the uncertainties at this time; however, we provide a range as a representation of overall uncertainties.

One major uncertainty is in the amount of production of ozone, in the troposphere, per unit 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 1.8–416 pptv. By comparison, the MLOPEX study (Mauna Loa Observatory Photochemistry Experiment) over the Pacific Ocean found a range of 2.4–358 pptv (Carroll et al., 1992). Measurements over polluted areas can be much larger, giving NO_x levels ≥ 1 ppbv. 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.

III. Radiative Forcing Models

A. Infrared Radiative Transfer Model

We have used an infrared radiative transfer model based on the correlated k-distribution algorithm (Grant et. al., 1992, Grossman and Grant, 1992) to calculate the radiative forcing at the tropopause. Calculations were done for a globally averaged atmosphere for CH_4 and O_3 at times between 1 and 30 years after a CH_4 impulse has been applied at the bottom of the atmosphere. Calculations have been made of the radiative forcing for CO_2 , in the globally-averaged atmosphere and at five different latitudes, 2 years after the pulse. This was done in order to determine the scaling factor with respect to the IPCC (1990) expression for CO_2 radiative forcing at the tropopause. Calculations have also been made at five different latitudes for CH_4 and O_3 , at a time of 2 years, in order to determine the differences between the radiative forcing in the globally-averaged atmosphere and latitude averaged radiative forcing. The tropospheric radiative forcing of H_2O , caused by the methane pulse, has been calculated at five different

latitudes for times of 5, 10, 15, and 20 years after pulse. An appropriate latitudinal average is calculated to determine the globally-averaged tropospheric radiative forcing. The parameters of the calculations are;

O₃, CH₄, wave number range of 900–1650 cm⁻¹, 25 cm⁻¹ subintervals,

CO₂, wave number range of 550–1200, 2000–2525 cm⁻¹, 25 cm⁻¹ subintervals,

H₂O, wave number range of 25–3000 cm⁻¹, 25 cm⁻¹ subintervals,

Tropopause of globally averaged atmosphere at 166 mb,

Ground Temperature of 291K (Peixoto and Oort, 1992).

The radiative forcing is defined as the difference between the net infrared flux at the tropopause in the ambient, globally averaged atmosphere, and the net flux at the tropopause in the atmosphere with changed CH₄, H₂O, and O₃ profiles calculated at the various times after the CH₄ impulse.

A test of the ability of correlated k-distribution model to calculate O₃ tropospheric forcing was performed using an LLNL generated model for an annually-averaged, mid latitude, clear sky atmosphere. A perturbation of 15% of the tropospheric O₃ was added and the tropospheric forcing calculated. The result of 0.266 W/m² agreed to within about 10 percent of the Ramanathan et al. (1987) value for a similar test case, assuming a 20 percent correction factor for clouds. A test calculation for CH₄ radiative forcing in a mid-latitude summer, clear sky approximation, was made by Grossman et al. (1993) and the result agreed with the Ramanathan et al. (1987) value to within about 4 percent. A calculation of the tropospheric radiative forcing for CH₄ in a globally and annually averaged atmosphere both with and without a representative cloud distribution was made by Grossman and Grant (1993). The results with clouds agreed to within 1 percent of the IPCC (1990) value. These tests indicate that our correlated k-distribution model has the ability to provide consistent tropospheric radiative forcing results. Table 3 shows the radiative forcing values in W/m² at representative times between 1 and 30 years after the CH₄ impulse for both the direct CH₄ and the indirect O₃ radiative forcing. Also shown are the results of direct CO₂ tropospheric radiative calculations for year 2 (maximum O₃ radiative forcing) using CO₂ concentrations of 1.29 and 2 times normal CO₂ abundance. The CO₂ calculations were made to test the systematic differences between the IPCC (1990) formula for CO₂ tropospheric radiative forcing and the results obtained using the LLNL model atmosphere. For both cases shown in Table 3 the results of our calculation produce a radiative forcing which is approximately 25 percent higher than that calculated using the IPCC (1990) formula. IPCC (1990) notes that calculations which do not use a cloud cover model, which is the case for our calculations, will result in radiative forcing values which are of the order of 20 percent too high. Thus the agreement of our CO₂ radiative forcing values with the IPCC (1990) values would be of the order of 5 percent if we had included a cloud cover model in our calculations. It is important for the GWP calculations, which will be discussed later, that the CO₂ forcing values derived from the IPCC (1990) formula contain a 25 percent adjustment in order to be comparable with the

O₃ and CH₄ forcing values given in Table 3. The results for the time variation of the indirect O₃ radiative forcing, given in Table 3 show that the peak forcing occurs at a time of 2 years after the initial methane impulse. This is indicative of the radiative forcing being correlated with the time variation of the tropospheric ozone column density which peaks at a time of two years (Fig. 5) rather than the total ozone column density which peaks at a time of about 6 years (Fig. 4). The reason for this behavior of the O₃ radiative forcing is that the upward IR flux change is much larger than the downward flux difference at the tropopause at all times and this drives the temporal behavior of the O₃ forcing even though the change in the stratospheric ozone column is much larger than the change in the tropospheric ozone column.

Two interesting aspects of the use of a 2-D latitudinally averaged model atmosphere are the question of the variation of the tropospheric radiative forcing as a function of latitude and the difference between the latitudinally averaged value of the tropospheric radiative forcing and the tropospheric radiative forcing calculated for the globally averaged model atmosphere. We have calculated the direct CH₄ and indirect O₃ tropospheric for five different latitudes between +71 deg. and -71 deg for the time at which maximum O₃ radiative forcing occurs, year 2 after the CH₄ impulse. The results are shown in Table 4. The radiative forcing for O₃ and CH₄ has been shown, for a CH₄ impulse of 2.83 times the concentration of the lowest atmospheric level for each latitude (25 percent of the total tropospheric CH₄ mass), at the actual tropopause at that latitude. There are significant differences between the radiative forcing values calculated in the polar regions and those calculated for the mid latitude and the equatorial regions. The polar values are lower and the mid latitude values are higher than the average value of the forcing. The maximum latitudinal variations are +12, -9 percent for the CH₄ forcing and +29, -49 percent for the O₃ forcing. These excursions from the average may have significant climatological consequences which will be discussed later from the point of view of the GWP results. It is interesting to note that the results shown in Table 4 indicate that the radiative forcing values calculated for the globally averaged atmosphere, 0.2455 for CH₄ and 0.1180 for O₃, differ by ~5 percent (CH₄) and ~9 percent (O₃) with the average of the forcing values for each latitude. We consider these differences to be small and thus the use of the globally averaged atmosphere to determine the average radiative forcing is a reasonable approach to the GWP calculation.

Table 5 shows the latitude effect of the tropospheric CO₂ radiative forcing for a CO₂ impulse of twice the normal concentration (350 ppm). The CO₂ factor in Table 5 is the ratio of the IPCC (1990) value of the CO₂ forcing (4.3668 W/m²) to the CO₂ forcing obtained in this paper (Column 2, Table 5). This factor must be applied to the CH₄ and O₃ forcing results to make them compatible with the IPCC (1990) CO₂ formulation for the GWP calculations to be discussed later. In addition to this factor, the results shown in Table 4 indicate a latitude variation of the direct CH₄ and indirect O₃ radiative forcing. The CH₄ and O₃ factors shown in Table 5 are the product of 1, the ratio of the value of the CH₄ and O₃ tropospheric radiative forcings at the various latitudes to the global average values (Table 4), and 2, the CO₂ factor of Table 5. The variation of these factors represent a rough estimate of the latitude variation of the radiative forcing part of the GWP calculation. The results indicate roughly a ± 10 percent variation of the CH₄ GWP

with latitude and a larger effect for the O₃ forcing of about 50 percent at the high latitudes.

Table 6 shows the latitude variation of the H₂O radiative forcing due to changes in the stratospheric H₂O as well as the latitude averaged value of the radiative forcing. Since H₂O is a very strong greenhouse gas, the tropopause must be carefully defined since the H₂O tropospheric radiative forcing will strongly depend on the height of the tropopause. The lower the tropopause the smaller the radiative forcing. In order to compare the latitude averaged radiative forcing for H₂O with the radiative forcing in a globally averaged atmosphere a test calculation of the radiative forcing in the global averaged atmosphere at year 10 was made. The tropospheric radiative forcing for H₂O in the globally averaged atmosphere (166 mb tropopause) was approximately 30 percent less than the globally averaged radiative forcing for year 10 given in Table 6. Since the location of the tropopause is a critical factor in the radiative forcing it is recommended, for the case of H₂O forcing, that the radiative forcing should be calculated as a function of latitude and then averaged as opposed to the calculation of the radiative forcing in the globally averaged atmosphere.

B. UV Effects On O₃ Radiative Forcing

Since O₃ has an absorption band in the UV spectral region the possibility exists that there may be a significant contribution to the total radiative forcing by the differential UV absorption. We make an estimation of the UV radiation forcing contribution in the following manner. The atmosphere is considered as a two component system. The stratosphere is taken to be a pure absorption region while the troposphere is taken to be a scattering and absorbing layer. The spectral region over which the UV radiative forcing will be calculated is taken to be 250–340 nm in 5 nm spectral sub intervals. The O₃ absorption cross sections and Rayleigh scattering cross sections are given by WMO-16 (1985). The radiative forcing calculation is done for the year 2 model atmosphere (the maximum O₃ forcing model). The downward UV flux at the tropopause is calculated using a simple Beer's Law exponential attenuation of the zero air mass solar flux (Goody and Yung, 1989). The upward flux at the tropopause is calculated using a delta-Eddington scattering model in the troposphere which takes the troposphere as a single scattering layer. In addition to the diffuse, reflected flux component from the troposphere additional upward flux components due to the attenuated direct and downward scattered beams that are reflected from the ground are also considered. The ground albedo was taken to be 0.2. The UV radiative forcing calculated in this way amounted to about 9 percent of the IR radiative forcing. Thus UV forcing effects should be a 10 percent effect at most.

IV. Carbon Cycle Model and CO₂ Response Curves.

Unlike many of the greenhouse gases emitted to the atmosphere, CO₂ does not have a chemical or photochemical sink within the troposphere or stratosphere. Removal of CO₂ is therefore dependent on exchanges with other carbon reservoirs. Following the emissions of a hypothetical pulse of CO₂ into the atmosphere, about 10% will be removed within 2 to 3 years through gaseous diffusion into the mixed layer of the ocean.

Subsequent removal is dependent on downward mixing into the deeper ocean. Ultimately, the rest of the initial pulse can be removed by mixing into the ocean, but only over a time period of hundreds of years (Maier-Reimer and Hasselmann, 1987). To avoid the need to use a single lifetime for CO₂, we have used a coupled climate-carbon cycle model of Jain and Bach (1994) to calculate the decay rate of 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. 4000 m). The model ocean is treated as a diffusive 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). The model includes stimulation of net photosynthesis or net primary productivity by enhanced atmospheric CO₂ using the fertilization factor β .

To correctly estimate the GWP values and the past and future CO₂ concentrations, it is important to use carbon cycle models that properly balance the carbon budget. 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, it will give the correct history of CO₂ concentration changes. However, the carbon cycle model used to calculate the GWPs given by IPCC (1990, 1992) does not properly balance the carbon budget. In a separate study (Wuebbles et al., 1993) we have assessed the effects of balancing the carbon budget on GWP values. The CO₂ variations can be made to fit observations by assuming the larger ocean flux, and/or accounting for feedbacks in the terrestrial component of the carbon cycle and/or assuming the existence of an additional CO₂ sink. The present model is sufficiently flexible that all three methods may be used; we chose to use only the first two methods. In Figure 7, the observed CO₂ concentrations are compared with the results of the carbon cycle model. The carbon cycle model including the biospheric feedbacks satisfactorily reproduces the observed atmospheric CO₂ concentration (balanced case). Excluding the effects of the biosphere (i.e. unbalanced case) results in an overestimation of CO₂ concentration. The time variation of the fraction of CO₂ concentration remaining after an atmospheric impulse is shown in Figure 8. It will be used in the GWP calculation described in the following section.

V. Global Warming Potential Model

A. Basic Model

Global warming potentials (GWPs) are evaluated according to the concept of IPCC (1990). A concentration change of trace gas X, arising from an impulse of a unit mass of the trace gas X (for direct GWPs) or from chemical processing due to an impulse of gas Y (for indirect GWPs), in the atmosphere produces a tropospheric radiative forcing change $\Delta f_X(t)$, which decreases with time as X is removed from the atmosphere. This radiative forcing change is considered as directly proportional to the temperature change at the surface via a climate sensitivity factor. Commitment to radiative forcing from a unit mass of X is the integral of $\Delta f_X(t)$ from the time of an impulse to the user-selected GWP time horizon, T. The GWP of X is the radiative forcing commitment from a unit mass of

X divided by the radiative forcing commitment from a unit mass of CO₂, or a CO₂ like molecule,

$$GWP_X = \frac{\int_0^T \Delta f_X(t) dt}{\int_0^T \Delta f_{CO_2}(t) dt} \quad (2)$$

The IPCC (1990)-derived GWPs assume that the background atmosphere is in equilibrium (that background concentrations are constant over the GWP integration period). In our calculations, the chemical processes are allowed to operate on the background concentrations for the trace gases that are present in the atmosphere just before the impulse. This has, as will be discussed later, a significant effect on the equivalent lifetime of the decay of the impulse of the trace gas X to the atmosphere.

The definition of GWP (1990) requires integration of radiative forcing (or tropospheric temperature change) resulting from a unit mass release of trace gas, usually one kilogram, and of CO₂. A small change in atmospheric concentration resulting from such a small release can produce computational errors, so larger mass releases are usually applied and then the radiative forcing is scaled to a one kilogram release. Radiative forcing scales linearly for many gases at reasonable concentrations (IPCC, 1990); only for releases of gas much greater than one gigaton of CO₂, CH₄, or N₂O does nonlinearity occur (Wuebbles *et al.*, 1993). The radiative forcing of CO₂ is obtained from the IPCC (1990) formula,

$$\Delta F_{CO_2} = 6.3 \log_e \left(\frac{c_{CO_2}(t)}{c_{CO_2}^0} \right) \quad (3)$$

for which $c_{CO_2}(t)$ is the concentration of CO₂ at time t and $c_{CO_2}^0$ is the concentration of CO₂ which would exist in the absence of the pulse. In the equilibrium case used here, $c_{CO_2}^0$ is constant with respect to time, so that the argument of the log_e is replaced by one plus the impulse response function for CO₂, $i_{CO_2}(t)$:

$$\begin{aligned} \Delta F_{CO_2} &= 6.3 \log_e (1 + i_{CO_2}(t)); \\ i_{CO_2}(t) &= \frac{c_{CO_2}(t) - c_{CO_2}^0}{c_{CO_2}^0} \end{aligned} \quad (4)$$

The impulse response function used in this study was discussed in the previous section (Figure 8). Mass-scaled, integrated radiative forcing for CO₂ is then calculated by the procedure described in Wuebbles *et al.* (1993) at time horizons of 20, 50, 100, 200, and 500 yr.

B. Extrapolation and integration of radiative forcing

The radiative forcing values of Tables 3 and 6 must be fitted before numerical integration in Equation 2 due to the uneven timestep required by computer limitations and to time horizons exceeding the longest time after pulse for which the atmospheric and line models were run. IPCC (1990) states that CH_4 radiative forcings are proportional to $c_{\text{CH}_4}(t)^{1/2}$, while tropospheric O_3 radiative forcings are linear in $c_{\text{O}_3}(t)$. In turn, the concentration perturbations of the two trace species may be taken as negative exponentials in time t . However, as seen by Figures 9 and 10, the initially perturbed atmosphere produces concentrations inconsistent with a negative exponential in t . Points for which this is the case, the first year of the CH_4 radiative forcings and years 1–4 after the pulse for O_3 , are excluded from fitting for this reason. The fits after weighting by CH_4 mass are:

$$\Delta f_{\text{CH}_4} = (\exp(-58.841 \pm 0.028 - 0.1189 \pm 0.0024 t))^{1/2} \quad , \quad (5a)$$

$$\Delta f_{\text{O}_3} = \exp(-30.0410 \pm 0.0035 - 0.05663 \pm 0.00022 t) \quad , \quad (5b)$$

$$\Delta f_{\text{H}_2\text{O}} = \exp(-3.9645 \pm 0.040 - (0.05991 \pm 0.0017)t) \quad . \quad (5c)$$

For the integration of the radiative forcing of CH_4 , the value in Table 3 is used for the first year after the pulse. Years 1 to 3 after the pulse also are used in the O_3 Δf integration, and the value at year 4 is replaced by a linear interpolation of years 3 and 5. Fit values are used for all years afterward. Simpson's Rule (Press et al., 1992, equ. 4.1.13) is then applied to integrate the radiative forcing over time. The radiative forcing for zero time after the pulse is set to zero in each case for integration. Integrated radiative forcings for CH_4 , H_2O , and O_3 are each multiplied by a factor of 0.8 to reconcile the clear sky approximation with the IPCC (1990) cloud parameterization as discussed previously. Table 7 lists the integrated radiative forcings per kilogram derived for each of the gases.

C. GWP Results

Table 8 shows the results of the GWP calculations. The CH_4 GWP values are significantly larger than those given by IPCC (1990, 1992) and Wuebbles et al. (1993). In the IPCC calculations the CH_4 lifetime was given as 10.5 years, which implies that the OH abundance was held fixed at the ambient value. In the present calculation, the chemical processes which affect CH_4 , O_3 , and H_2O abundances are allowed operate and as a result the OH abundance changes as the chemical equilibrium is perturbed by the CH_4 pulse. Equation 1 predicts a lifetime of CH_4 which is dependent on the OH abundance. This long apparent lifetime of the pulse is the result of the slower destruction of all CH_4 from the decrease in OH. The radiative forcing fits for CH_4 given by Equation 5a and shown in Figure 9 indicate an apparent lifetime on the order of 17 years for the decay of the CH_4 pulse. Wuebbles et al. (1992) showed that when the CH_4 lifetime is increased, the GWP values also increase towards the results obtained in the present

calculation. For a lifetime of 12.6 years, GWP's at 20, 100, and 500 years of 41.7, 15.9, and 7.1 were obtained. A simple extrapolation of the GWP vs. CH_4 lifetime results Wuebbles et al. (1992) predicts a GWP of approximately 52 at 20 years which is the same as that obtained in this paper. The results obtained for the O_3 indirect radiative forcing are on the order of 10 to 20 percent higher than those given in IPCC (1990) and Wuebbles et al. (1993). Given the uncertainties of the calculations, at least 20 to 30 percent, this is a reasonable agreement. The indirect GWP's for stratospheric H_2O obtained in this paper are lower by factors of 3 to 5 than those given in IPCC (1990). This is probably due to an overestimation of the tropospheric radiative forcing of H_2O in IPCC (1990). The ratio of the indirect H_2O GWP to the direct CH_4 GWP, for the calculations in this paper is about 4 percent and agrees quite well with the results obtained by Lelieveld and Crutzen (1992) who give a value of 5 percent for this ratio. This effect is strongly dependent on the height of the tropopause since H_2O is such a strong IR absorber and should have a sharp mixing ratio gradient at the tropopause. The overall uncertainty in the GWP calculations is due to the uncertainties in the lifetime of CH_4 , the amount of NO_x present in the atmosphere, and the radiative forcing calculations. The best estimate of the overall uncertainty in the calculations is on the order of 20 percent.

VI. Conclusions

We have calculated the direct CH_4 GWP and the indirect O_3 and stratospheric H_2O GWPs resulting from a CH_4 pulse equal to ~36 percent of the total atmospheric mass of CH_4 . The direct CH_4 GWP is significantly larger than previous estimates as a result of the effect on the pulse response time due to the variation of the OH abundance. The agreement of the indirect O_3 GWP effect with previous estimates is within the uncertainty bounds of the calculation. The indirect H_2O GWP is much less than the estimate given in IPCC (1990, 1992) but agrees very well with more recent calculations Lelieveld and Crutzen (1992). The H_2O effect is very strongly dependent on the location of the tropopause because of the strong IR absorption of H_2O . Future calculations need to be made to determine the effect of the magnitude of the CH_4 impulse on the impulse decay time and the effect of the presence of hydrocarbons and NO_x on the direct and indirect GWP's.

Acknowledgment

Work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48 and was supported in part by the Department of Energy Environmental Sciences Division and the Gas Research Institute under contract No. 5091-254-2167. One of us K. P. wishes to acknowledge the support of a Global Change Distinguished Postdoctoral Fellowship sponsored by the U. S. DOE, Office of Health and Environmental Research and administered by Oak Ridge Associated Universities.

References

- Allen, M. and J.E. Frederick, 1982: Effective photodissociation cross sections for molecular oxygen and nitric oxide in the Schumann-Runge bands, *J. Atmos. Sci.*, 39, 2066–2075.
- Barnett, J.J., and M. Corney, 1984: A middle atmosphere temperature reference model from satellite measurements, *Adv. Space Res.*, 5, 125–134.
- Carroll, M.A., B.A. Ridley, D.D. Montzka, G. Hubler, J.G. Walega, R.B. Norton, B.J. Huebert, and F.E. Grahek, 1992: Measurement of nitric oxide and nitrogen dioxide during the Mauna Loa Observatory Photochemistry Experiment, *J. Geophys. Res.*, 95, 10361–10374.
- DeMore, W.B., S.P. Sander, R.F. Hampson, M.J. Kurylo, D.M. Golden, C.J. Howard, A.R. Ravishankara, C.E. Kolb, and M.J. Molina, 1992: *Chemical kinetics and photochemical data for use in stratospheric modeling: Evaluation number 10*, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.
- Fisher, D. A., 1993, NASA/NOAA/AFEAS Workshop, Boulder Co. and *Geophys. Res. Letts.* (in press).
- Fleming, E.L., S. Chandra, M.R. Schoeberl, and J. J. Barnett, 1988: Monthly mean global climatology of temperature, wind, geopotential height, and pressure for 0–120 km, NASA Technical Memorandum 1000697.
- Fung, I., J. John, J. Lerner, E. Matthews, M. Prather, L.P. Steele, and P.J. Fraser, 1991: Three-dimensional model synthesis of the global methane cycle, *J. Geophys. Res.*, 96, 13033–13065.
- Garcia, R. R., and S. Solomon, 1983: A numerical model of the zonally averaged dynamical and chemical structure of the middle atmosphere, *J. Geophys. Res.*, 88, 1379–1400.
- Gillotay D. and P.C. Simon, 1991a: Temperature-dependence of ultraviolet absorption cross-sections of alternative chlorofluoroethanes, *Journal of Atmospheric Chemistry*, 12, 269–285.
- Gillotay D. and P.C. Simon, 1991b: Temperature-dependence of ultraviolet absorption cross-sections of alternative chlorofluoroethanes: 2. The 2-chloro-1,1,1,2-tetrafluoroethane—HCFC-124, *Journal of Atmospheric Chemistry*, 13, 289–299.
- Goody, R.M., and Y.L. Yung, 1989: *Atmospheric Radiation, Theoretical Basis*, 2nd. Ed, 519 pp., Oxford, New York, NY.
- Grant, K. E., A. S. Grossman, R. Freedman, and J. B. Pollack, 1992: A correlated k-distribution model of the heating rates for CH₄ and N₂O in the atmosphere between 0 and 60 km., *Proceedings of the 5th Annual Review Conference on Atmospheric Transmission Models*, in press, LLNL Report UCRL-JC-110364.
- Grossman, A. S., and Grant, K. E., 1992: A correlated k-distribution model of the heating rates for H₂O and a molecular mixture in the 0–2500 cm⁻¹ wavelength region in the atmosphere between 0 and 60 km., LLNL Report UCRL-ID-112296.

- Grossman, A. S., K. E. Grant, 1993: Tropospheric radiative forcing of CH₄, LLNL Report UCRL-ID-116533.
- Grossman, A. S., and D. J. Wuebbles, 1992: Global warming potential of SF₆, LLNL Report UCRL-ID-112944.
- Grossman, A. S., K. E. Grant, and D. J. Wuebbles, 1993: Radiative forcing calculations for SF₆ and CH₄ using a correlated k-distribution transmission model., LLNL Report UCRL- ID-115042.
- Harshvardhan, R. Davies, D.A. Randall, and T.G. Corsetti, 1987: A fast radiation parameterization for atmospheric circulation models, *J. Geophys. Res.*, 92, 1009–1016.
- Harvey, L. D. D., 1989: Managing atmospheric CO₂, *Climatic Change*, 15, 343–381.
- Hough, A.M., 1991: The development of a two-dimensional global tropospheric model: the model chemistry, *J. Geophys. Res.*, 96, 7325–7362.
- Intergovernmental Panel on Climate Change (IPCC): Climate Change; The IPCC Scientific Assessment, Cambridge University Press, Cambridge, UK, 1990.
- Intergovernmental Panel on Climate Change (IPCC): Climate Change 1992; The Supplementary Report to the IPCC Scientific Assessment, Cambridge University Press, Cambridge, UK, 1992.
- Jain, A. K. and W. Bach, 1994: The effectiveness of measures to reduce the man-made greenhouse effect: the application of a climate-policy-model. *Theoretical and Applied Climatology* (in press).
- Joseph, J. H., W. J. Wiscombe, and J. A. Weinman, 1976: The delta eddington approximation for radiative flux transfer. *J. Atmos. Sci.*, 33, 2452–2459.
- Kinnison, D.E., K.E. Grant, P.S. Connell, and D.J. Wuebbles, 1994: The chemical and radiative effects of the Mt. Pinatubo eruption, submitted to *J. Geophys. Res.*, in revision.
- Lacis, A. A., D. J. Wuebbles, and J. A. Logan, 1990: Radiative forcing by changes in the vertical distribution of ozone, *J. Geophys. Res.*, 95, 9971–9981.
- Lelieveld, J., and P. J. Crutzen, 1992: Indirect effects of methane in climate warming. *Nature*, 355, 339–342.
- Lelieveld, J., P. J. Crutzen, and C. Bruhl, 1993: Climate effects of atmospheric methane. *J. Chemosphere*, 26, 739–758.
- Maier-Reimer, E. and K. Hasselmann, 1987: Transport and storage of CO₂ in the ocean—an inorganic ocean circulation carbon cycle model, *Climate Dynamics*, 2, 63–90.
- Newman, P.A., M.R. Schoeberl, R.A. Plumb, J. Rosenfield, 1988: Mixing rates calculated from potential vorticity, *J. Geophys. Res.*, 93, 5221–5240.

- Patten, K.O., P.S. Connell, D.E. Kinnison, D.J. Wuebbles, L. Froidevaux, and T.G. Slanger, 1994: Effect of vibrationally excited oxygen on ozone in the upper stratosphere, *J. Geophys. Res.*, 99, 1211–1223.
- Peixoto, J. P., and A. H. Oort, 1992: *Physics Of Climate*, 520pp, AIP, New York.
- Prather, M., 1993: Lifetimes and eigenstates in atmospheric chemistry. *Geophys. Res. Letts.* (in press).
- Press, W. H., S. A. Teukolsky, W. T. Vetterling, B. P. Flannery, 1992: *Numerical Recipes in C: The Art of Scientific Computing*, 2nd ed. (Cambridge Univ. Press. Cambridge, UK), 134.
- Ramanathan, V., L. Callis, R. Cess, J. Hansen, I. Isaksen, W. Kuhn, A. Lacis, F. Luther, J. Mahlman, R. Reck, and M. Schlesinger, 1987: Climate-chemical interactions and effects of changing atmospheric trace gases. *Revs. of Geophys.*, 25, NO. 7, pp 1441–1482.
- Sagan, C., and J. B. Pollack, 1967, On isotropic nonconservative scattering and the clouds of Venus. *J. Geophys. Res.*, 72, 469–477.
- Smolarkiewicz, P. K., 1984: A fully multidimensional positive definitive advection transport algorithm with small implicit diffusion, *J. Comput. Phys.*, 54, 325–362.
- Vaghjiani, G.L. and A.R. Ravishankara, 1991: New measurement of the rate coefficient for the reaction of OH with methane, *Nature*, 350, 406–409
- World Meteorological Organization, Atmospheric Ozone, 1985: WMO Global Ozone Research and Monit. Proj. Report 16, Geneva.
- World Meteorological Organization, Scientific Assessment of Stratospheric Ozone, 1989: Global Ozone Research and Monit. Proj. Report 20, Geneva.
- World Meteorological Organization, 1991: Scientific Assessment of Ozone Depletion: 1991, Global Ozone Research and Monitoring Project Report 25, Geneva.
- Wuebbles, D.J., D.E. Kinnison, K.E. Grant, and J. Lean, 1991: The effect of solar flux variations and trace gas emissions on recent trends in stratospheric ozone and temperature, *J. Geomag. Geoelectr.*, 43, 709–718.
- Wuebbles, D. J., and A. S. Grossman, 1992: Global warming potential for CF₄, LLNL Report UCRL-ID-112295.
- Wuebbles, D.J. and J.S. Tamareis, 1993: The role of methane in the global environment, in *Atmospheric Methane: Sources, Sinks, and Role in Global Change*, edited by M.A.K. Khalil, Springer-Verlag, Germany.
- Wuebbles, D. J., K. O. Patten, K. E. Grant, A. K. Jain, 1993: "Sensitivity of Direct Global Warming Potentials to Key Uncertainties", submitted for publication to *Climatic Change*, LLNL Report UCRL-ID-111461.
- Wuebbles, D. J., J. S. Tamareis, and K. O. Patten 1993: Quantified estimates of total GWP's for greenhouse gases taking into account tropospheric chemistry, LLNL Internal Document UCRL-ID-115850.

Figure Captions

Figure 1. Globally and annually averaged profiles of water vapor, ozone, and methane as a function of altitude for the ambient atmosphere.

Figure 2. Pressure-temperature profile for the ambient atmosphere. The temperatures are globally and annually averaged.

Figure 3. 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 equal to the equilibrium increase of CH_4 produced by a constant 25% increase in total emissions. Feedbacks in the lifetime of methane result in about a 36% peak increase in total atmospheric methane. The ambient value of the methane mass is indicated by the dashed line.

Figure 4. Annual average total ozone column after the pulse increase of methane. The ambient value of the ozone column is indicated by the dashed line.

Figure 5. Annually averaged tropospheric ozone column after the pulse increase of methane. The ambient value of the tropospheric ozone column is indicated by the dashed line.

Figure 6. Increase in annually averaged stratospheric water vapor burden (kg) before and after the pulse emission of methane.

Figure 7. The time variation of the observed CO_2 concentration (+), the carbon cycle model prediction including biospheric feedbacks (____), and the carbon cycle model prediction excluding the biosphere (-----).

Figure 8. The response of atmospheric CO_2 to a pulse of 1 GTC (gigatons of Carbon).

Figure 9. Radiative forcing of methane vs. time (years) after the pulse emission of methane. The correlated k-distribution radiative forcing model calculations are denoted by the symbols. The solid line is the fit to the model calculations given by Equation 4.

Figure 10. Radiative forcing of ozone vs. time (years) after the pulse emission of methane. The correlated k-distribution radiative forcing model calculations are denoted by the symbols. The solid line is the fit to the model calculations given by Equation 4.

Table 1. Chemical reaction mechanism for LLNL two-dimensional model. The reference used for all photochemical data is Demore et al. (1992).

(a) Two-body reactions (Arrhenius rate constant expression $k = A \cdot \exp\left(\frac{-E}{RT}\right)$)

No.	Reaction	A ¹	E/R ²
1	$O + O_3 \rightarrow 2^*O_2$	8.00E-12	2,060
2	$O_1D + N_2 \rightarrow O + N_2$	1.80E-11	-110
3	$O_1D + O_2 \rightarrow O + O_2$	3.20E-11	-70
4	$O_1D + O_3 \rightarrow 2^*O_2$	1.20E-10	0
5	$O_1D + O_3 \rightarrow O_2 + 2^*O$	1.20E-10	0
6	$H_2O + O_1D \rightarrow 2^*OH$	2.20E-10	0
7	$H_2 + O_1D \rightarrow OH + H$	1.00E-10	0
8	$N_2O + O_1D \rightarrow N_2 + O_2$	4.90E-11	0
9	$N_2O + O_1D \rightarrow 2^*NO$	6.70E-11	0
10	$CH_4 + O_1D \rightarrow CH_2O + H_2$	1.40E-11	0
11	$CH_4 + O_1D \rightarrow CH_3O_2 + OH$	1.40E-10	0
12	$CF_2Cl_2 + O_1D \rightarrow 2^*Cl$	1.12E-10	0
13	$CF_3CCl_3 + O_1D \rightarrow 3^*Cl$	1.60E-10	0
14	$CF_3CFCl_2 + O_1D \rightarrow 2^*Cl$	1.28E-10	0
15	$CF_3CF_2Cl + O_1D \rightarrow Cl$	7.12E-11	0
16	$CHF_2Cl + O_1D \rightarrow Cl$	7.00E-11	0
17	$H + O_3 \rightarrow OH + O_2$	1.40E-10	470
18	$H_2 + OH \rightarrow H_2O + H$	5.50E-12	2,000
19	$OH + O_3 \rightarrow HO_2 + O_2$	1.60E-12	940
20	$OH + O \rightarrow O_2 + H$	2.20E-11	-120
21	$HO_2 + O \rightarrow OH + O_2$	3.00E-11	-200
22	$HO_2 + O_3 \rightarrow OH + 2^*O_2$	1.10E-14	500
23	$HO_2 + OH \rightarrow H_2O + O_2$	4.80E-11	-250
24	$H_2O_2 + OH \rightarrow H_2O + HO_2$	2.90E-12	160
25	$N + O_2 \rightarrow NO + O$	1.50E-11	3,600
26	$N + NO \rightarrow N_2 + O$	3.40E-11	0
27	$NO + O_3 \rightarrow NO_2 + O_2$	2.00E-12	1,400
28	$NO + HO_2 \rightarrow NO_2 + OH$	3.70E-12	-250
29	$NO_2 + O \rightarrow NO + O_2$	6.50E-12	-120
30	$NO_2 + O_3 \rightarrow NO_3 + O_2$	1.20E-13	2,450
31	$N_2O_5 + H_2O \rightarrow 2^*HNO_3$	5.00E-22	0
32	$HO_2NO_2 + OH \rightarrow H_2O + NO_2 + O_2$	1.30E-12	-380
33	$Cl + O_3 \rightarrow ClO + O_2$	2.90E-11	260
34	$Cl + HO_2 \rightarrow HCl + O_2$	1.80E-11	-170
35	$Cl + HO_2 \rightarrow OH + ClO$	4.10E-11	450
36	$ClO + O \rightarrow Cl + O_2$	3.00E-11	-70
37	$ClO + OH \rightarrow HO_2 + Cl$	1.10E-11	-120
38	$ClO + HO_2 \rightarrow O_2 + HOCl$	4.80E-13	-700
39	$ClO + NO \rightarrow NO_2 + Cl$	6.40E-12	-290
40	$ClO + ClO \rightarrow Cl + ClOO$	4.00E-13	1,250
41	$ClO + ClO \rightarrow Cl_2 + O_2$	4.00E-13	1,250

¹Units are cm³/molecule-sec.

²Unit is degrees Kelvin.

No.	Reaction	A ³	E/R ⁴
42	OCIO + Cl → 2*ClO	3.40E-11	-160
43	OCIO + O → O ₂ + ClO	2.50E-12	950
44	OCIO + OH → HOCl + O ₂	4.50E-13	-800
45	OCIO + NO → NO ₂ + ClO	2.50E-12	600
46	ClOO + Cl → Cl ₂ + O ₂	2.30E-10	0
47	Cl ₂ O ₂ + Cl → Cl ₂ + ClOO	1.00E-10	0
48	HCl + OH → H ₂ O + Cl	2.60E-12	350
49	HOCl + OH → H ₂ O + ClO	3.00E-12	500
50	ClONO ₂ + O → ClO + NO + O ₂	3.19E-13	800
51	ClONO ₂ + O → ClO + NO ₂ + O	2.58E-12	800
52	ClONO ₂ + OH → HOCl + NO + O ₂	1.32E-13	333
53	ClONO ₂ + OH → HOCl + NO ₂ + O	1.07E-12	333
54	ClONO ₂ + Cl → Cl ₂ + NO + O ₂	7.48E-13	-160
55	ClONO ₂ + Cl → Cl ₂ + NO ₂ + O	6.05E-12	-160
56	Br + O ₃ → BrO + O ₂	1.70E-11	800
57	Br + HO ₂ → HBr + O ₂	1.50E-11	600
58	Br + NO ₃ → BrO + NO ₂	1.60E-11	0
59	Br + OCIO → BrO + ClO	2.60E-11	1,300
60	Br + Cl ₂ O ₂ → BrCl + ClOO	3.00E-12	0
61	Br + CH ₂ O → HBr + HO ₂ + CO	1.70E-11	800
62	BrO + O → Br + O ₂	3.00E-11	0
63	BrO + HO ₂ → HOBr + O ₂	6.20E-12	-500
64	BrO + OH → Br + HO ₂	1.10E-11	0
65	BrO + NO → Br + NO ₂	8.80E-12	-260
66	BrO + NO ₃ → NO ₂ + Br + O ₂	1.00E-12	0
67	BrO + ClO → Br + OCIO	1.60E-12	-430
68	BrO + ClO → Br + ClOO	2.90E-12	-220
69	BrO + ClO → BrCl + O ₂	5.80E-13	-170
70	BrO + BrO → 2*Br + O ₂	1.40E-12	-150
71	HBr + O → Br + OH	5.80E-12	1,500
72	HBr + OH → Br + H ₂ O	1.10E-11	0
73	CH ₄ + OH → CH ₃ O ₂ + H ₂ O	2.90E-12	1,820
74	CH ₂ O + OH → H ₂ O + HO ₂ + CO	1.00E-11	0
75	CH ₃ O ₂ + O → CH ₂ O + HO ₂	3.00E-11	0
76	CH ₂ O + O → HO ₂ + OH + CO	3.40E-11	1,600
77	CH ₃ O ₂ + NO → HO ₂ + CH ₂ O + NO ₂	4.20E-12	-180
78	Cl + CH ₄ → CH ₃ O ₂ + HCl	1.10E-11	1,400
79	Cl + CH ₂ O → HCl + HO ₂ + CO	8.10E-11	30
80	CH ₃ Cl + OH → Cl + H ₂ O + HO ₂	2.10E-12	1,150
81	CH ₃ CCl ₃ + OH → H ₂ O + 3*Cl	1.80E-12	1,550
82	CHF ₂ Cl + OH → Cl + H ₂ O	1.20E-12	1,650
83	CH ₃ Cl + Cl → HO ₂ + CO + 2*HCl	3.30E-11	1,250
84	CH ₃ Br + OH → Br + H ₂ O	3.60E-12	1,430

³Units are cm³/molecule-sec.

⁴Unit is degrees Kelvin.

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

Number	Reaction
1	$O + O_2 \rightarrow O_3$
2	$H + O_2 \rightarrow HO_2$
3	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
4	$HO_2 + HO_2 + H_2O \rightarrow H_2O_2 + O_2 + H_2O$
5	$NO_2 + HO_2 \rightarrow HO_2NO_2$
6	$NO_3 + NO_2 \rightarrow N_2O_5$
7	$N_2O_5 \rightarrow NO_2 + NO_3$
8	$NO_2 + OH \rightarrow HNO_3$
9	$HNO_3 + OH \rightarrow H_2O + NO + O_2$
10	$HNO_3 + OH \rightarrow H_2O + NO_2 + O$
11	$HO_2NO_2 \rightarrow HO_2 + NO_2$
12	$ClO + NO_2 \rightarrow ClONO_2$
13	$ClO + ClO \rightarrow Cl_2O_2$
14	$ClOO \rightarrow Cl + O_2$
15	$Cl_2O_2 \rightarrow 2*ClO$
16	$BrO + NO_2 \rightarrow BrONO_2$
17	$CO + OH \rightarrow H$
18	$N_2O_5 \rightarrow 2*HNO_3$
19	$ClONO_2 \rightarrow HOCl + HNO_3$

(c) Photolysis reactions

Number	Reaction
1.	$O_2 + hv \rightarrow 2^*O$
2.	$O_3 + hv \rightarrow O + O_2$
3.	$O_3 + hv \rightarrow O_1D + O_2$
4.	$H_2O_2 + hv \rightarrow 2^*OH$
5.	$H_2O + hv \rightarrow H + OH$
6.	$NO_2 + hv \rightarrow NO + O$
7.	$N_2O + hv \rightarrow N_2 + O_1D$
8.	$NO + hv \rightarrow N + O$
9.	$NO_3 + hv \rightarrow NO_2 + O$
10.	$NO_3 + hv \rightarrow NO + O_2$
11.	$N_2O_5 + hv \rightarrow NO_2 + NO + O_2$
12.	$N_2O_5 + hv \rightarrow 2^*NO_2 + O$
13.	$N_2O_5 + hv \rightarrow NO_2 + NO + 2^*O$
14.	$N_2O_5 + hv \rightarrow 2^*NO + O_2 + O$
15.	$HO_2NO_2 + hv \rightarrow OH + NO_2$
16.	$HO_2NO_2 + hv \rightarrow OH + NO + O_2$
17.	$HO_2NO_2 + hv \rightarrow OH + NO_2 + O$
18.	$HO_2NO_2 + hv \rightarrow HO_2 + NO_2$
19.	$Cl_2 + hv \rightarrow 2^*Cl$
20.	$ClO + hv \rightarrow Cl + O$
21.	$ClO + hv \rightarrow Cl + O_1D$
22.	$OCIO + hv \rightarrow O + ClO$
23.	$ClOO + hv \rightarrow ClO + O$
24.	$Cl_2O_2 + hv \rightarrow Cl + ClOO$
25.	$HOCl + hv \rightarrow OH + Cl$
26.	$ClONO_2 + hv \rightarrow Cl + NO + O_2$
27.	$ClONO_2 + hv \rightarrow Cl + NO_2 + O$
28.	$ClONO_2 + hv \rightarrow Cl + NO_2 + O$
29.	$BrCl + hv \rightarrow Br + Cl$
30.	$BrO + hv \rightarrow Br + O$
31.	$HBr + hv \rightarrow H + Br$
32.	$HOBr + hv \rightarrow Br + OH$
33.	$BrONO_2 + hv \rightarrow Br + NO_2 + O$
34.	$BrONO_2 + hv \rightarrow Br + NO + O_2$
35.	$CH_2O + hv \rightarrow CO + H_2$
36.	$CH_2O + hv \rightarrow HO_2 + CO + H$
37.	$CH_3Cl + hv \rightarrow CH_3O_2 + Cl$
38.	$CCl_4 + hv \rightarrow 4^*Cl$
39.	$CH_3CCl_3 + hv \rightarrow 3^*Cl$
40.	$CFCl_3 + hv \rightarrow 3^*Cl$
41.	$CF_2Cl_2 + hv \rightarrow 2^*Cl$
42.	$CF_3CCl_3 + hv \rightarrow 3^*Cl$
43.	$CF_3CFCl_2 + hv \rightarrow 2^*Cl$
44.	$CF_3CF_2Cl + hv \rightarrow Cl$
45.	$CHF_2Cl + hv \rightarrow Cl$
46.	$CH_3Br + hv \rightarrow Br + CH_3O_2$
47.	$CF_3Br + hv \rightarrow Br$
48.	$CF_2ClBr + hv \rightarrow Br + Cl$

Table 2. Surface emission inventory for the LLNL two-dimensional model. (teragrams per year)

Model Zone	Latitude Center	Methane	Carbon Monoxide	Nitrogen Dioxide
1	-80.1	0.00	0.60	0.00
2	-70.9	0.00	1.00	0.00
3	-62.3	0.00	8.45	0.00
4	-53.1	0.15	18.64	1.98
5	-42.5	4.08	35.62	7.27
6	-30.0	18.99	84.83	10.35
7	-17.5	24.67	136.09	15.63
8	-5.7	39.25	154.50	11.67
9	5.7	42.43	145.11	12.67
10	17.5	54.99	167.10	10.69
11	30.0	81.71	197.88	20.37
12	42.5	70.41	209.05	27.09
13	53.1	57.51	126.63	8.88
14	62.3	30.00	34.40	4.83
15	70.9	15.92	5.02	0.00
16	80.1	12.77	3.01	0.00
TOTALS (Tg/yr):		452.9	1328	131.4

Table 3. Radiative Forcing W/m²

Year	Direct CH ₄	Indirect O ₃	CO ₂ (1.29)	CO ₂ (2.0)
1	0.2500	0.0947		
2	0.2455	0.1180	1.956	5.453
3	0.2312	0.1165		
6	0.1950	0.1013		
7	0.1844	0.0957		
8	0.1744	0.0909		
9	0.1649	0.0861		
10	0.1558	0.0818		
15	0.1176	0.0614		
20	0.0884	0.0462		
25	0.0665	0.0348		
30	0.0500	0.0261		

Table 4. Latitude Variation Of Radiative Forcing (W/M²) For Year 2

LATITUDE (DEG)	DIRECT CH ₄ (P. TROP.)	INDIRECT O ₃ (P. TROP.)
-71	0.2403 (292mb)	0.0625 (292mb)
-30	0.2755 (139mb)	0.1518 (139mb)
+5.7	0.2628 (123mb)	0.1516 (123mb)
+30	0.2659 (135mb)	0.1406 (135mb)
+71	0.2244 (302mb)	0.0603 (302mb)
Avg.	0.2603	0.1297
% Diff.	+5 (0.2455)	+9 (0.1180)

Table 5. Latitude Effect Of CO₂ Forcing For An Impulse Doubling Of CO₂

LATITUDE	FORCING (W/m ²)	CO ₂ FACTOR	CH ₄ FACTOR	O ₃ FACTOR
Average	5.453	0.8	0.8	0.8
-71	4.418	0.988	0.967	0.523
-30	5.735	0.76	0.852	0.977
+5.7	5.976	0.73	0.781	0.939
+30	5.773	0.76	0.823	0.906
+71	4.624	0.944	0.863	0.482

Table 6. Latitude Variation Of H₂O Radiative Forcing (W/M²)

LATITUDE (DEG)	H ₂ O Forcing		
	Year 5	Year 10	Year 20
-60 (278mb)	2.085 (-3)	5.302 (-3)	3.761 (-3)
-30 (139mb)	4.179 (-3)	1.021 (-3)	7.270 (-3)
Eq. (123mb)	2.995 (-3)	6.456 (-3)	4.715 (-3)
+30 (135mb)	5.295 (-3)	1.251 (-2)	8.911 (-3)
+60 (278mb)	1.741 (-3)	4.032 (-3)	2.932 (-3)
Avg.	3.629 (-3)	8.535 (-3)	6.099 (-3)

Table 7. Radiative Forcing Integrals per Kilogram Mass of the Trace Gases

	20 yr	50 yr	100 yr	200 yr	500 yr
CH ₄	1.505e-12 ^a	2.074e-12	2.183e-12	b	b
O ₃ (CH ₄)	7.931e-13	1.127e-12	1.198e-12	b	b
H ₂ O(CH ₄)	5.624e-14		1.012e-13		1.016e-13
CO ₂	3.117e-14	6.303e-14	1.073e-13	1.832e-13	3.612e-13

^aRead "e-" as an exponent, thus 1.505e-12 = 1.505 × 10⁻¹². Units are W yr m² kg⁻¹ at the tropopause.

^bTaken as identical to the value for time horizon of 100 yr.

Table 8. Global Warming Potentials and the Indirect GWP Total Uncertainty Estimate

	source	20 yr	50 yr	100 yr	200 yr	500 yr
CH ₄	current	52.6		22.9		7.0
	a	37.7	21.7	12.9	7.5	3.8
	b	34		9		2
	c	35		11		4
O ₃ (CH ₄)	current	26.7		11.7		3.58
	b	24		8		3
	a	23.1		10.4		3.1
H ₂ O(CH ₄)	current	1.9		1.01		0.31
	b	10		4		1

Sources:

(a) Wuebbles *et al.*, 1993

(b) IPCC, 1990

(c) IPCC, 1992.

Figure 1 Globally- and annually-averaged profiles of water vapor, ozone, and methane as a function of altitude for the ambient atmosphere.

Figure 2 Pressure-temperature profile for ambient atmosphere. The temperatures are globally- and annually-averaged.

Figure 3 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 equal to the equilibrium increase of CH_4 produced by a constant 25% increase in total emissions. Feedbacks in the lifetime of methane result in about a 36% peak increase in total atmospheric methane. The ambient value of the methane mass is indicated by the dashed line.

Figure 4 Annual average total ozone column after the pulse increase of methane.

Figure 5 Annually averaged tropospheric ozone column after the pulse increase of methane.

Figure 6

Figure B. Radiative forcing of CH₄ versus time after pulse release of CH₄. ○: line model calculations. Solid line: fit of Equation 5.4a.

DATE

FILMED

10 / 5 / 94

END