

CHAPTER 6

Model Simulations of Stratospheric Ozone

Author:

M.K.W. Ko

Co-authors:

A. Ibrahim

I. Isaksen

C. Jackman

F. Lefèvre

M. Prather

P. Rasch

R. Toumi

G. Visconti

Contributors:

S. Bekki

G. Brasseur

C. Brühl

P. Connell

D. Considine

P.J. Crutzen

E. Fleming

J. Gross

L. Hunt

D. Kinnison

S. Palermi

Th. Peter

G. Pitari

K. Sage

T. Sasaki

X. Tie

D. Weisenstein

D.J. Wuebbles

CHAPTER 6

MODEL SIMULATIONS OF STRATOSPHERIC OZONE

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SUMMARY

Model Simulations of Stratospheric Ozone

- Multi-dimensional models are designed to provide simulations of the large-scale transport in the stratosphere. This transport rate is combined with the local chemical production and removal rates of ozone to determine the distribution of ozone as a function of longitude, latitude, height, and season.
- There is strong observational evidence that heterogeneous chemistry (hydrolysis of N_2O_5 and ClONO_2) is operating on surfaces of the aerosol particles in the stratospheric sulfate layer. There is a general agreement on how this should be represented in the models. Models that include these reactions produce calculated ozone decreases (between 1980 and 1990) that are larger and in better agreement with the observed trend than those produced by models that include only gas-phase reactions. All model simulations reported here include these two reactions.
- Both three-dimensional and two-dimensional models have been used in simulating polar stratospheric cloud (PSC) chemistry in the vortex and how the equatorward transport of chemically perturbed polar air may affect ozone at midlatitudes. Our lack of understanding of the detailed mechanisms for denitrification, dehydration, and transport processes reduces our confidence in these model predictions.
- No multi-year simulation has been performed to date using three-dimensional models. Two-dimensional (latitude-altitude) models remain the primary tools for extensive diagnostic studies and multi-year simulations.

How well do models simulate the distributions and trends of ozone in the stratosphere?

UPPER STRATOSPHERE

- The model-simulated ozone concentration in the upper stratosphere is typically 20% smaller than the observed values, a problem that has been identified previously. This suggests that there is a problem with our understanding of the photochemistry in that region.
- The model-calculated ozone trends above 25 km due to emission of halocarbons between 1980 and 1990 are in reasonable agreement with the trends (both in the altitude profile and latitudinal variation) derived from the satellite measurements. Most of the model results did not consider radiative feedback and temperature trends that are likely to reduce the predicted ozone decreases by about a factor of 0.8.

LOWER STRATOSPHERE

- The models underestimate the amount of ozone in the lower stratosphere at high latitudes during winter and spring. This, coupled with the model-calculated behaviors of other trace gases, indicates that the models do not have a good representation of the transport processes in those seasons.
- The partitioning of the radical species in the lower stratosphere is influenced to a large extent by the hydrolysis rates of N_2O_5 and ClONO_2 . This, in turn, affects the calculated ozone response in the lower stratosphere to increases in chlorine and bromine. The trend in the polar region is also affected by PSC chemistry in the vortex as well as heterogeneous conversion of HCl on sulfate particles at cold temperatures.
- Comparison with the local trend derived from observations indicates that models that include only hydrolysis of N_2O_5 and ClONO_2 on sulfate particles underestimate the trend between 15 and 20 km at all latitudes. Including PSC processing and the heterogeneous conversion of hydrochloric acid (HCl) on cold sulfate aerosol in model simulations gives larger trends at high latitudes.

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COLUMN ABUNDANCE

- The model-simulated ozone columns in the tropics are within 10% of the observed values. However, some models underestimate the spring maximum in the Northern Hemisphere by as much as 30%.
- The models calculate a trend in the tropics of about -1% per decade in the column abundance of ozone due to emissions of halocarbons between 1980 and 1990. This is consistent with the trend derived from the Dobson stations, the Solar Backscatter Ultraviolet (SBUV) instrument, and the Total Ozone Mapping Spectrometer (TOMS). The model-calculated trend in the tropics is largely a result of the calculated ozone decrease above 25 km.
- The decreases in column ozone at high latitudes calculated by models that include hydrolysis of N_2O_5 and ClONO_2 as the only heterogeneous reactions are between 2% to 3% per decade. This is smaller than the observed negative trends of 4%-8% per decade at the northern high latitudes, and 8%-14% at southern high latitudes outside the vortex.
- Models with PSC chemistry calculate a trend at high latitudes comparable to observation. However, the trend at midlatitudes is still small compared to the observed decrease of 4%-6% during winter and spring (Northern Hemisphere) and winter and summer (Southern Hemisphere).
- A larger trend can be obtained at midlatitudes by including the effects from export of chemically perturbed air from the polar region, by adjusting the transport, or by invoking additional chemical ozone removal cycles. The importance of the processes has not been resolved because of the lack of laboratory and field data.
- The increase in aerosol loading due to the eruption of Mt. Pinatubo was predicted to perturb the lower stratosphere. An idealized simulation was designed to isolate the effect of the photochemical response to a uniform thirty-fold increase in aerosol loading starting in June that decays with a time constant of 1 year. The model-calculated decreases range from 2% to 8% around 50°N in the spring after the prescribed increase, with the calculated decrease diminishing to zero over a five-year period.

Model Predictions of Future Trends

- Using an emission scenario that is designed to represent global compliance with the international agreements, the calculated chlorine loading in the stratosphere reaches its maximum value about 3-5 years after the prescribed tropospheric organic chlorine concentration achieves its maximum value. The maximum calculated chlorine and bromine concentrations and the lowest ozone values occur within 2 years of each other in this scenario.
- Comparison of the model results indicates that although there are significant differences among the model-calculated local photochemical rates and transport rates, the rates from each individual model combine to produce reasonable present-day ozone distributions and the 1980 to 1990 ozone trend. However, as the atmosphere is perturbed farther away from its present state (*e.g.*, large increase in aerosol loading, changes due to long-term trends of N_2O , CH_4 , and halocarbons), the model-predicted responses differ by larger amounts. Current efforts aimed at direct validation of the transport process and photochemical process will help to resolve the differences and bolster our confidence in the model predictions.

6.1 INTRODUCTION

Ozone concentrations in the atmosphere are maintained by the balance between photochemical production (mainly the photolysis of O_2) and removal by photochemical reactions associated with the hydrogen (HO_x), nitrogen (NO_x), chlorine (ClO_x), and bromine (BrO_x) radicals. However, this balance is not always local because an ozone molecule created at one location can be transported to another location before it is photochemically destroyed. Ozone concentration in the lower stratosphere is maintained by a balance among the following processes: production in the tropics, transport to mid- and high latitudes, photochemical removal in the mid- and high latitudes, and removal from the stratosphere by stratosphere/troposphere (strat/trop) exchange. The magnitude of each term changes with seasons and their combined value determines the seasonal behavior of ozone. In the tropical upper stratosphere (above 30 km between $30^\circ N$ and $30^\circ S$), the photochemical reactions are sufficiently fast that local balance holds and the local ozone concentration is determined by the local production and removal rates. However, transport still affects ozone indirectly by modulating the concentrations of the radical species.

The role of the radical species in the removal of ozone has been confirmed by process studies using *in situ* observations. The concentrations of the radical species are maintained by photodegradation of the corresponding source gases: H_2O and methane (CH_4) for HO_x , nitrous oxide (N_2O) for NO_x , and halogen source gases for ClO_x and BrO_x . The large-scale circulation that transports ozone is also responsible for the redistribution of source gases, radicals, and other trace gases that can affect the partitioning of the radical species. Increases in radical concentrations (*e.g.*, increases in ClO_x due to chlorofluorocarbons (CFCs) emitted at the Earth's surface, and increases in NO_x due to N_2O emitted at the ground and stratospheric injection of NO_x by aircraft) lead to changes in ozone.

In this chapter, we discuss modeling of the seasonal behavior of ozone in the stratosphere using multi-dimensional models. The amount of ozone in the atmosphere may be separated into three layers according to the processes controlling the concentrations: 1000 mb (ground) to 100 mb (16 km) in the tropics and 200 mb (11 km) in the extra tropics; from the first layer to 10 mb

(30 km); and 10 mb to 1 mb (45 km) (*see, e.g.*, Jackman *et al.*, 1989). Ninety percent of the ozone resides in the upper two layers, with more than two-thirds in the middle layer. Although the models include a simple version of the troposphere, representation of many of the processes is incomplete (*see* Chapter 5 and Chapter 7 in this report for discussions of ozone in the troposphere). In the upper layer, where ozone is controlled by local production and removal, the ozone concentration can be simulated by box models if the concentrations of the radical species and overlying ozone column are known. The middle layer has received the most attention for several reasons. It is where the aerosol layer and the polar stratospheric clouds reside. The observations from the various aircraft campaigns and satellite observations (*see* Chapters 3 and 4, this report) have provided a wealth of data for studying this middle layer.

Because of limitations in computer resources, it is not practical to use three-dimensional models to perform multi-year simulations to study the response of stratospheric ozone to perturbations of the source gases and the radical species. These calculations have been done using two-dimensional (latitude-altitude) zonal-mean models. They incorporate processes that have been proven to be important. The same models are used to compute the atmospheric lifetimes of various trace gases (*see* Kaye *et al.*, 1994) and the ozone depletion potential indices for the halocarbons (*see* Chapter 13). While questions can be raised regarding some aspects of the formulation and representation of the processes in two-dimensional (2-D) models, model results from individual models that appeared in the literature are found to be in reasonable agreement with the present-day atmosphere (within 20% of the observed ozone column away from the polar region).

This chapter reviews the recent improvements in model formulation and discusses the strengths and weaknesses of these models. An open letter was sent to modeling groups to solicit results for a number of prescribed calculations. Different models have reported the results of their calculations in the scientific literature. More often than not, the results are not in agreement with each other. The purpose of the prescribed calculations is to ask each model to do the same calculations with the same input so that the model results can be compared. For this reason, the criterion for choosing the prescribed conditions is that they can be easily imple-

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Table 6-1. Models providing results in this chapter.

Model Name	Institution	Investigators
AER	Atmospheric and Environmental Research Inc., USA	M. Ko and D. Weisenstein
CAMBRIDGE	University of Cambridge, United Kingdom	S. Bekki
GSFC	NASA Goddard Space Flight Center, USA	C. Jackman, D. Considine, E. Fleming
ITALY	Universita degli Studi L'Aquila, Italy	G. Pitari, S. Palmeri, G. Visconti
LLNL	Lawrence Livermore Laboratory, USA	D. Kinnison, P. Connell
MPIC	Max Planck Institute for Chemistry, Germany	C. Brühl, J. Gross, P.J. Crutzen, Th. Peter
MRI	Meteorological Research Institute, Japan	T. Sasaki
NCAR	National Center for Atmospheric Research, USA	G. Brasseur, X. Tie
OSLO	University of Oslo, Norway	I. Isaksen

mented, rather than being faithful to what actually occurs in the atmosphere. For these calculations, it is more meaningful for the model results to be compared with each other rather than with observations. Clearly, comparison with observation still remains as the only real test on the reliability of model results.

Modeling groups that submitted results are listed in Table 6-1. They are all 2-D models. Most of these models (with the exception of the CAMBRIDGE model) have participated in one or more of the intercomparison exercises, the latest of which took place in 1991 and 1992 (see Prather and Remsberg, 1993). This intercomparison involved 14 different groups from 6 countries. The intercomparison was comprehensive and included: 1) source, radical, and reservoir gases important in ozone photochemistry; 2) radioactive tracers ^{14}C and ^{90}Sr and the Mt. Ruiz volcanic cloud, which tested the models' transport; and 3) a detailed model intercomparison of photodissociation rates, transport fluxes, and idealized tracers that highlighted some of the models' similarities and differences. One result of these exercises was to help eliminate simple coding errors in the models and give more confidence that the range of predictions is due to differences in formulations and approaches. The remaining differences will ultimately have to be resolved by comparison with observations. The results from these calculations will show that there are substantial differences among the model predictions, particularly when perturbations are large. Unfortunately, the schedule of this report does not allow enough time

to resolve all the issues. It is hoped that this will be done soon.

6.2 COMPONENTS IN A MODEL SIMULATION

This section discusses how the models simulate the distributions of the source gases, the partitioning of the radical species, and the distribution of ozone in the stratosphere. To simulate the distribution of ozone, the models calculate the local production and removal rates for ozone, and combine them with the effect of transport to determine the ozone concentration as a function of longitude, latitude, altitude, and season. The local production and removal rates depend on the model-computed distributions of the source gases and the radical species, and the partitioning of the radicals (which in turn depends on the local temperature and solar insolation). One thing to note is that the photochemical removal rate for ozone in most of the lower stratosphere is about 10% per month in summer and 1% per month in winter. Thus, it is always necessary to consider the effect of transport and the combined cumulative effect over several years to assess the ozone response. This is to be contrasted with situations where activation of the chlorine radicals in the polar vortex leads to a rapid ozone removal rate of 1% per day.

6.2.1 Source Gases and Radical Species

The models simulate the following processes in the life cycle of a source gas released in the troposphere: the cycling of the source gas between the troposphere and the stratosphere via strat/trop exchange; the photochemical reactions that release the radical species; the subsequent redistribution of the radical species by the large-scale transport; and the partitioning of the radical species into the active and reservoir species. A molecule in the stratosphere can either be photochemically removed, or it will spend, on average, about three years before it is transported back to the troposphere (see *e.g.*, Holton, 1990). The three-year residence time corresponds to the average for all material in the stratosphere. Clearly, material introduced to the stratosphere near the tropopause will have a much shorter residence time. The exchange between the troposphere and stratosphere is simulated in the models in terms of the large-scale advection and eddy transport. This is probably adequate for source gases such as N_2O and the CFCs, and the radical families Cl_y , Br_y , and NO_y , whose distributions are relatively uniform. A more sophisticated treatment is needed for cases involving direct injection of radical species, such as injection of chlorine radicals by the space shuttle solid rocket engine and injection of NO_x by high-flying aircraft.

6.2.1.1 HALOGEN SPECIES

The odd chlorine (Cl_y) and bromine (Br_y) species in the stratosphere come from degradation of the source gases. Among the source gases that have been measured in the atmosphere, the atmospheric burdens of methyl chloride (CH_3Cl), methyl bromide (CH_3Br), and other bromomethanes are thought to be maintained, in part, by natural sources. Other man-made sources include the chlorofluorocarbons (CFCs), the hydrochlorofluorocarbons (HCFCs), the bromomethanes (mainly methyl bromide), and the halons in the stratosphere. Photodegradation of the CFCs takes place almost exclusively in the stratosphere. The hydrogenated halogen species can be broken down by photochemical reactions in both the troposphere and stratosphere. The Cl_y and Br_y species released in the troposphere will be washed out relatively quickly and will not be transported to the stratosphere. Thus, source gases that react in the troposphere will deliver less of their chlorine or bromine to

the stratosphere. The radical species released in the stratosphere are redistributed in the stratosphere and eventually removed from the stratosphere by the large-scale transport that parameterizes strat/trop exchange in the models. While in the stratosphere, they will be partitioned into the active species (Cl , ClO , Cl_2O_2 , BrO) and the reservoir species (HCl , $ClONO_2$, $HOCl$, HBr , $BrONO_2$, $HOBr$). The active species participate directly in the ozone removal cycles. Observed concentrations of the reservoir species provide an important check for the model results.

Model calculations have been used to simulate the distribution of the chlorine radicals released by specific source gases in the present-day stratosphere (see Weisenstein *et al.*, 1992). This can be used to estimate the individual contribution of a specific source gas to chlorine loading and ozone depletion. A similar breakdown can also be obtained using observed concentrations of the source gases in the lower stratosphere (Kawa *et al.*, 1992; Woodbridge *et al.*, 1994).

Two other sources for chlorine radicals were discussed in Chapter 2. These are deposition of chlorine by solid-fuel rockets and injection of HCl into the stratosphere by violent volcanic eruptions. These sources are not included in the model simulations. The estimated input of 0.7 kiloton (Cl)/yr from solid-fuel rockets is small compared to the annual input of 300 kiloton (Cl)/yr from the current inventory of organic halocarbons in the atmosphere (Prather *et al.*, 1990a). Theoretical calculations discussed in Chapter 3 show that HCl will be scavenged in the volcanic plume (Tabazadeh and Turco, 1993). This, together with the lack of observed increase in HCl after eruptions (Wallace and Livingston, 1992; Mankin *et al.*, 1992), supports the conclusion that volcanic eruptions contribute little to stratospheric chlorine.

6.2.1.2 THE ODD NITROGEN SPECIES

The odd nitrogen species are introduced into the stratosphere by several sources. The major natural source of NO_y is from the reaction of N_2O with $O(^1D)$, producing two NO molecules (Crutzen, 1970; McElroy and McConnell, 1971). This is why changes in concentration of N_2O will affect the concentration of NO_y radicals and ozone. Reaction of N_2O with excited O_2 molecules has been suggested as a possible source (Toumi, 1993) but cannot be quantified because of lack of rate data. Other suggested continuous natural sources

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Table 6-2. Comparison of sources and sinks for odd nitrogen species in the stratosphere.

SOURCES	Magnitude (kiloton(N)/yr)
Nitrous oxide oxidation $N_2O + O(^1D) \rightarrow 2NO$	600
Transport of NO_x produced by lightning in the troposphere	250
Galactic cosmic rays (solar minimum)	86
(solar maximum)	63
Solar proton events (1972, solar maximum)	35
(1975, solar minimum)	0.01
Input from mesosphere and thermosphere, relativistic electron precipitations, meteors	?
Nuclear explosions (1961 & 1962 nuclear tests)	550
Stratospheric-flying aircraft	depends on emission index, fleet size, and flight paths
Rocket launches	?
SINKS	
Reforming of molecular nitrogen $N + NO \rightarrow N_2 + O$	195
Rainout of HNO_3 transported to the troposphere	750

of stratospheric NO_y that have a regional impact are galactic cosmic rays for the polar lower stratosphere (Warneck, 1972; Nicolet, 1975; Legrand *et al.*, 1989), lightning for the lower equatorial stratosphere (Noxon, 1976; Tuck, 1976; Liu *et al.*, 1983; Ko *et al.*, 1986; Kotamarthi *et al.*, 1994), and the downward flux of odd nitrogen from the thermosphere (Strobel, 1971; McConnell and McElroy, 1973) especially in the polar region during winter (Solomon *et al.*, 1982; Garcia *et al.*, 1984; Russell *et al.*, 1984). Sporadic natural sources of stratospheric NO_x include meteors (Park and Menees, 1978), solar proton events (Zadorozhny *et al.*, 1992; Jackman, 1993), and precipitation by relativistic electrons (Callis *et al.*, 1991). The frequency and magnitude of these sporadic sources are not well quantified. Most models include the lightning source in addition to N_2O oxidation, but ignore other sources. Mankind also influences stratospheric NO_x production through atmospheric nuclear explosions (Johnston *et al.*, 1973; Foley and Ruderman, 1973), rocket launches (Karol *et al.*, 1992; Chapter 10 in WMO, 1992), and high-flying aircraft (CIAP, 1975; Albritton *et al.*, 1993).

The odd nitrogen species introduced into the stratosphere are redistributed by the large-scale transport. They are partitioned into N, NO, NO_2 , NO_3 , N_2O_5 ,

HNO_3 , HNO_4 , $ClONO_2$, and $BrONO_2$. The active species ($NO_x = NO + NO_2$) are important in ozone control. Besides reacting with ozone, the NO_x constituents are also important in interference reactions with other families (HO_x , Cl_x , Br_x) involved in ozone regulation through reactions with OH (forming HNO_3), with ClO (forming $ClONO_2$), and with BrO (forming $BrONO_2$).

Photochemical removal occurs in the upper part of the stratosphere via the reaction of N with NO forming N_2 . The rest of the production is balanced by transport removal. Table 6-2 (from Jackman *et al.*, 1980, 1990; Prather *et al.*, 1992) shows a comparison of the magnitude of some of these suggested sources and sinks of odd nitrogen. Nitrous oxide oxidation is believed to be the largest source, with lightning also contributing substantially in the lower equatorial stratosphere. The transport to the troposphere is thought to be the largest sink, with the reforming of N_2 also contributing significantly.

6.2.1.3 THE HO_x SPECIES

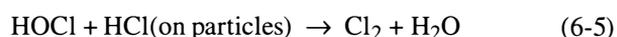
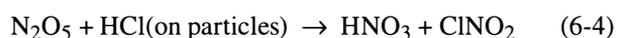
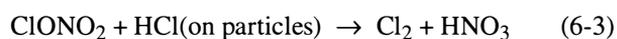
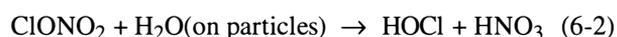
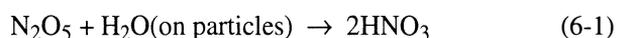
The HO_x species are produced from the reaction of $O(^1D)$ with H_2O and CH_4 . Reaction of excited O_2 molecules with H_2 has been suggested as a source (Toumi, 1993) but cannot be quantified because of lack of rate

data. The reaction $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$ occurs on the surfaces of the aerosol particles. After the HNO_3 molecules are released to the atmosphere, they can either react with OH or be photolyzed to produce OH and NO_2 . Thus, depending on the fate of the HNO_3 molecules, the reaction can be a source of OH. Model calculations show that there is a net increase in OH when the reaction is included (see discussion in Rodriguez *et al.*, 1991). Removal of the HO_x species in the stratosphere is dominated by reaction of OH with HO_2 , HNO_3 , HNO_4 , and HCl. The species OH and HO_2 participate in the ozone removal reactions and modulate the partitioning of the NO_y , Cl_y , and Br_y species.

The H_2O concentration in the stratosphere is maintained by oxidation of CH_4 and import of H_2O from the troposphere. The exchange of H_2O across the tropopause is not well understood. Some models (ITALY, LLNL, MPIC, MRI, NCAR) parameterized this by imposing a boundary condition along the tropopause. Other models (AER and GSFC) keep the stratospheric H_2O concentration fixed at observed values (see section B in Prather and Remsberg, 1993) and make adjustments for future changes from CH_4 increase and from engine emissions of stratospheric aircraft.

6.2.2 Heterogeneous Reactions and Partitioning of the Radical Species

Studies of the Antarctic ozone hole pointed to the importance of heterogeneous reactions in affecting ozone in the lower stratosphere. These early modeling studies, laboratory experiments, and field measurements were summarized in a review paper by Solomon (1990). Subsequent studies were reviewed in WMO (1992). Chapters 3 and 4 presented more recent evidence that shows that heterogeneous reactions do occur on particles in the atmosphere at rates that are consistent with rate constants determined in the laboratory. These reactions are



In each reaction, a gas molecule (*e.g.*, N_2O_5) is assumed to collide with a particle and proceed to react with another molecule (H_2O or HCl) already on the particle. As discussed in Chapter 3, these reactions occur on liquid or frozen sulfate particles and on polar stratospheric clouds (PSCs) at different rates. The effectiveness of each reaction in altering the partitioning of the radical species depends on how fast the heterogeneous conversion rate is compared to the gas-phase reactions that control the partitioning in specific regions of the atmosphere. Because HCl is much more soluble on PSCs, reactions (6-3) through (6-5) are more effective on PSCs than on liquid sulfate particles. A common effect of the first four reactions is to decrease the NO_x/NO_y ratio, with the net effect of reducing the ozone destruction due to the NO_x loss cycle. At the same time, the reduction in NO_x also inhibits the formation of ClONO_2 , leaving more of the active chlorine in the form of ClO, and increases the ClO_x removal of ozone. The additional HNO_3 produced in the reaction also increases OH and the removal of ozone due to the HO_x cycle. The last three reactions involve direct activation of chlorine species by converting HCl to active chlorine. The inclusion of these reactions in the models has brought the model results in closer agreement with observations (see Chapters 3 and 4).

The information on the reaction rate constants indicates that reaction (6-1) has the dominant effect at normal stratospheric temperatures at midlatitudes (see discussion in Hanson *et al.*, 1994). Reaction (6-1) reduces the efficiency of the NO_x cycle, while both the HO_x and ClO_x cycles are enhanced. As a result, the HO_x cycle is the dominant ozone removal cycle in the lower stratosphere. This has been confirmed using direct observations of OH and HO_2 in the lower stratosphere (Wennberg *et al.*, 1994). The net effect on the local removal rate of ozone is small for normal aerosol loading, so that the present-day ozone abundances calculated with and without heterogeneous chemistry are within 10% of each other (Rodriguez *et al.*, 1991; Weisenstein *et al.*, 1991, 1993; McElroy *et al.* 1992). However, these same reactions make the model-calculated ozone more sensitive to increases in chlorine and less sensitive to added nitrogen-containing radicals.

Reaction (6-2) has a more noticeable impact on the partitioning of the radical species for temperatures less than 200 K and/or under enhanced aerosol loading

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(Hanson *et al.*, 1994). Indirect evidence for this reaction was reported in Solomon *et al.* (1993) and Sanders *et al.* (1993), who detected enhanced OCIO in the Antarctic, consistent with ClONO₂ hydrolysis on Mt. Pinatubo aerosols before the onset of PSCs. The effect of reactions (6-3) through (6-5) appears to be limited to ice surfaces, but could be important on sulfate particles at high latitudes under very cold temperatures (Hanson *et al.*, 1994). We discuss below how models attempt to simulate the effects of these reactions.

6.2.2.1 HETEROGENEOUS CHEMISTRY ON THE SULFATE LAYER

Reactions (6-1) and (6-2) proceed on liquid sulfate aerosol particles that are present in the global sulfate layer throughout the lower stratosphere. Molina *et al.* (1993) reported experimental results that show that if the temperature is below 200 K, the activation may also take place on solid H₂SO₄ hydrates. The rates of the reactions depend on the surface area density and the water content of the aerosol, and possibly the phase of the aerosol particle. In the models, a first-order reaction rate constant is defined for each reaction as the product of the collision frequency of the gas-phase reactant with the aerosol particles in the sulfate layer and the sticking coefficient (γ), which is the reaction probability per collision. The collision frequency depends on the surface area density of the sulfate particles. The effect of the varying water content and phase of the aerosol is parameterized in the models by defining an effective γ in terms of the local temperature and concentration of water vapor. However, there is observational evidence that indicates that the phase of the aerosol particles may also depend on the history of the particles, and not just on local conditions. A final assumption made in the models is that the products of the reaction are released to the atmosphere. Thus, there is no sequestering of the reaction products.

Most model studies have assumed a γ value of 0.1 for reaction (6-1). Recent results reported by Fried *et al.* (1994) indicate that γ for (6-1) may vary between 0.077 to 0.15 at 230 K for H₂SO₄ weight percent between 64% to 81%. The extrapolated rate in the atmosphere based on their semi-empirical model ranges from 0.03 to 0.15. Other studies (Tolbert *et al.*, 1993; Fried *et al.*, 1994) discussed whether uptake of formaldehyde may change

the composition of the aerosol and affect the γ values. The effect of such variation for reaction (6-1) has not been explored.

Hanson *et al.* (1994) recommended the following expression for γ for reaction (6-2) :

$$\gamma(\text{ClONO}_2 + \text{H}_2\text{O}) = 10^{(1.86 - 0.0747W)}$$

where W is the weight percent of acid, defined as

$$W = \frac{T(0.6246Z - 14.458) + 3565}{T(-0.19988) + 1.3204Z + 44.777}$$

with $Z = \ln(\text{partial pressure H}_2\text{O (mb)})$, T is the temperature in K. Hanson *et al.* (1994) also provided parameters for reactions (6-3) and (6-5). They concluded from their model calculation that the reactions should be included in simulating the ozone behavior at high latitude winter under enhanced aerosol conditions. The calculations in this chapter include reactions (6-1) and (6-2) as the only heterogeneous reactions on sulfate particles.

There are additional problems specific to simulating the effects of these reactions in a 2-D zonal-mean model. The model results presented in this chapter use a prescribed zonal-mean aerosol surface density specified as a function of altitude and latitude (Chapter 8, WMO, 1992) derived from the Stratospheric Aerosol and Gas Experiment (SAGE) observations. If we assume that the surface area density is constant in the zonal direction, a constant value for γ in (6-1) would mean that the conversion rate can be represented reasonably well as a zonal-mean rate. On the other hand, the parameterization for reaction (6-2) depends on local temperature and partial pressure of H₂O. As the dependence on these zonally varying quantities become more nonlinear, simulating the effect of the conversion as a zonal-mean quantity becomes more problematic (Murphy and Ravishankara, 1994; Considine *et al.*, 1994). The effects of longitudinal temperature fluctuation on the zonal-mean rate of reaction (6-2) has been studied by Pitari (1993a). The conversion rate experienced by an air parcel following the actual trajectory in the polar vortex was found to be as much as a factor of 10 larger than the rate calculated using the zonal-mean temperature.

6.2.2.2 HETEROGENEOUS CHEMISTRY ON PSCs

Modeling the effects of polar stratospheric clouds (PSCs) involves two steps. The model must simulate the removal of H₂O and HNO₃ vapor when the particles are

formed, and the effects of heterogeneous conversions that occur on the surfaces. Inside the polar vortex, the conversion rates due to PSC chemistry are so fast that the amount converted is limited by the availability of the reactants (N_2O_5 , ClONO_2 , HOCl , HCl) once the particles are formed. As a result, the calculated repartitioning depends less on the details of how the reactions are parameterized.

Early 2-D model studies of the effects of polar heterogeneous processes parameterized the heterogeneous reactions as first-order conversion rates for the gas-phase reactants triggered by location and season (Chipperfield and Pyle, 1988; Isaksen *et al.*, 1990) or by the zonal-mean temperature falling below a threshold value (Granier and Brasseur, 1992). In the latter case, the threshold zonal mean temperature was picked to give a reasonable PSC frequency of occurrence. Denitrification was included in Isaksen *et al.* (1990) by ad hoc removal of 50% of the HNO_3 in the PSC regions. Granier and Brasseur (1992) included denitrification and dehydration for Type II PSCs by introducing a first-order removal rate for H_2O and HNO_3 with a time constant of 5 days when the zonal-mean temperature falls below the threshold value. Denitrification was included for Type I PSCs using a first-order removal rate for HNO_3 with a time constant of 30 days. To obtain the surface area density, a log-normal size distribution was assumed. In the 3-D model studies of Chipperfield *et al.* (1993) and Lefèvre *et al.* (1994), the amounts of H_2O , and HNO_3 condensed to form Type I and Type II PSCs were calculated assuming thermodynamic equilibrium using the local model temperature, H_2O , and HNO_3 concentrations. The surface area densities were calculated assuming that the particles have radii of $1\ \mu\text{m}$ and $10\ \mu\text{m}$ for Type I and Type II PSCs, respectively. Sedimentation was included for Type II particles in the transport of the condensed material. Pitari *et al.* (1993) developed a code in their 2-D model in which PSC occurrence and surface area were calculated rather than prescribed. They used a tracer continuity equation for condensed material with a production term that included terms parameterizing condensation, coagulation, sedimentation, and rainout. Different treatments for the uptake of HCl were used in the models. Pitari *et al.* (1993) ignored the uptake of HCl . Chipperfield *et al.* (1993) and Lefèvre *et al.* (1994) assumed that HCl is incorporated in the PSCs using the mole fractions given by Hanson and Mauers-

berger (1988). In all cases, it is assumed that the reaction rate can be represented by an effective γ .

Modeling such processes on PSCs in 2-D models presents special challenges. First, the motions of air-parcels are typically not zonally symmetric. The effectiveness of reactions (6-3) through (6-5) depends on the availability of sunlight to photolyze Cl_2 and ClONO_2 to form Cl and ClO . It is not clear whether a full air-trajectory calculation is needed to take into account the solar insolation experienced by the air parcel, or whether the situation can be approximated by an average exposure to PSCs over several trips around the globe. The problems will likely be most severe at the beginning and end of the polar winters, especially in the Arctic, which experiences large temperature fluctuations and azonal motions throughout the winter. The Southern Hemisphere vortex in the depth of the winter is more uniformly cold and zonally symmetric. Secondly, it is not clear that using the zonal-mean temperature alone can capture the complexity of the different temperatures experienced by an air parcel. Peter *et al.* (1991) developed a way to use climatological temperature statistics to derive probabilities for PSC formation as a function of latitude and altitude for both Type I and Type II PSCs. This formed the basis of methods that other studies used to predict surface area densities without relying solely on zonal mean temperatures (Pitari *et al.*, 1993; Grooss *et al.*, 1994; Considine *et al.*, 1994).

6.2.3 Transport and Ozone

If ozone is calculated assuming local photochemical equilibrium (*i.e.*, local production balanced by local removal), the calculated column abundance will have its maximum value of 700 Dobson units (DU) in the tropics, decreasing to about 200 DU in the summer high latitudes. The observed behavior of the column abundance of ozone (minimum at the tropics and maximum at high latitude) is a good indication that transport plays an important role in redistributing ozone from the production region in the tropics to high latitudes.

Transport of trace gases in three-dimensional chemistry-transport models (CTMs) is based on either three-dimensional winds from general circulation models (GCMs) or data-assimilated winds derived from observations. Because of the limitation in computational resources, it is not yet practical for 3-D CTMs to

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predict evolution of chemical species over time periods much longer than a few years. The same limitation also precludes incorporating full chemistry into a GCM to calculate ozone and winds interactively. Thus, the GCM winds are calculated using prescribed ozone based on observation.

In 2-D models, transport is represented by advection from the zonal-mean velocities and eddy mixing coefficients. Most models used prescribed velocity and eddy coefficients with seasonal variations. The same circulation and temperature are used year after year to simulate the climatological mean state. However, previous studies (Tung and Yang, 1988; Schneider *et al.*, 1991; Jackman *et al.*, 1991; Yang *et al.*, 1991) have shown that the observed interannual variations in temperature would induce corresponding variations in the transport circulation leading to changes in ozone of about 3% to 4%. Variations in the circulation can also come from the quasi-biennial oscillation (QBO) in the equatorial winds. Gray and Pyle (1989) and Gray and Dunkerton (1990) produced a QBO in ozone in their 2-D model with interactive dynamics by parameterizing the QBO in the equatorial winds through specification of damping of waves. In Gray and Ruth (1993), a QBO in the equatorial winds was introduced into the model by relaxing the model winds toward the monthly mean observed winds. The calculated ozone QBO showed anomalies of ± 6 Dobson units ($\pm 3\%$) at the tropics and ± 12 DU ($\pm 2\%$) at midlatitudes. The broad patterns were shown to be in agreement with the anomalies derived from TOMS (Lait *et al.*, 1989), although the amplitude was larger in the model.

6.2.3.1 RELATION TO OBSERVATION

Most applications of 3-D CTMs are formulated as initial value problems where the concentrations of the trace gases are first initialized from observations, and the models are then used to simulate the evolution of the trace gases (typically for a season) for comparison with observations. Granier and Brasseur (1991) used a mechanistic 3-D model with rather detailed chemistry to investigate the mechanisms responsible for ozone depletion over the Antarctic and the Arctic. Kaye *et al.* (1991), Douglass *et al.* (1991), and Rood *et al.* (1991) used a simple parameterized chemistry to assess the importance of chemical processing in polar regions during the winters of 1979 and 1989. The transport of chemical

tracers in those studies was driven by winds from the STRATAN assimilated system (Rood *et al.*, 1989). Chipperfield *et al.* (1993) and Lefèvre *et al.* (1994) simulated the behavior of chemical constituents in the Arctic lower stratosphere during the winters of 1989-1990, and 1991-1992, respectively. These models used analyzed winds and temperature from the European Centre for Medium-Range Weather Forecasts (ECMWF). The simulations reproduce successfully the activation of atmospheric chlorine in polar regions and predict the depletion of ozone in PSC-processed air. While the simulations cannot be used to predict the long-term behavior of the trace gases, they provide the opportunity to diagnose observations and to quantify the different processes that have led to the observed ozone depletion. Chipperfield *et al.* (1993), for example, quantified the respective contribution of the different catalytic cycles responsible for the destruction of ozone in the Arctic lower stratosphere during the 1989-1990 winter.

In 2-D models, the relation to observation is less straightforward. In models that use the residual mean formulation, the velocity and eddy mixing coefficient can be related to observed quantities as follows. The vertical velocity is related to the ratio of the local diabatic heating rate and the lapse rate. Comparison of the vertical velocity in the model with the diabatic heating rate calculated from observed ozone and temperature (Rosenfield *et al.*, 1987) and the lapse rate provides a reference point (see Prather and Remsberg, 1993). The values of the eddy diffusion coefficient K_{yy} can be compared with values derived using mixing rates for potential vorticity (Newman *et al.*, 1988). The interaction between the vertical velocity and the eddy mixing determines the shapes of the surfaces of constant mixing ratios in the lower stratosphere. Measured concentrations of different trace gases indicate that they share the same mixing surfaces in the lower stratosphere when the local photochemical time constant is longer than the transport time constant. This sharing of the mixing ratio surfaces is evident in that an x-y plot of the mixing ratios of two long-lived trace gases shows a compact curve (Plumb and Ko, 1992). This feature is present in both observations and model results (see section H in Prather and Remsberg, 1993). The mixing ratio surfaces in a model defined by the advection velocity and the eddy diffusion coefficient help to determine the latitudinal

gradient of the model-calculated column abundance of ozone.

Finally, the simulated distributions of the long-lived trace gases from 2-D models can be compared to observations. Simulations of source gases N_2O and CH_4 were reasonable when compared to SAMS (Stratospheric and Mesospheric Sounder), ATMOS (Atmospheric Trace Molecule Spectroscopy), and balloon measurements at mid- to high latitudes between 20 and 30 km; however, the variabilities near the winter poles were more difficult to simulate (see Prather and Remsberg, 1993). It was noted in Prather and Remsberg (1993) that direct comparison of model results for the source gases or transient tracers (such as the radioisotopes ^{14}C and ^{90}Sr from nuclear weapons tests) with observation is difficult because the transport can vary significantly from year to year, with the quasi-biennial oscillation leading to two distinctly separate modes of stratospheric circulation. The transport as formulated in the 2-D models can, at best, represent the averaged transport on a seasonal time scale and does not provide any specific information on the transport of the trace gases on shorter time scales. Such information has to come from 3-D CTMs using three-dimensional winds from a data assimilation procedure or similar analysis using observations. Analysis of such results should provide the information necessary to assess the appropriateness of the transport parameterization in the 2-D models.

6.2.3.2 TRANSPORT BETWEEN THE POLAR VORTICES AND MIDLATITUDES

The representation of either a closed or a leaky vortex is a major challenge for models. This is particularly problematic for 2-D models, where the inherent dependence on diffusion coefficients does not allow for a completely satisfactory representation of either process. Previous attempts by 2-D models (Sze *et al.*, 1989; Chipperfield and Pyle, 1988) to simulate the effect of export of ozone-poor air from the breakdown of the Antarctic vortex suggest that the dilution process could have a large effect on the ozone behavior year-round in the southern midlatitudes. The results of Sze *et al.* (1989) showed that for an imposed ozone hole with 50% reduction in the column, the calculated ozone column at 30°S and in the tropics decreased year-round by 3% and 0.5%, respectively. In contrast, the results from Chipperfield and Pyle (1988) showed a decrease of less than 0.5%

northward of 40°S . Prather *et al.* (1990b) used the Goddard Institute for Space Studies (GISS) 3-D CTM to assess the magnitude of the dispersion of ozone-depleted air over several months following the breakdown of the Antarctic polar vortex and obtained a 2% decrease in total ozone year-round at 30°S .

Prather and Jaffe (1990) used a 3-D CTM to look at the effects of the export of chemically perturbed air. Toumi *et al.* (1993) suggested that polar-processed air reaching midlatitudes is expected to contain large amounts of ClONO_2 and may also play a part in affecting the ozone trend. Cariolle *et al.* (1990) used the 3-D general circulation model of Meteo-France (Emeraude) to examine the evolution of the Antarctic polar vortex. They found ozone reduction (about 2%) at midlatitudes in September well before the vortex breakdown. More recently, Mahlman *et al.* (1994) used the Geophysical Fluid Dynamics Laboratory (GFDL) SKYHI GCM to show that, with the 25% depletion in total ozone calculated over Antarctica during the spring season, the ozone column abundance at the equator was reduced by 1% by the end of a 4.5-year model experiment, and the local ozone concentration in the lower stratosphere was reduced by 5%.

The studies of Kaye *et al.* (1991) and Douglass *et al.* (1991), in which the transport of chemical tracers was driven by assimilated winds, concluded that the transport of processed air in the Arctic to midlatitudes was limited. Lefèvre *et al.* (1994) reported the simulation of the behavior of the chemical constituents in the Arctic lower stratosphere during the winter of 1991-1992. The model used analyzed winds and temperature (from ECMWF) and included a comprehensive scheme for gas-phase reactions, as well as a parameterization of heterogeneous reactions occurring on the surface of nitric acid trihydrate (NAT) and ice particles in polar stratospheric clouds, and heterogeneous processes on the surface of sulfate aerosol particles. The model results showed that the combined effects of PSC processing in the vortex, vortex erosion, and aerosol processing at midlatitudes led to significant ozone reductions in the Northern Hemisphere during January 1992. However, chemical processes produced only a limited fraction of the ozone deficit observed at high latitudes during a period dominated by a strong blocking anticyclone over the North Atlantic.

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6.2.3.3 MODELS WITH INTERACTIVE DYNAMICS

The results presented in this chapter are mostly from model simulations in which the temperature and circulation are kept fixed. It is clear that the thermal structure and the transport circulation will change as the trace gas concentrations change. Changes can be due to changes in ozone or changes in other greenhouse gases. Decrease of ozone in the stratosphere and increases in greenhouse gases will cause a cooling of the stratosphere. In addition, changes in ozone near the tropopause and increases in greenhouse gases will cause a warming of the troposphere. We will restrict the discussion in this section to the effect of the cooling in the stratosphere. The effects from changes in the troposphere will be discussed in Section 6.4.3.

First-order effects on the coupling of ozone, temperature, and wave feedback are relatively well understood, and much of the relevant work is summarized in earlier WMO publications. However, the thermal structure of the atmosphere is controlled by a delicate balance between radiative processes (which are related to ozone) and dynamical processes. At the same time, ozone is controlled by a delicate balance between chemical production and destruction (which depends on the thermal structure) and dynamical transport. Thus, processes that appear to be of secondary importance can act to tip the balance in perturbation studies.

Previous studies ignoring heterogeneous reactions (Nicoli and Visconti, 1982; Schneider *et al.*, 1993) suggested that the cooling of the middle atmosphere could be a mechanism for increasing ozone because the ozone-removing cycles are less efficient at lower temperatures. Thus, this temperature feedback is a negative feedback in that the model-calculated ozone decrease will be reduced. However, a cooler stratosphere could lead to an enhanced occurrence of PSCs (Peter *et al.*, 1991; Austin *et al.*, 1992) resulting in increased chlorine activation, giving rise to the possibility of a Northern Hemisphere ozone hole. Pitari *et al.* (1992) used results from a simple 3-D model to show that the ozone response to CO₂ doubling is distinctly different if PSCs are present and heterogeneous reactions on PSCs are included. They showed that the large stratospheric cooling caused by the CO₂ increase would induce a substantial polar ozone decrease despite the fact that the rates of homogeneous catalytic cycles are reduced.

The changes in local heating will also lead to changes in the circulation, and have an attendant effect on the transport of heat, momentum, and trace species. For example, latitudinal changes in the ozone distribution (*i.e.*, the ozone hole) can lead to substantial changes in the persistence and strength of the polar vortex, and thus enhance the chlorine-catalyzed ozone reduction in polar regions. Several GCM studies examined the coupling between temperature change and the ozone hole. Kiehl *et al.* (1988), using the National Center for Atmospheric Research (NCAR) Community Climate Model (CCM2), found that the introduction in the model of a prescribed Antarctic ozone hole produced in the polar stratosphere a cooling of approximately 5 K during the month of October, and introduced a possible delay in the timing of the final warming. A similar cooling was calculated by Cariolle *et al.* (1990) and Prather *et al.* (1990b) using the Meteo-France model and the GISS model, respectively. However, the results of Mahlman *et al.* (1994) show a larger sensitivity, where a 25% reduction in ozone produces a temperature reduction of 8 K.

While attempts to implement full chemistry schemes in GCMs are still limited by computational resources, there has been important progress in including interactive dynamics in 2-D models. Interactive models can be separated into groups according to the treatment of the forcing term for the zonal-momentum equation. The first group uses externally specified momentum fluxes (Harwood and Pyle, 1975; Vupputuri, 1978; Garcia and Solomon, 1983) or calculates the fluxes from the gradient of the zonal mean potential vorticity from externally specified K_{yy} (Ko *et al.*, 1993). Feedback in these models is limited to changes induced by changes in local heating rates. A second group of models calculates the forcing term explicitly from the zonal waves computed in the model. This latter approach can, in principle, account for the effect of the interaction between the waves and mean circulations. Examples in these groups are the models of Brasseur *et al.* (1990), Garcia *et al.* (1992), Garcia and Solomon (1994), and Kinnersly and Harwood (1993).

6.3 COMPARISON OF MODEL RESULTS WITH OBSERVATION

If the models are designed to simulate the behavior of ozone, an obvious question concerns how well they

simulate the ozone behavior in the present-day atmosphere and the observed changes in the past decades. Another question is to what extent we can trust the model predictions. Ironically, one cannot answer those questions by simply comparing the model-simulated ozone directly with the observations. The reasons are as follows. The winds and temperature in the global models represent climatological averaged states. It would not be appropriate to compare the model simulations with the observed behavior in any one particular year. The behavior of ozone is the net effect from many competing mechanisms. Thus, it is difficult to come to any definitive conclusion about the role of any specific mechanism by simply looking at whether the model-simulated ozone values agree with observations. The balance among these mechanisms in the future atmosphere could be very different from that in the present-day atmosphere. The important thing is not only whether we have the proper balance in the present-day atmosphere, but whether the correct physics has been included so that we can predict with confidence how changes in these terms will affect ozone.

Comparison of model results with observations has to be done indirectly after further processing of the observations and/or model-simulated results. One example is the process study that prescribes values for winds, temperature, and concentrations of some of the trace gases based on observations. A more restricted simulation is performed to calculate the remaining trace gases. A comparison is then made for the restricted set to test the few mechanisms that control the behavior of those species. Examples of these are the studies that use data-assimilated winds to isolate the short-term transport, and modeling studies associated with aircraft campaigns that test the mechanisms for the photochemical partitioning. Another example is the intercomparison exercise in Prather and Remsberg (1993) that calculates the relative abundance of the odd-nitrogen and chlorine species in the altitude range of 20 to 40 km, constrained by observed concentrations from ATMOS. Other methods have been developed specifically for ozone. In previous studies to obtain trends in the column abundance of ozone, analyses were performed to take out the quasi-biennial oscillations and the 11-year solar cycle effects to obtain an ozone trend that can be ascribed to changes in trace gases (see, *e.g.*, Bojkov 1987; Reinsel *et al.*, 1994; Stolarski *et al.*, 1992). The derived trend is

then compared to a model simulation that examines the effect of changes in trace gases on ozone. We will discuss some of the model results in Section 6.3.2.

6.3.1 Present-Day Atmosphere

In the comparisons shown below, the University of Oslo (OSLO), NCAR, and Max Planck Institute for Chemistry (MPIC) modeling groups submitted results from calculations that include chemical reactions on PSC surfaces. The Goddard Space Flight Center (GSFC) group submitted two sets of results, one with and one without polar heterogeneous processes.

6.3.1.1 OZONE IN THE UPPER STRATOSPHERE

Several problems identified previously in the upper stratosphere have not been resolved. The Model & Measurement Intercomparison Workshop (Prather and Remsberg, 1993) confirmed previous findings that model-calculated O₃ around 40 km is 20% to 40% smaller than the values derived from the Solar Backscatter Ultraviolet (SBUV) measurement (see Figure 6-1). Recent analysis by Eluszkiewicz and Allen (1993) indicates a deficit of 8% to 20% even when observations are used to constrain the concentrations of the radical species.

Previous suggestions that vibrationally excited oxygen molecules may produce ozone in the upper stratosphere (Slanger *et al.*, 1988; Toumi *et al.*, 1991; Toumi, 1992) are found to be ineffective because of rapid quenching (Patten *et al.*, 1994). The values for the ClO/HCl ratio derived from measurements (Stachnik *et al.*, 1992) are found to be smaller than model-calculated values. Recent model simulations show that the effects of assuming a branching that produces HCl from the reaction of ClO with OH (McElroy and Salawitch, 1989; Natarajan and Callis, 1991) are to increase the calculated ozone concentration at 2 mb (Chandra *et al.*, 1993) and to decrease the calculated decadal ozone trend at the same altitude (Toumi and Bekki, 1993). However, the results from Chandra *et al.* (1993) show that even with the branching, the calculated ozone concentration is still 20% too small in the summer months.

Although the amount of ozone in the upper layer is relatively small and the error may not affect the model-calculated ozone column, the discrepancy may be an indication that there is missing chemistry in the models. There is a need to obtain simultaneous measurements of

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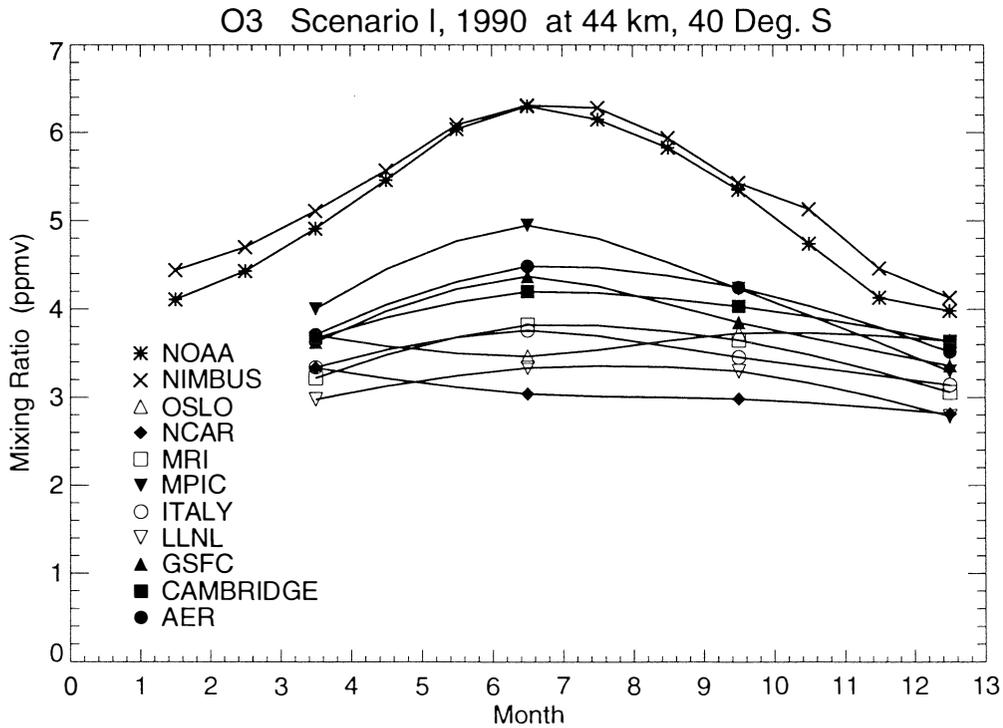
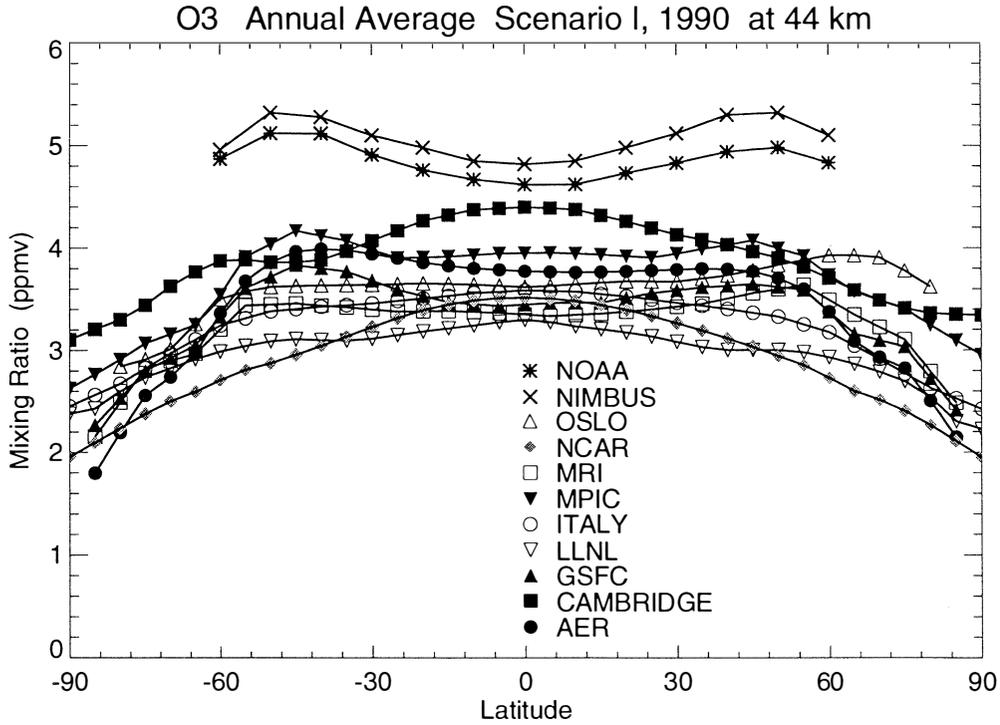


Figure 6-1. Comparison of the model-calculated ozone concentrations at 44 km (2 mb) for 1990 with observations. The observations are the 1989 and 1990 averages from the NOAA-11 SBUV/2 and the Nimbus-7 SBUV as compiled by Chandra *et al.* (1993). The upper panel shows the annual averaged concentrations as a function of latitude. The lower panel shows the calculated concentrations at 40°S for four seasons.

ozone, temperature, and radical species such as OH, HO₂, ClO, and NO₂ in the upper stratosphere to help resolve this.

6.3.1.2 OZONE COLUMN

Figure 6-2a shows the calculated column abundance of ozone for the 1990 condition. The model results are within 20% of the observations away from the polar region. The zonal-mean total ozone derived from the Total Ozone Mapping Spectrometer (TOMS) observation indicates that the spring maximum in the Northern Hemisphere extends all the way to the pole, while the Southern Hemisphere shows a sub-polar maximum, with the largest value occurring at about 60°S. This has been attributed to the different surface topographies in the two hemispheres inducing different circulations, resulting in a more stable vortex that encircles the pole in the Southern Hemisphere. By adjusting the circulation and the eddy diffusion coefficients, most models succeeded in producing these features. Hou *et al.* (1991) discussed the relative roles of the circulation and eddy diffusion coefficients in determining the result in the Atmospheric and Environmental Research, Inc. (AER) model. However, none of the models simulates the isolation of the air in the vortex. Thus, it is questionable whether the models produce the observed ozone behavior by simulating the actual mechanisms occurring in the atmosphere.

In Prather and Remsberg (1993), the model-calculated ozone distributions were compared with the average of the 1979 and 1980 observed distribution. This was done to minimize the ozone QBO in the observation. The difference (in Dobson units) between the model-calculated total ozone for 1980 and the averaged observed abundance is plotted in Figure 6-2b. The calculated total ozone values in most models are within 20 Dobson units (10%) of the observed value in the tropics. The models also calculate smaller column ozone than the observed values during the spring maxima in polar regions, up to 100 DU (30%) smaller in some cases.

6.3.2 Ozone Trends Between 1980 and 1990

6.3.2.1 MECHANISMS THAT CAN AFFECT THE OZONE TREND

The distribution of ozone can be modified in many ways. The concentrations of the radical species can be

increased by the introduction of additional source gases or direct introduction of radical species, such as injection of chlorine radicals by the space shuttle solid rocket engine (WMO, 1992) and injection of NO_x by high-flying aircraft (WMO, 1992; this report). The partitioning of the radical species can be affected by changes in temperature, which affect the reaction rate constants and the frequency of occurrence of the PSCs. Analyses of temperature records (see, *e.g.*, Spencer and Christy, 1993; Oort and Liu, 1993) suggested a cooling trend of about 0.4 K/decade. This cooling may be a result of the increase in CO₂ and ozone depletion that occurred in this period. The partitioning can also be affected by changes in surface areas of the sulfate layer that affect the rate of heterogeneous conversion. Observations (see Chapter 3, WMO [1992]) showed that the aerosol loading has been decreasing after the eruption of El Chichón in 1982. Other works suggested that aircraft emission of SO₂ from combustion of aviation fuel may have increased the sulfate loading in the past decade (see Hofmann, 1991; Bekki and Pyle, 1992).

Other mechanisms that can affect the ozone trend are the QBO in equatorial winds (which has a period of 2 years), the 11-year solar cycle, and the El Niño/Southern Oscillation (ENSO) with a period of about 4 years. Modeling of the ozone QBO was reviewed in Section 6.2.3. Previous studies using 2-D models (Brasseur and Simon, 1981; Garcia *et al.*, 1984; Callis *et al.*, 1985) provided quantitative estimates for the sensitivity of ozone to long-term variations in solar flux at ultraviolet (UV) wavelengths. Results from four 2-D models containing gas-phase chemistry only that were reported in WMO (1990) indicate that the global ozone content is 2% larger at solar maximum than at solar minimum. Results from models with heterogeneous chemistry are available from several recent studies. Unfortunately, it is difficult to compare the results because each work used different assumptions on the variation of the solar flux. Huang and Brasseur (1993) reported that total ozone at solar maximum is 0.5% smaller at winter high latitudes and 0.5% larger at the tropics compared to the values at solar minimum. Brasseur (1993) reported that total ozone is 1% larger at the tropics and 1.5% larger at high latitudes at solar maximum compared to solar minimum when a 3% change in solar flux between 208-265 nm is assumed. Fleming *et al.* (1994) estimated that annual averaged total ozone between 45°N and 45°S is about

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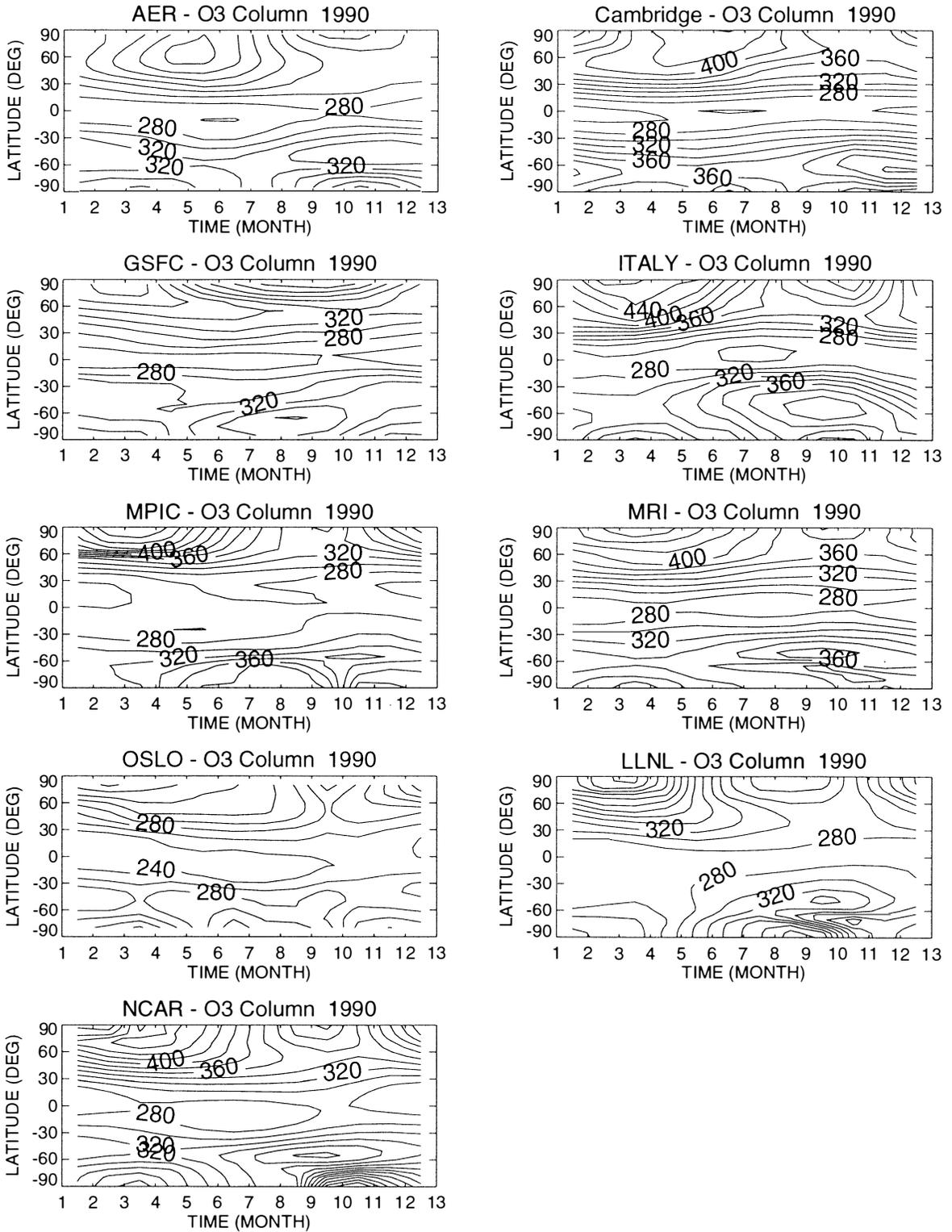


Figure 6-2a. Model-simulated column abundance of ozone for 1990 conditions. The contour levels are in steps of 20 Dobson units.

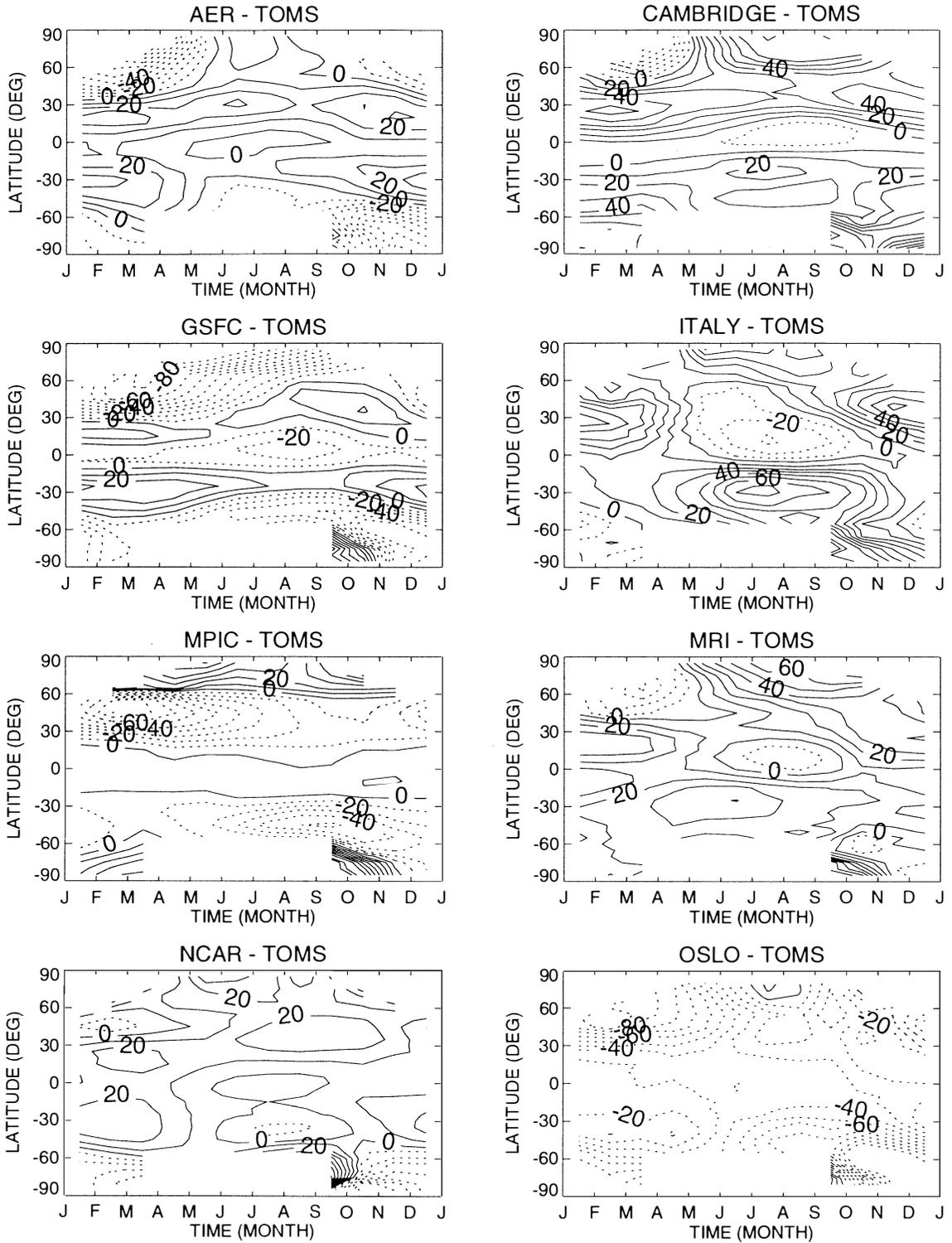


Figure 6-2b. The differences (in Dobson units) between the model-calculated column abundance of ozone for 1980 and the average of the 1979 and 1980 observed column from TOMS. The contour levels are in steps of 10 Dobson units.

Table 6-3. Surface concentrations for halocarbons (pptv), HCFCs (pptv), N₂O (ppbv), and CH₄ (ppbv) for Scenario I.

year	CFC-11	CFC-12	CFC-113	CCl ₄	CH ₃ CCl ₃	CH ₃ Br	H-1301	H-1211	HCFC-22	HCFC-141b	HCFC-142b	HCFC-123	HCFC-124	N ₂ O	CH ₄
1970	59.5	119.8	0.0	85.7	6.5	10.9	0.0	0.1	8.1	0.0	0.0	0.0	0.0	295.0	1420.0
1975	116.1	204.3	10.7	92.0	44.0	11.3	0.1	0.4	30.7	0.0	0.0	0.0	0.0	298.0	1495.0
1980	169.1	286.0	22.1	97.5	93.9	11.9	0.4	0.9	51.1	0.0	0.0	0.0	0.0	302.0	1570.0
1985	216.1	370.6	40.3	102.4	123.1	12.7	1.1	1.7	74.6	0.0	0.0	0.0	0.0	306.0	1650.0
1990	270.1	465.3	70.5	108.2	153.2	13.6	1.7	2.9	105.8	0.3	0.0	0.0	0.2	310.0	1715.0
1995	278.5	502.7	86.0	110.5	148.6	14.5	1.9	3.0	138.5	2.7	3.1	0.2	1.6	313.9	1780.0
2000	257.4	496.9	81.9	98.1	59.1	14.2	1.8	2.4	176.5	10.2	10.3	0.7	4.2	317.8	1845.0
2005	236.2	478.6	77.3	87.1	23.4	14.2	1.7	1.8	214.8	13.8	17.0	1.1	6.9	321.8	1910.0
2010	216.2	457.5	73.0	77.3	9.3	14.2	1.5	1.4	248.2	14.2	21.8	1.6	9.3	325.9	1975.0
2015	197.6	436.3	68.9	68.7	3.7	14.2	1.4	1.1	258.5	14.6	18.7	2.0	9.3	330.0	2040.0
2020	180.4	415.8	64.9	61.0	1.5	14.2	1.3	0.9	263.6	15.0	16.4	1.8	4.2	334.1	2105.0
2025	164.5	396.1	61.3	54.1	0.6	14.2	1.2	0.7	248.1	17.6	14.8	1.6	2.0	338.3	2170.0
2030	149.9	377.2	57.8	48.0	0.2	14.2	1.1	0.5	221.5	21.0	13.8	1.5	1.1	342.6	2235.0
2035	136.5	359.2	54.5	42.6	0.1	14.2	1.0	0.4	152.1	12.3	10.7	0.0	0.5	346.9	2300.0
2040	124.3	342.1	51.4	37.9	0.0	14.2	1.0	0.3	104.4	7.2	8.3	0.0	0.2	351.2	2365.0
2045	113.0	325.7	48.4	33.6	0.0	14.2	0.9	0.3	71.7	4.3	6.4	0.0	0.1	355.6	2430.0
2050	102.8	310.2	45.7	29.8	0.0	14.2	0.8	0.2	49.2	2.5	5.0	0.0	0.0	360.1	2495.0

3.5% larger in 1985 and 1979 (solar maxima) than in 1985 (solar minimum). These values are to be compared with the value of 1.2% derived from the statistical analysis of the Dobson data on ozone and the $F_{10.7}$ solar flux through 1984 (Reinsel *et al.*, 1987), and the 1-2% value cited in Chapter 7 of WMO (1990). A review of the effects of ENSO on ozone can be found in Zerefos *et al.* (1992). Analyses of the observations indicate that there was a 2% ozone decrease in the tropics after the large ENSO event in 1982-1983. No modeling work has been done to simulate the suggested mechanisms to produce the ozone response.

6.3.2.2 MODEL RESULTS

As discussed in the beginning of Section 6.3, the effects of the 11-year solar cycle and QBO are subtracted from the ozone trend using statistical techniques. Here, we compare this remaining trend to the model-calculated trend due to changes in other trace gases. The trends in the surface concentrations of the halocarbons, CH_4 , and N_2O are discussed in Chapter 2 of this report. The modelers were asked to perform a calculation in which the changes in the surface concentrations of the source gases are as given in Table 6-3. With the exception of the CAMBRIDGE model, all models kept the temperature, circulation, and surface area of the sulfate particles constant in the calculation. The CAMBRIDGE model includes dynamics feedback in its calculation.

The model-calculated changes in ozone between 1980 and 1990 are shown in Figure 6-3a. The effect of PSC chemistry is included in the OSLO, NCAR, and MPIC models. The GSFC model results shown correspond to the case without PSC chemistry. Note that most models show a calculated decrease of about 1-2% in the tropics, increasing to 4% at the high latitudes. Compared to the derived trend reported in Stolarski *et al.* (1992), models without PSC chemistry fail to reproduce the following features: the over 6% decrease north of 50°N during March; the 6% decrease south of 40°S throughout the year; and the large decrease in the Antarctic polar vortex. Including PSC chemistry in the model will help to produce some of these features. The OSLO, NCAR and MPIC results all showed decreases of about 7% at northern high latitudes. The calculated decreases for the southern high latitudes range from 7% to 9%. The GSFC model with PSC chemistry shows calculated decreases of about 3% at northern high latitudes

and up to 9% in the south. Figure 6-3b shows the calculated trend as a function of latitude compared to the derived trend between 1980 and 1990. The model results agree well with the derived trend in the tropics. Only models with PSC chemistry calculate the large trend at high latitudes. Around 40° latitudes, the observed ozone trend is between -4% to -8% per decade in winter, and -4% to -6% per decade in spring and fall. These are to be compared with the model-calculated values of -2% to -3% per decade year round. Thus, the model-calculated trends are a factor of 1.3 to 3 smaller than the observed trends, depending on season.

Figure 6-4 shows the calculated percentage change in the local concentration of ozone between 1980 and 1990. The model-calculated ozone trends for the past decade are typically 8% to 12% between 30°N and 50°N at 40 km. These values are too large compared to the trend derived from SAGE I and SAGE II (McCormick *et al.*, 1992) and that derived from the Umkehr data (see WMO, 1992). However, a recent study (Hood *et al.*, 1993) of the SBUV data indicates that the trend may be larger and somewhat closer to the model-calculated trends. As discussed in Section 6.3.1, a smaller trend can be obtained if a branching for production of HCl is assumed for the reaction of OH with ClO (Toumi and Bekki, 1993). The model-calculated trend would also be smaller if the feedback effects from the cooling of the stratosphere due to the ozone decrease were included in the models. This temperature feedback is included in the CAMBRIDGE model only. Calculations from models (Schneider *et al.*, 1993) indicate that the feedback will provide a 20% compensation in the calculated ozone decrease.

Results in Figure 6-4 show that none of the models reproduced the 5% to 10% per decade decrease in ozone in the midlatitude lower stratosphere derived from the SAGE data (McCormick *et al.*, 1992). There are suggestions as to how a larger decrease can be calculated in the models. One suggestion is that the transport parameterizations in the models fail to represent how ozone at high latitudes can affect the midlatitude region. A more realistic representation of the transport may give a larger ozone decrease. Another suggestion is that there may be missing photochemistry. Solomon *et al.* (1994a) showed that if IO is assumed to react with ClO and BrO at sufficiently fast rates, the calculated ozone decrease in the lower stratosphere will be larger.

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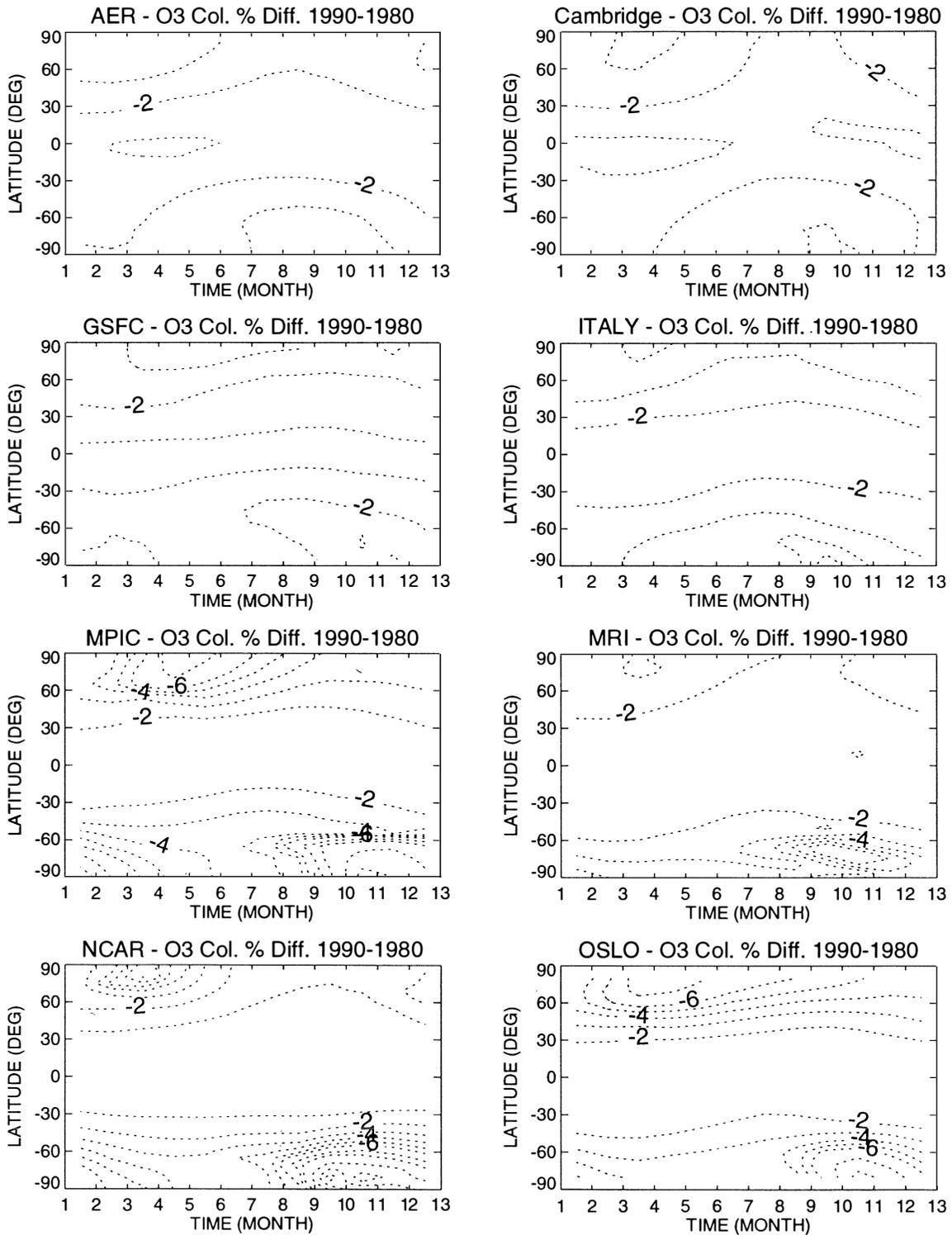


Figure 6-3a. Model-calculated changes in column ozone between 1980 and 1990. The models simulate the effect of chlorine increase with the aerosol kept at the background values. PSC chemistry is excluded except for the OSLO, MPIC, and NCAR models. Contour levels are in 1% steps.

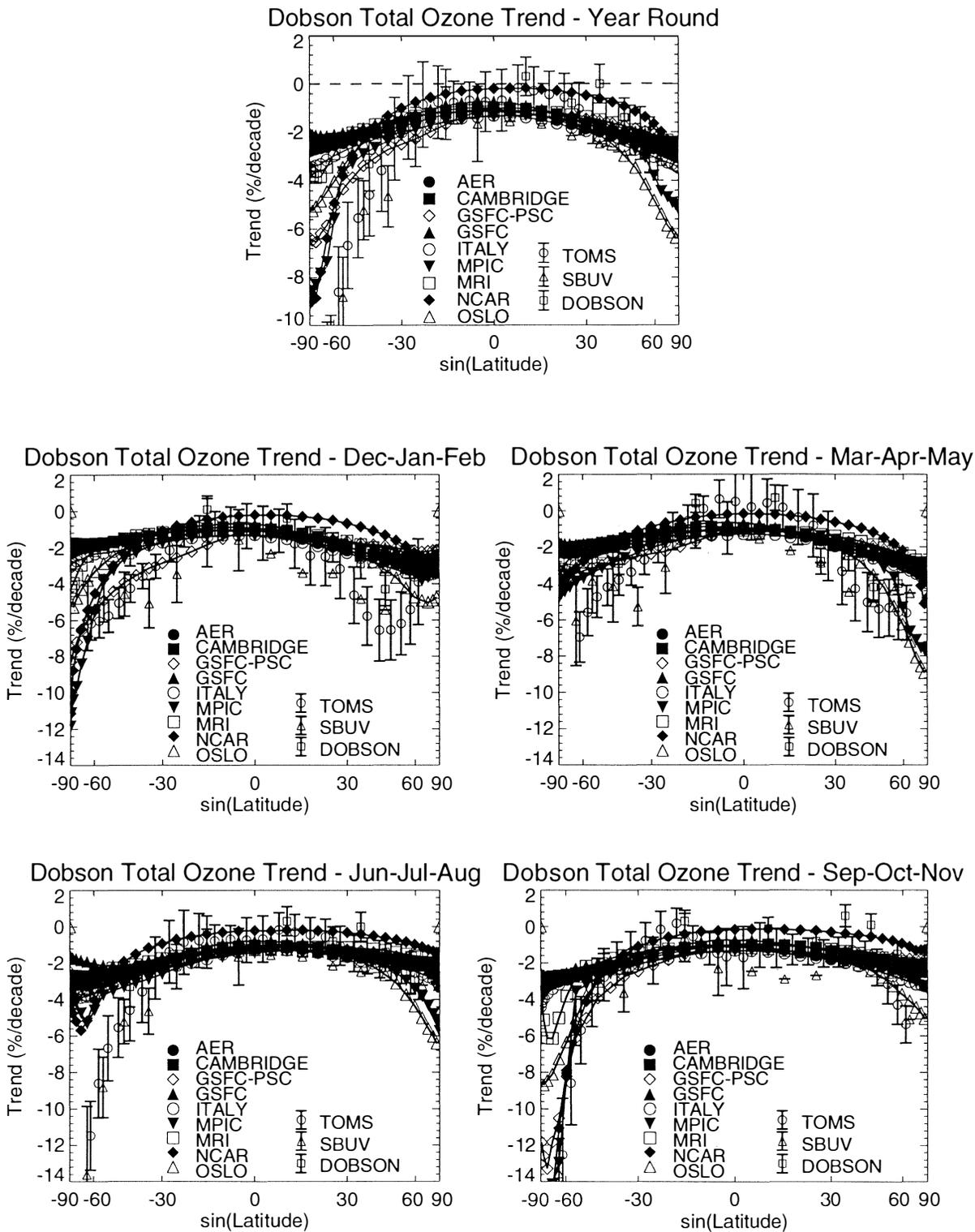


Figure 6-3b. Model-calculated changes in column ozone between 1980 and 1990 compared to derived trends.

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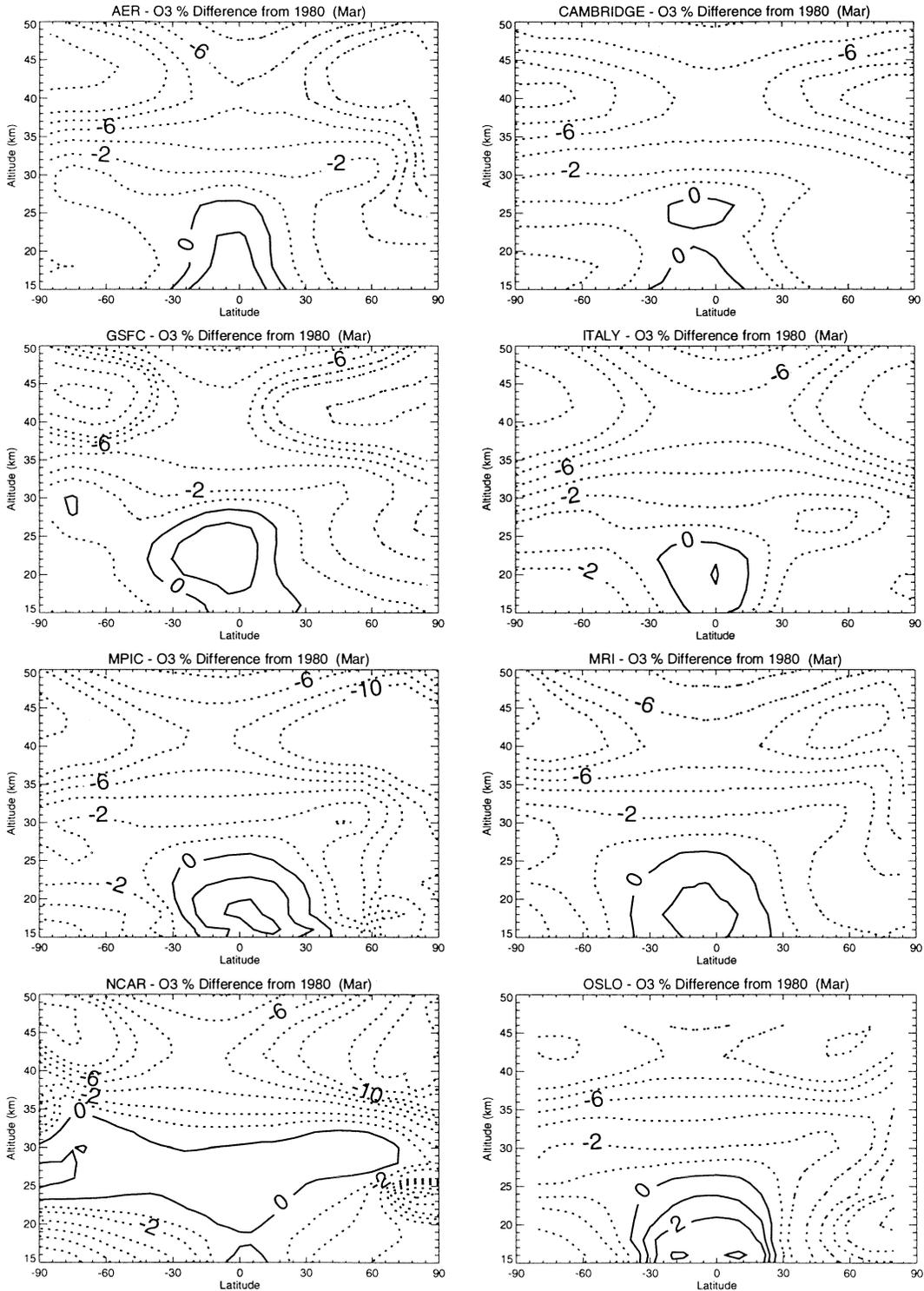


Figure 6-4. Model-calculated local change in ozone between 1980 and 1990 for March condition. PSC chemistry is excluded except for the OSLO, MPIC, and NCAR models. Contour levels are 2%, 1%, 0, -1%, -2%, and -4%, and in steps of 2% thereafter.

6.3.3 Effects of the Mt. Pinatubo Eruption

Volcanic eruptions introduce large amounts of SO₂ into the stratosphere that will be oxidized to form sulfate aerosol. Model simulations (Golombek and Prinn, 1993; Pitari *et al.*, 1993) have shown that the background stratospheric aerosol layer can be explained in terms of the present input of SO₂, and OCS (carbonyl sulfide). However, the lack of detailed knowledge on the microphysics of particle formation precludes a detailed prediction on how the surface area will change.

Prior to the formation of the volcanic aerosol, SO₂ chemistry can affect the photochemical removal rate of ozone in the tropics for the initial months after the eruption (Bekki *et al.*, 1993). The increase of the aerosol surface area available for heterogeneous processes is the most immediate effect of aerosol changes (Hofmann and Solomon, 1989). However, modeling studies (Michelangelo *et al.*, 1989; Brasseur and Granier, 1992; Kinne *et al.*, 1992; Pitari, 1993b; Pitari and Rizi, 1993; Schoeberl *et al.*, 1993) have shown that other effects may be as important. The UV flux is increased substantially above the aerosol layer and may decrease below, thus affecting the photolysis rates. Another effect is related to the heating of the aerosol layer due to the absorption of solar and terrestrial radiation. The additional heat source can modify the dynamics and affect the reaction rates of those catalytic cycles whose reaction rates depend on temperature.

6.3.3.1 RADICAL SPECIES

The effects of the volcanic aerosol on several radical species were reviewed in Chapter 4. The observations and the accompanying modeling studies indicate that the behaviors of the radical species are in qualitative agreement with enhanced processing on the surface of the volcanic aerosols. These include observation of NO_x/NO_y ratios from aircraft (Fahey *et al.*, 1993; Kawa *et al.*, 1993), observation of N₂O₅ and HNO₃ from ATMOS (Rinsland *et al.*, 1994), measurement of ClO from aircraft (Avalone *et al.*, 1993; Wilson *et al.*, 1993), and measurement of ClO, NO, and O₃ (Dessler *et al.*, 1993) and NO₂ and HNO₃ (Webster *et al.*, 1994) from balloons. In addition, there are column measurements of ClONO₂, HCl, and HNO₃ from aircraft (Toon *et al.*, 1993) and ground-based measurements of NO₂ (Johnston *et al.*, 1992; Mills *et al.*, 1993; Coffey and

Mankin, 1993; Koike *et al.*, 1994; Solomon *et al.*, 1994b) and HNO₃ (Koike *et al.*, 1994). Solomon *et al.* (1993) reported that the enhanced level of OClO observed over McMurdo Station during autumn of 1992 is consistent with expected effects from the enhanced conversion of ClONO₂ via reaction (6-2).

6.3.3.2 OZONE BEHAVIOR IN THE TROPICS IN LATE 1991

Using satellite and lidar measurements, Labitzke and McCormick (1992) concluded that the monthly averaged zonal mean 30-mb (24 km) temperatures at 20°N in September and October 1991 are as much as 2.5 K warmer than the 26-year average. Warming in the equatorial region was measured to be as high as 4 K. DeFoor *et al.* (1992) deduced from lidar data that there was a total lift of 1.8 km in the tropics 100 days after the eruption. There are some disagreements on how the eruption has affected ozone because of the difficulty in isolating the effects of the QBO and other mechanisms that cause interannual variations of ozone. Using the Nimbus-7 TOMS and the NOAA-11 satellite Solar Backscatter Ultraviolet/2 (SBUV/2) spectrometer data, Chandra (1993) suggests that the maximum change in column ozone attributed to the Mt. Pinatubo eruption may not be greater than a 2-4% decrease at mid- and low latitudes a few months after the eruption after removing the effect of the QBO. Schoeberl *et al.* (1993) used a different method in analyzing the Nimbus 7 TOMS data and derived a decrease of 5-6% in column ozone between 12°N and 12°S between June and December 1991. Grant *et al.* (1992, 1994) compared the electrochemical concentration cell (ECC) sondes data and the airborne UV Differential Absorption Lidar (DIAL) data to Stratospheric Aerosol and Gas Experiment II (SAGE II) climatology and deduced a column ozone decrease in the tropics of 9% ± 4% in September, 1991.

Bekki *et al.* (1993) investigated the role of gas-phase sulfur photochemistry on ozone in the first month following the eruption. Most other studies did not include this on the assumption that its effect is short-lived. Kinne *et al.* (1992), Brasseur and Granier (1992), Pitari and Rizi (1993), Kinnison *et al.* (1994), and Tie *et al.* (1994) investigated the coupled radiative-dynamical perturbation on ozone following the eruption and provided diagnostics to estimate the contributions from dynamics, radiation, and heterogeneous processing. All models estimated a net increase in heating of about 0.3 to 0.4 K/

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day. However, different approaches were used to determine how this extra heating is to be partitioned into warming or enhanced vertical motion. The studies of Brasseur and Granier (1992), Tie *et al.* (1994), and Pitari and Rizi (1993) used the dynamics equations in their respective models to apportion the heating. The calculated decrease in tropical ozone in late 1991 is 9% in Pitari and Rizi (1993), which results from a 4% decrease from changes in photolysis rate, a 4% decrease from increased heterogeneous processing, and 1% decrease from temperature and circulation changes. The calculated decrease in Tie *et al.* (1994) is 2%, which results from a 2% decrease caused by changes in photolysis rates, a 2% decrease from changes in temperature and circulation, and a 2% increase from changes in heterogeneous processing. The studies of Kinnison *et al.* (1994) provided separate estimates under the assumption that all the heating is dissipated either by local warming or by enhanced upward motion. The calculated decrease is 2% (-1.5% from motion and -0.5% from heterogeneous processing) if it is assumed that the extra heating goes to enhanced upward motion, and 1% (-0.5% from temperature change and -0.5% from heterogeneous processing) if it is assumed that all the heating is balanced by warming. The work of Kinne *et al.* (1992) estimated an uplifting of 1.7 km after accounting for the warming using the observed temperature change. They used a simple 1-D mechanistic model to estimate an ozone decrease of 10%.

6.3.3.3 OZONE BEHAVIOR IN 1992 AND 1993

Gleason *et al.* (1993) reported that during 1992, TOMS on the Nimbus-7 satellite measured global average total ozone to be 1-2% lower than expected if ozone is assumed to be decreasing at the same linear trend in the past decade. These results are consistent with analysis of the TOMS and Meteor 3 data (Herman and Larko, 1994), which showed that the 1993 ozone amount is 12.5% below the historical mean (from 1979) at high latitude, 7% at midlatitude, and 4% at low latitude. Low ozone for the winter of 1992-1993 was also reported from the Microwave Limb Sounder (MLS) instrument on the Upper Atmosphere Research Satellite (UARS) (Froidevaux *et al.*, 1994) and the NOAA-11 SBUV/2 instrument (Planet *et al.*, 1994). Froidevaux *et al.* (1994) also emphasized examining the latitude and height be-

havior of the observed ozone decrease to try to identify the causes for the lower values.

In Pitari and Rizi (1993), the model calculated a decrease in ozone of about 12% at 60°N in March 1992. Diagnostic results showed that this is a combination of a 12% decrease due to heterogeneous chemistry, a 4% decrease due to changes in photolysis rate, and a 4% increase due to changes in transport. In contrast, the additional ozone (about 4%) transported into the region from the strengthening of the mean circulation in the Kinnison *et al.* (1994) study tends to cancel the reduction of ozone due to the increase in heterogeneous conversion rates, producing changes in ozone that do not agree well with observed data. Tie *et al.* (1994) showed that the changes in ozone at northern high latitudes are -10% in spring of 1992 and -8% in spring of 1993. Because so many different mechanisms can change ozone after the eruption, it is difficult to understand the ozone response by comparison of model-simulated ozone with observations alone. Additional diagnostics based on observations are needed to isolate the effects of the different mechanisms.

6.3.3.4 ISOLATING THE EFFECTS OF HETEROGENEOUS PROCESSING

Results from Rodriguez *et al.* (1994) and Kinnison *et al.* (1994) showed that the effects of increased heterogeneous processing from the Mt. Pinatubo aerosol caused an additional 2-5% decrease in ozone at mid- to high latitudes in the winter of 1993. However, the results of Pitari and Rizi (1993) and Granier and Brasseur (1992) indicated that the change in aerosol would lead to a 10% decrease in ozone column due to heterogeneous chemistry alone. It is difficult to compare the model predictions because each model used a different set of parameters to describe the aerosol loading and its decay. In an attempt to see if the model predictions will agree better if the models use uniform input, we prescribed the following set of simulations. The first simulation calculates the behavior of ozone using the surface concentrations for trace gases as prescribed in Table 6-3 while keeping the aerosol surface area at the background value. The second calculation uses the same surface concentrations but assumes the aerosol surface area increases by a factor of 30 in June 1991. The excess surface area is assumed to decay with an exponential

Table 6-4. Mixing ratios for halocarbons (in pptv) for Scenario II.

year	CFC-11	CFC-12	CFC-113	CCl ₄	CH ₃ CCl ₃	CH ₃ Br
1992	281.8	487.6	79.1	110.5	178.1	14.1
1995	290.4	513.7	87.5	113.7	159.3	14.7
2000	284.6	528.6	85.5	118.5	75.8	15.4
2005	278.0	532.4	82.9	122.8	42.5	16.4
2010	264.3	526.9	79.6	117.7	22.0	17.6

time constant of 1 year. The simulation is to include only the effect of enhanced heterogeneous processing. The differences between the ozone in the two simulations (second simulation minus the first) are given in Figure 6-5.

Prather (1992) investigated the potential for a non-linear, catastrophic loss of stratospheric ozone if the aerosol density were greatly increased following a massive eruption. None of the models indicates that such a situation was reached in the Mt. Pinatubo case. Figure 6-5a shows the results for northern midlatitudes, indicating that the effect of enhanced processing is to decrease the ozone. The results fall into three groups: about -3% (AER and LLNL), about -5% (GSFC and MPIC), and about -8% (ITALY and NCAR). The results for the tropics are given in Figure 6-5b. The ozone decrease ranges from less than 0.5% to 2.5%.

It is unclear what the causes are for the differences in the model predictions. Possible explanations include the different treatments used in calculating the concentration of N₂O₅ and the different effects of reaction (6-2) in the models caused by different temperatures being used. The AER model and the LLNL model use an explicit diurnal variation in calculating N₂O₅, while other models use various methods to estimate the N₂O₅ concentration from an averaged sun condition.

6.4 RESULTS FROM SCENARIO CALCULATIONS

For the purpose of a model intercomparison, we have prescribed two scenarios for the source gases. The surface concentrations of the species are specified as functions of time as given in Tables 6-3 and 6-4. Values prior to 1990 are based on available observations. The growth rate for N₂O is based on previous estimates of 0.25% per year. Khalil and Rasmussen (1992) showed

that the actual increase in the past decade has been very variable, ranging from 0.5 ppbv per year to 1.2 ppbv per year. For CH₄, a linear growth rate of 13 ppbv per year is assumed after 1992. Recent observations for CH₄ (Dlugokencky *et al.*, 1994; Khalil and Rasmussen, 1993) indicate that the CH₄ growth rate has slowed to as little as 2 ppbv per year.

The surface concentration for the CH₃Cl is set at 600 pptv. Surface concentrations for the CFCs, HCFCs, halons, and CH₃Br were calculated using a box model with assumed emissions and the reference lifetimes given in Chapter 13. In Scenario I (Table 6-3), the emissions for the halocarbons follow the guidelines in the Amendments to the Montreal Protocol. For CH₃Br, it is assumed that a background of 9 pptv is maintained by natural sources. Emission of anthropogenic CH₃Br assumes a schedule that maintains constant emission at the 1991 level. This, when combined with the natural sources, results in a surface concentration of 14.2 pptv after the year 2000. The substitute HCFCs are a combination of HCFC-22, HCFC-141b, HCFC-142b, HCFC-123, and HCFC-124. The Ozone Depletion Potential (ODP)-weighted annual production is taken to be 3.1% of the ODP-weighted emissions in 1990. In addition to the basic scenario, results are also presented for a second scenario (Table 6-4) where we assume partial compliance with the Protocol for CFC-11, CFC-12, CFC-113, CH₃CCl₃, and CCl₄. The emission for CH₃Br is also assumed to be larger, resulting in a surface concentration of 17.6 pptv in 2010. The Scenario II calculation extends only to 2010.

6.4.1 Chlorine and Bromine Loading

Figure 6-6a shows the model-calculated chlorine concentrations for 58 km at 50°N. The observed concentrations of HCl from the ATMOS instrument for 1985 (Zander *et al.*, 1990) and 1992 (Gunson *et al.*, 1994) are

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Ozone Column Monthly % Difference

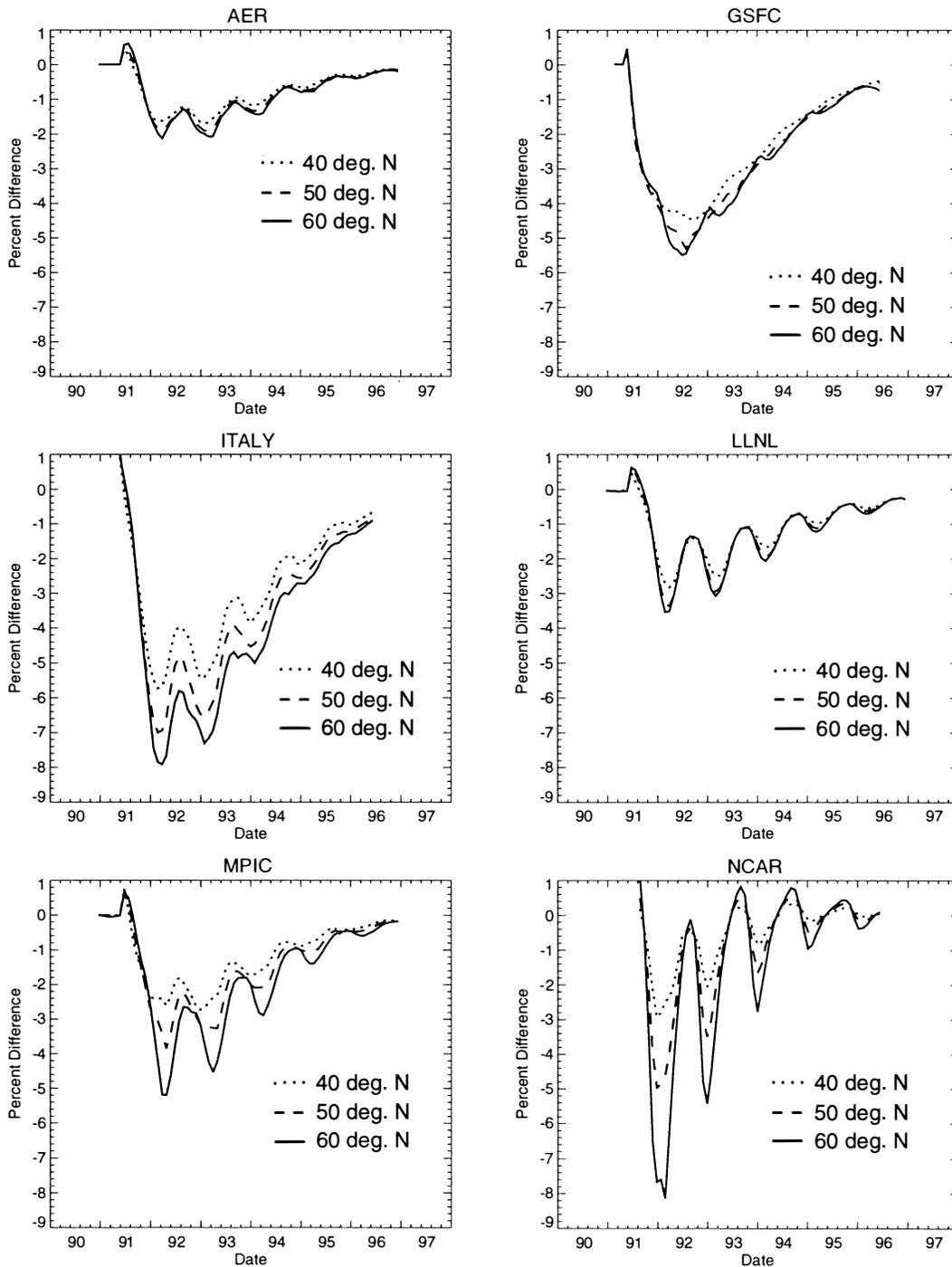


Figure 6-5a. Calculated percent change in ozone column at 40°N, 50°N, and 60°N for a thirty-fold increase in surface area. The values are obtained by comparing the column calculated using fixed background aerosol with the column calculated where there is a 30-fold increase in aerosol surface area in June 1991 with the excess aerosol decaying with a time constant of 1 year.

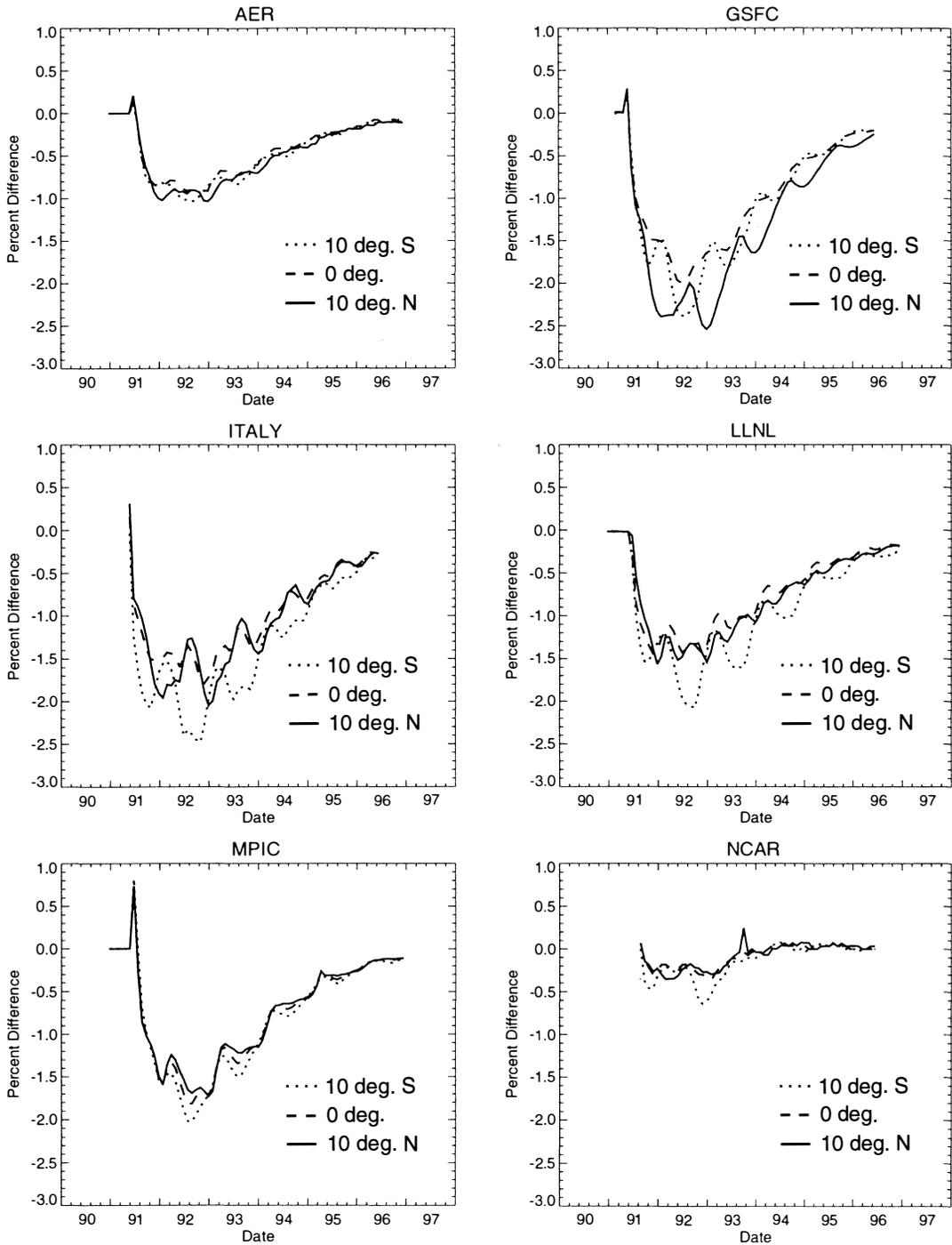


Figure 6-5b. Same as Figure 6-5a except for 10°S, Equator, and 10°N.

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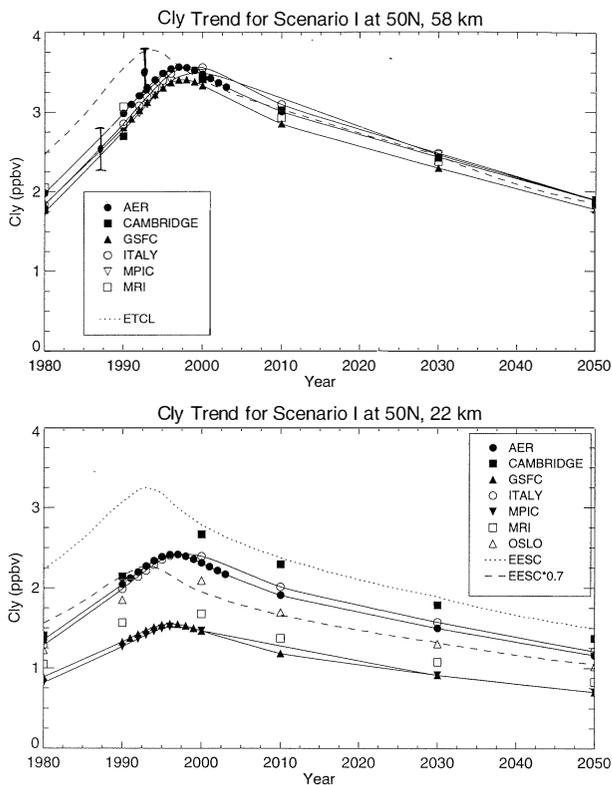


Figure 6-6a. Upper panel: Model-calculated concentration for chlorine for Scenario I at 58 km, 50°N for March. The ETCL is the mixing ratio of the chlorine atoms bound in the source gases at the surface. It is calculated using the boundary values given in Table 6-3. The measured value of HCl (∇) from the ATMOS instrument for the 1985 SL-3 mission (Zander *et al.*, 1990) and the 1992 ATLAS-1 mission (Gunson, *et al.*, 1994) are shown for comparison.

Figure 6-6b. Lower panel: Model-calculated concentration for chlorine for Scenario I at 22 km, 50°N for March. The EESC curves are calculated using the boundary values of the chlorine source gases. It corresponds to the mixing ratio of the chlorine atoms bound in the sources gases and weighted by the ODP of the source gas. The second curve is multiplied by 0.7, which is the fraction of CFC-11 dissociated at that altitude.

included in the figure for comparison. Also included in the graph is the curve labeled the equivalent tropospheric chlorine loading (ETCL), which is defined as the sum of the mixing ratios of the chlorine atoms in the source molecules at the ground. The model-calculated Cl_y concentrations can be compared with the ETCL curve after allowing for the time lag to transport the source gases to the stratosphere and the redistribution of the radical species. With the prescribed surface concentrations of the halocarbons given in Table 6-3, the ETCL reaches a maximum in 1994. The calculated chlorine concentration reaches the maximum around the year 1998.

The model-calculated Cl_y concentrations at 22 km are shown in Figure 6-6b. Estimates for the chlorine concentrations at 20 km between 60°N and 80°N based on measured concentrations of the organic chlorine species range from 1 to 2 ppbv for outside and inside the vortex, respectively (Kawa *et al.*, 1992). The observed value inside the vortex should be more representative of the concentration at 22 km because of the occurrence of diabatic descent in the vortex. The EESC (equivalent effective stratospheric chlorine) curve is defined by the sum of the mixing ratios of the chlorine atoms in the source molecules at the ground, weighted by the respective ODPs. It corresponds to the chlorine loading values used in Chapter 13 of this report. It can be compared with the chlorine concentration in the lower stratosphere. One of the curves in Figure 6-6b is obtained by multiplying the EESC values by 0.7, approximately the fraction of CFC-11 dissociated at 22 km and 50°N. The calculated Cl_y concentrations at 22 km among the models differ by about 1 ppbv. The models that calculate smaller concentrations of Cl_y also calculate smaller concentrations of ozone. This is probably related to the position of the tropopause and the strength of the circulation in the models.

The time behavior of the ETCL and EESC curves agrees well with the model-calculated curve except that the calculated concentration in the lower stratosphere lags the EESC curve by 3-4 years and the calculated concentration in the upper stratosphere lags the ETCL curve by 4-5 years.

The calculated bromine concentrations are shown in Figure 6-7. The curve representing the equivalent tropospheric bromine loading (ETBL) is included in Figure 6-7a. As in the case of the model-calculated Cl_y, the

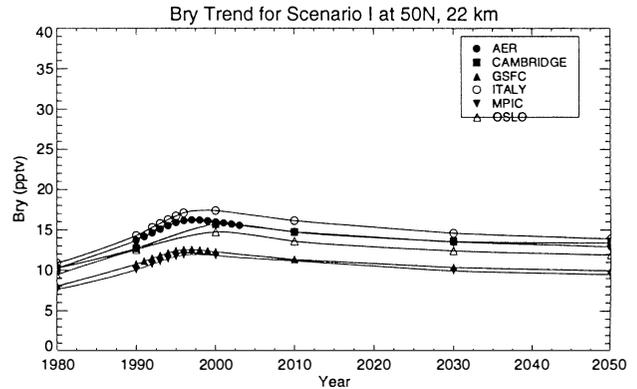
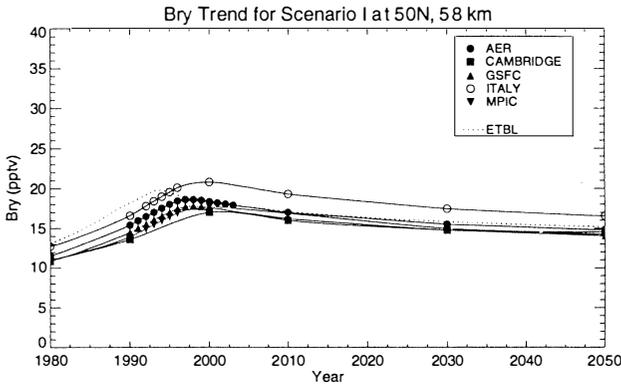


Figure 6-7a. Model-calculated bromine concentration for Scenario I at 58km 50°N for March. The ETBL is the mixing ratio of the bromine atoms bound in the source gases at the surface. It is calculated using the boundary values given in Table 6-3.

Figure 6-7b. Model-calculated bromine concentration for Scenario I at 22km 50°N for March.

model-calculated Br_y values in the lower stratosphere separate into the same two groups.

A comparison of the chlorine loading and bromine loading between Scenarios I and II is shown in Figures 6-8 and 6-9, respectively, for the AER and GSFC models. At 2010, the calculated concentrations of chlorine and bromine in the lower stratosphere for Scenario II are larger than those calculated for Scenario I by 200 pptv and 2 pptv, respectively.

6.4.2 Calculated Ozone Trend

Figure 6-10 shows the calculated trends for column ozone between 1980 and 2050 for Scenarios I and II. Note that the calculated ozone columns in 1980 are quite different among the models, ranging from 380 Dobson units to 470 DU at 60°N; and 300 DU to 420 DU at 40°N. The calculated percent change relative to 1980 is plotted in Figure 6-11. The maximum decrease of about 6% to 9% is calculated around the year 2000. Larger decreases are calculated by the OSLO and MPIC models, which include PSC chemistry. The extra Cl_y and Br_y in Scenario II cause an extra 1.5% decrease in ozone at high latitudes for the AER and GSFC models, which do not include PSC chemistry. The MPIC and OSLO models, which include PSC chemistry, calculate an additional 3% decrease in ozone at 60°N in March.

The models also show different results in the rate of recovery. Figure 6-12 shows the model-calculated ozone behavior for 50°N. The CAMBRIDGE, GSFC, and MRI models reach the 1980 ozone values before

2030, while the other models show a much slower recovery. Additional calculations were performed to check the sensitivity of the ozone response to changes in N_2O , CH_4 , and aerosol surface area. With the chlorine concentration fixed at the 2050 level, approximately 2 ppbv, calculations were performed to determine how the model-calculated ozone will change under the assumptions listed in Table 6-5. All the models agree that a decrease in CH_4 would produce a decrease in column ozone. The GSFC model and the LLNL model are more sensitive to changes in CH_4 . All the models agree that a decrease in N_2O would produce an increase in column ozone. A doubling of aerosol surface area in 2050 has an effect ranging from neutral to a slight increase in column ozone. The models do not agree on the sign of the ozone column change when these perturbations are combined.

6.4.3 Effects from Greenhouse Gases

In Section 6.3.2.2, we discussed dynamics feedback as a negative feedback in the upper stratosphere, *i.e.*, including the effect of stratospheric cooling would modulate the model-calculated ozone decrease by a factor of 0.8. However, the effect on the lower stratosphere is less certain, where a cooler temperature may promote formation of PSCs, leading to additional ozone decrease. Here, we discuss the effect from other greenhouse gases. Global increases in the greenhouse gases (particularly CO_2) due to anthropogenic emissions are expected to influence the Earth's climate. The first-order effect is expected to be a warming of the surface/troposphere sys-

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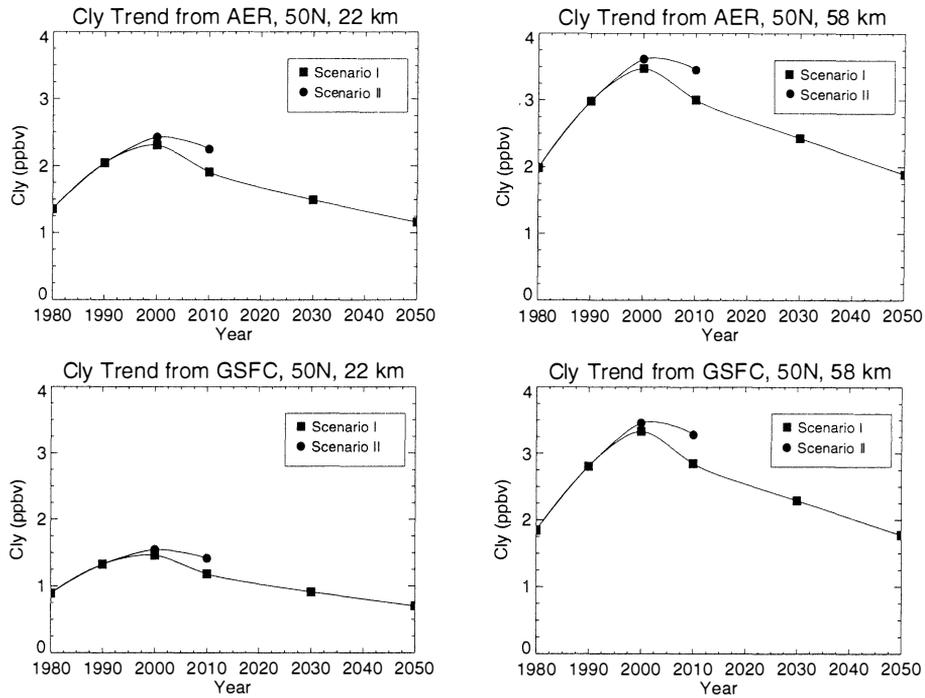


Figure 6-8. Model-calculated chlorine loading for Scenarios I and II.

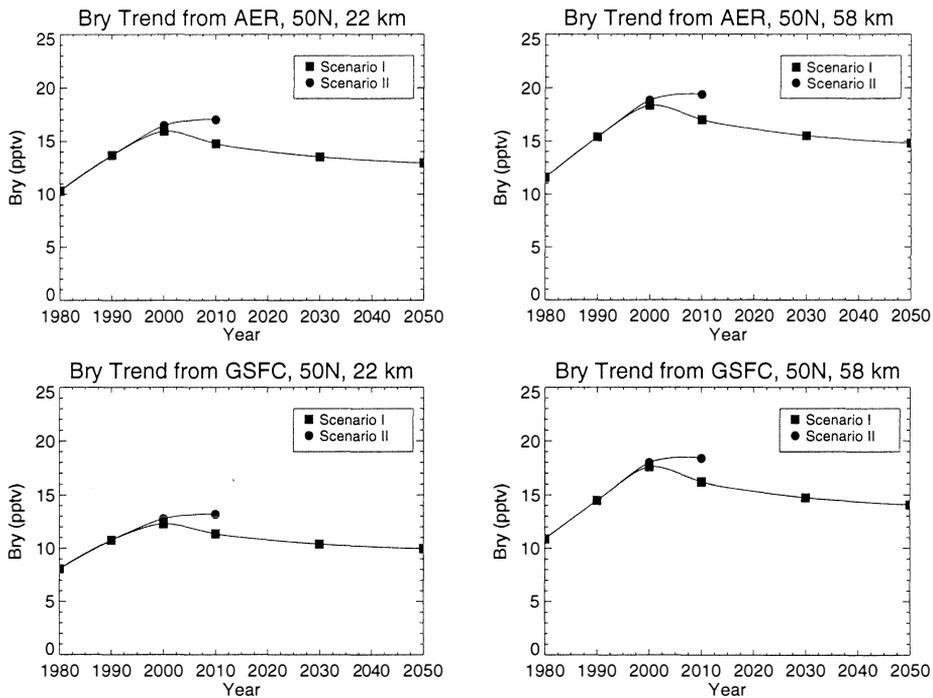


Figure 6-9. Model-calculated bromine loading for Scenarios I and II.

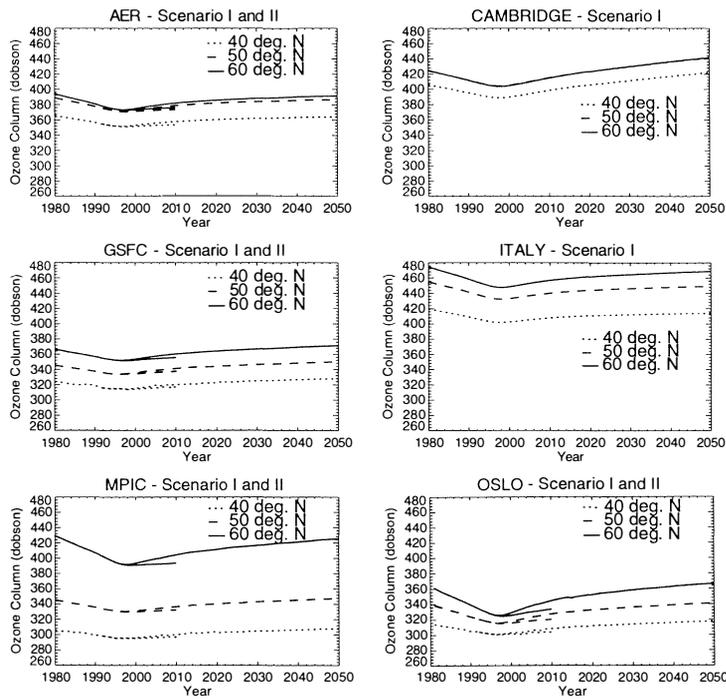


Figure 6-10. Model-calculated ozone trend for March for Scenarios I and II.

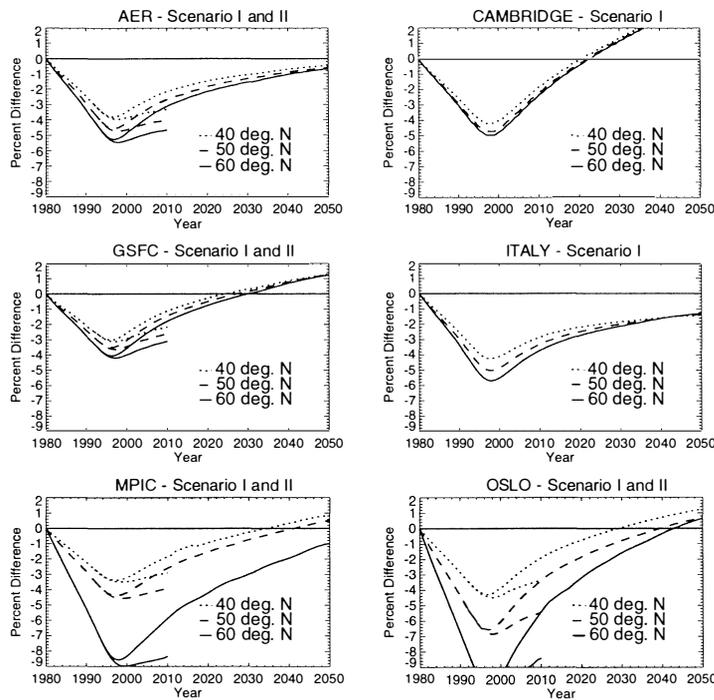


Figure 6-11. Model-calculated percent change in ozone for March for Scenarios I and II.

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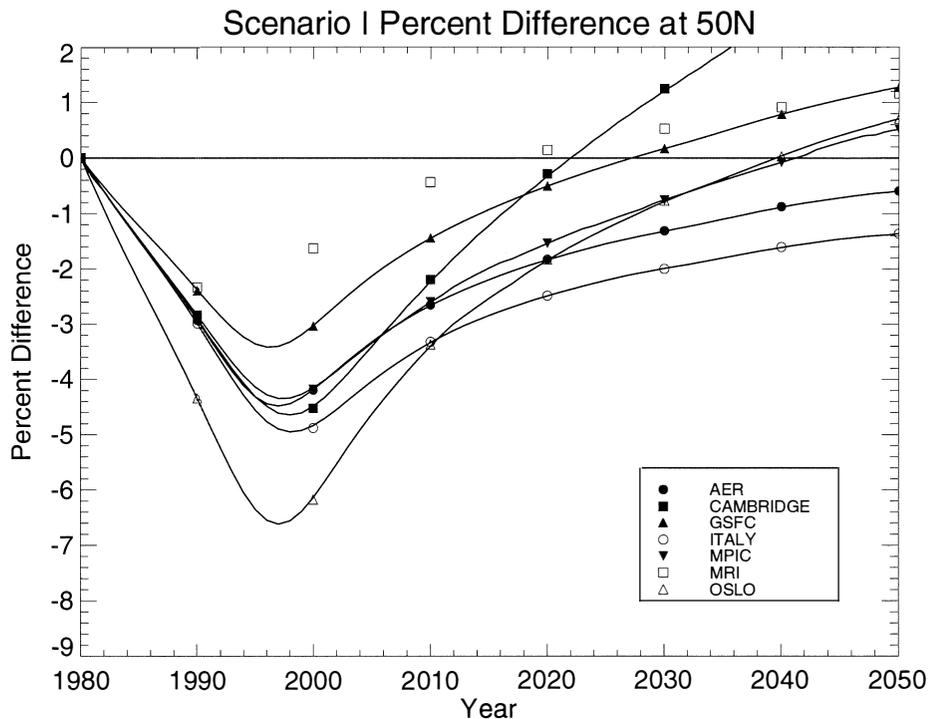


Figure 6-12. Model-calculated percent change in ozone for March at 50°N for Scenario I. The results from MRI are derived from steady-state calculations using the boundary conditions appropriate for the years.

tem and cooling of the middle atmosphere. Ozone is a primary absorber of solar radiation, warming the middle atmosphere and reducing the solar radiation reaching the surface. It is also a greenhouse gas, and thus acts to warm the surface/troposphere system. Studies (Ramswamy *et al.*, 1992; Wang *et al.*, 1993) have shown that the latitudinal distribution of the total greenhouse warming effect due to CO₂, CH₄, N₂O, and CFCs decreases more sharply at mid- and high latitudes when the observed changes in the ozone distribution were considered.

Using results from a GCM, Rind *et al.* (1990) found that both the vertical and latitudinal structure of the temperature change following a doubling of CO₂ results in increases in the propagation of planetary waves into the stratosphere, and increased potential energy in the lower stratosphere. These processes generated an increase in the eddy energy in the middle atmosphere with an attendant increase in wave forcing and residual circulation, tending to warm high latitudes. This change in the transport circulation should affect the ozone distribution and, consequently, the thermal forcing of the

atmosphere. This effect on ozone was not included in the Rind *et al.* (1990) calculation but was acknowledged to be of potential importance. Austin *et al.* (1992) used a middle atmosphere GCM, which included a relatively comprehensive ozone photochemistry that was radiatively interactive, in a CO₂ doubling scenario. The model was found to respond very differently to the CO₂ doubling when fully interactive ozone was included, particularly with respect to the occurrence of a stratospheric warming. They also found a much larger ozone response to CO₂ doubling, with reductions in ozone by as much as 150 Dobson units during Arctic spring. In contrast, Pitari *et al.* (1992) found only a 10 Dobson unit reduction in column ozone amounts during the Northern Hemisphere spring minimum.

In addition to these changes in the middle atmosphere circulation, theoretical results (*e.g.*, Geller and Alpert, 1980) and modeling studies (*e.g.*, Hansen *et al.*, 1983; Boville, 1984) demonstrated a troposphere response to perturbations in the stratospheric dynamics. Both the stationary and transient components of tropospheric wave structures can be modulated by the

Table 6-5. Sensitivity studies illustrating the model-calculated ozone responses.

	N ₂ O ppbv	CH ₄ ppmv	aerosol	percent change in ozone column March 50°N			
				AER	GSFC	Italy	LLNL
2050 baseline	360	2.5	clean	-	-	-	-
A	360	1.8	clean	-0.48	-1.02	-0.18	-1.16
B	318	2.5	clean	1.38	0.89	1.34	1.41
C	360	2.5	2x	0.84	0.16	0.32	0.87
D	318	1.8	2x	1.51	-0.25	1.09	0.92

stratospheric circulation. Kodera *et al.* (1991) demonstrated that anomalies, initially created in the stratosphere, can propagate into the troposphere through wave-mean flow interactions. Kodera (1993) has shown that many of the changes in zonal mean winds first occur in the stratosphere, and then propagate into the troposphere, causing changes in the tropospheric subtropical jet. Because the troposphere is the fundamental source of wave energy for the middle atmosphere, these studies suggest that it is important to begin to study the complex feedback taking place between the stratosphere and troposphere through temperature and wave effects. It is unclear at this point whether 2-D models that calculate explicit wave forcing (Kinnersley and Harwood, 1993; Garcia and Solomon, 1994) can address some of these issues, or if one has to rely exclusively on GCMs.

6.5 CONCLUSIONS

Comparison of the model results indicates that although there are significant differences among the model-calculated local photochemical rates and transport rates, the rates from each individual model combine to produce reasonable present-day ozone distributions and the 1980-to-1990 ozone trend. However, as the atmosphere is perturbed farther away from its present state (*e.g.*, large increase in aerosol loading, changes due to long-term trends of N₂O, CH₄, and halocarbons), the model-predicted responses differ by larger amounts.

As shown in Figures 6-10 and 6-11, the differences in the model-predicted ozone responses are much smaller when considered on a percentage basis relative to each model's own baseline for 1980. This relative response is useful in assessing the relative impact among

different halocarbons and their substitute compounds and the merits of different emission scenarios. However, if we are to concern ourselves with understanding the response of ozone to all perturbations, it is important to understand the absolute response as well.

Confidence in model predictions is currently limited by the following factors:

- the need to validate the model-calculated local production and removal rates of ozone;
- the need to validate the model-simulated large-scale transport in the lower stratosphere;
- the ability to parameterize PSC chemistry and its effect on global ozone;
- the capability to consider temperature and dynamics feedback on ozone responses to perturbations.

REFERENCES

- Albritton, D.L., *et al.*, *The Atmospheric Effects of Stratospheric Aircraft: Interim Assessment Report of the NASA High-Speed Research Program*, prepared for The Panel on Atmospheric Effects of Stratospheric Aircraft, Committee on Atmospheric Chemistry, Board on Atmospheric Sciences and Climate, National Research Council, NASA Reference Publication 1333, June 1993.
- Austin, J., N. Butchart, and K.P. Shine, Possibility of an Arctic ozone hole in a doubled-CO₂ climate, *Nature*, 360, 221-225, 1992.
- Avallone, L.M., D.W. Toohey, M.H. Proffitt, J.J. Margitan, K.R. Chan, and J.G. Anderson, In situ measurements of ClO at mid-latitudes: Is there an effect from Mt. Pinatubo?, *Geophys. Res. Lett.*, 20, 2519-2522, 1993.

STRATOSPHERIC MODELS

- Bekki, S., and J.A. Pyle, Two-dimensional assessment of the impact of aircraft sulfur emissions on the stratospheric sulfate aerosol layer, *J. Geophys. Res.*, *97*, 15839-15847, 1992.
- Bekki, S., R. Toumi, and J.A. Pyle, Role of sulfur photochemistry in tropical ozone changes after the eruption of Mount Pinatubo, *Nature*, *362*, 331-333, 1993.
- Bojkov, R.D., The 1983 and 1985 anomalies in ozone distribution in perspective, *Mon. Wea. Rev.*, *115*, 2187-2201, 1987.
- Boville, B.A., The influence of the polar night jet on the tropospheric circulation in a GCM, *J. Atmos. Sci.*, *41*, 1132-1142, 1984.
- Brasseur, G., The response of the middle atmosphere to long-term and short-term solar variability: A two-dimensional model, *J. Geophys. Res.*, *98*, 23079-23090, 1993.
- Brasseur, G., and P.C. Simon, Stratospheric chemical and thermal response to long-term variability in solar UV irradiance, *J. Geophys. Res.*, *86*, 7343-7362, 1981.
- Brasseur, G., M.H. Hitchman, S. Walters, M. Dymek, E. Falise, and M. Pirre, An interactive chemical-dynamical radiative two-dimensional model of the middle atmosphere, *J. Geophys. Res.*, *95*, 5639-5655, 1990.
- Brasseur, G.P., and C. Granier, Mount Pinatubo aerosols, chlorofluorocarbons, and ozone depletion, *Science*, *257*, 1239-1242, 1992.
- Callis, L.B., J.C. Alpert, and M.A. Geller, An assessment of thermal, wind and planetary wave changes in the middle and lower atmosphere due to 11-year UV-flux variation, *J. Geophys. Res.*, *90*, 2237-2282, 1985.
- Callis, L.B., *et al.*, Precipitating relativistic electrons: Their long-term effect on stratospheric odd nitrogen levels, *J. Geophys. Res.*, *96*, 2939-2976, 1991.
- Cariolle, D., A. Lasserre-Bigorry, J.-F. Royer, and J.-F. Geleyn, A general circulation model simulation of the springtime Antarctic ozone decrease and its impact on mid-latitudes, *J. Geophys. Res.*, *95*, 1883-1898, 1990.
- Chandra, S., Changes in stratospheric ozone and temperature after the eruption of Mt. Pinatubo, *Geophys. Res. Lett.*, *20*, 33-36, 1993.
- Chandra, S., C.H. Jackman, A.R. Douglass, E.I. Fleming, and D.B. Considine, Chlorine catalyzed destruction of ozone: Implications for ozone variability in the upper stratosphere, *Geophys. Res. Lett.*, *20*, 351-354, 1993.
- Chipperfield, M.P., and J.A. Pyle, Two-dimensional modeling of the Antarctic lower stratosphere, *Geophys. Res. Lett.*, *15*, 875-878, 1988.
- Chipperfield, M.P., D. Cariolle, P. Simon, R. Ramorosan, and D.J. Lary, A three-dimensional modeling study of trace species in the Arctic lower stratosphere during winter 1989-1990, *J. Geophys. Res.*, *98*, 7199-7218, 1993.
- CIAP Monograph 3, *The Stratosphere Perturbed by Propulsion Effluents*, DOT-TST-75-53, U.S. Department of Transportation, Washington, D.C., 1975.
- Coffey M.T., and W.G. Mankin, Observations of the loss of stratospheric NO₂ following volcanic eruptions, *Geophys. Res. Lett.*, *20*, 2873-2876, 1993.
- Considine, D.B., A.R. Douglass, and C.H. Jackman, Effects of a PSC parameterization on ozone depletion due to stratospheric aircraft in a 2D model, *J. Geophys. Res.*, *99*, 18879-18894, 1994.
- Crutzen, P.J., The influence of nitrogen oxides on the atmospheric ozone content, *Quart. J. Roy. Meteorol. Soc.*, *96*, 320-325, 1970.
- DeFoor, T.E., E. Robinson, and S. Ryan, Early lidar observations of the June 1991 Pinatubo eruption plume at Mauna Loa Observatory, Hawaii, *Geophys. Res. Lett.*, *19*, 187-190, 1992.
- Dessler, A.E., *et al.*, Balloonborne measurements of ClO, NO and O₃ in volcanic cloud: An analysis of heterogeneous chemistry between 20 and 30 km, *Geophys. Res. Lett.*, *20*, 2527-2530, 1993.
- Dlugokencky, E.J., K.A. Masarie, P.M. Lang, P.P. Tans, L.P. Steele, and E.G. Nisbet, A dramatic decrease in the growth rate of atmospheric methane in the northern hemisphere during 1992, *Geophys. Res. Lett.*, *21*, 43-48, 1994.
- Douglass, A.R., R.B. Rood, J.A. Kaye, R.S. Stolarski, D.J. Allen, and E.M. Larsen, The influence of polar stratospheric heterogeneous processes on reactive chlorine at mid-latitudes: Three-dimensional model implications, *Geophys. Res. Lett.*, *18*, 25-28, 1991.

- Eluszkiewicz J., and M. Allen, Global analysis of the ozone deficit, *J. Geophys. Res.*, *98*, 1069-1082, 1993.
- Fahey, D.W., *et al.*, In situ measurements constraining the role of sulphate aerosols in mid-latitude ozone depletion, *Nature*, *363*, 509-514, 1993.
- Fleming, E.L., S. Chandra, C.H. Jackman, D.B. Considine, and A.R. Douglass, The middle atmospheric response to short and long term solar UV variations: Analysis of observations and 2D model results, *J. Atmos. and Terrestrial Phys.*, in press, 1994.
- Foley, H.M., and M.A. Ruderman, Stratospheric NO production from past nuclear explosions, *J. Geophys. Res.*, *78*, 4441-4450, 1973.
- Fried, A., B.E. Henry, J.G. Calvert, and M. Mozurkewich, The reaction probability of N₂O₅ with sulfuric acid aerosols at stratospheric temperatures and compositions, *J. Geophys. Res.*, *99*, 3517-3532, 1994.
- Froidevaux, L., J.W. Waters, W.G. Read, L.S. Elson, D.A. Flower, and R.F. Jarnot, Global ozone observations from UARS MLS: An overview of zonal mean results, *J. Atmos. Sci.*, in press, 1994.
- Garcia, R.R., and S. Solomon, A numerical model of the zonally averaged dynamical and chemical structure of the middle atmosphere, *J. Geophys. Res.*, *88*, 1379-1400, 1983.
- Garcia, R.R., S. Solomon, R.G. Roble, and D.W. Rusch, A numerical response of the middle atmosphere to the 11-year solar cycle, *Planet. Space Sci.*, *32*, 411-423, 1984.
- Garcia, R.R., F. Stordal, S. Solomon, and J.F. Kiehl, A new numerical model of the middle atmosphere 1. Dynamics and transport of tropospheric source gases, *J. Geophys. Res.*, *97*, 12967-12991, 1992.
- Garcia, R.R., and S. Solomon, A new numerical model of the middle atmosphere 2. Ozone and related species, *J. Geophys. Res.*, *99*, 12937-12951, 1994.
- Geller, M.A., and J.C. Alpert, Planetary wave coupling between the troposphere and the middle atmosphere as a possible sun-weather mechanism, *J. Atmos. Sci.*, *37*, 1197-1215, 1980.
- Gleason, J.F., *et al.*, Record low global ozone in 1992, *Science*, *260*, 523-526, 1993.
- Golombek, A., and R.G. Prinn, A global 3-D model of the stratospheric acid layer, *J. Atmos. Chem.*, *16*, 179-199, 1993.
- Granier, C., and G. Brasseur, Ozone and other trace gases in the Arctic and Antarctic regions: Three-dimensional model simulations, *J. Geophys. Res.*, *96*, 2995-3011, 1991.
- Granier, C., and G. Brasseur, Impact of heterogeneous chemistry on model predictions of ozone changes, *J. Geophys. Res.*, *97*, 18015-10833, 1992.
- Grant, W.B., *et al.*, Observations of reduced ozone concentrations in the tropical stratosphere after the eruption of Mt. Pinatubo, *Geophys. Res. Lett.*, *19*, 1109-1112, 1992.
- Grant, W.B., *et al.*, Aerosol-associated changes in tropical stratospheric ozone following the eruption of Mt. Pinatubo, *J. Geophys. Res.*, *99*, 8197-8211, 1994.
- Gray, L.J., and J.A. Pyle, A two-dimensional mean circulation model of the quasi-biennial oscillation of ozone, *J. Atmos. Sci.*, *46*, 203-220, 1989.
- Gray, L.J., and T.J. Dunkerton, The role of the seasonal cycle in the quasi-biennial oscillation of ozone, *J. Atmos. Sci.*, *47*, 2429-2451, 1990.
- Gray, L.J., and S. Ruth, The modeled latitudinal distribution of the ozone quasi-biennial oscillation using observed equatorial winds, *J. Atmos. Sci.*, *50*, 1033-1046, 1993.
- Grooss, J.U., T. Peter, C. Brühl, and P.J. Crutzen, The influence of high flying aircraft on polar heterogeneous chemistry, in *Impact of Emissions from Aircraft and Spacecraft upon the Atmosphere: Proceedings of an International Scientific Colloquium*, edited by U. Schumann and D. Wurzel, DLR-Mitteilung 94-06, 229-234, 1994.
- Gunson, M.R., *et al.*, Increase in levels of stratospheric chlorine and fluorine loading between 1985 and 1992, *Geophys. Res. Lett.*, *21*, 2223-2226, 1994.
- Hansen, J.G., *et al.*, Efficient three-dimensional global models for climate studies: Models I and II, *Mon. Wea. Rev.*, *111*, 609-662, 1983.
- Hanson, D., and K. Mauersberger, Solubility and equilibrium vapor pressures of HCl dissolved in polar stratospheric cloud material: Ice and the trihydrate of nitric acid, *Geophys. Res. Lett.*, *15*, 1507-1510, 1988.

STRATOSPHERIC MODELS

- Hanson, D.R., A.R. Ravishankara, and S. Solomon, Heterogeneous reactions in sulfuric acid aerosol: A framework for model calculations, *J. Geophys. Res.*, *99*, 3615-3629, 1994.
- Harwood, R.S., and J.A. Pyle, A two-dimensional mean circulation model for the atmosphere below 80 km, *Quart. J. Roy. Meteorol. Soc.*, *101*, 723-748, 1975.
- Herman, J.R., and D. Larko, Low ozone amounts during 1992-1993 from Nimbus 7 and Meteor 3 total ozone mapping spectrometers, *J. Geophys. Res.*, *99*, 3483-3496, 1994.
- Hofmann, D.J., Aircraft sulphur emissions, *Nature*, *349*, 659, 1991.
- Hofmann, D.J., and S. Solomon, Ozone destruction through heterogeneous chemistry following the eruption of El Chichón, *J. Geophys. Res.*, *94*, 5029-5041, 1989.
- Holton, J.R., On the global exchange of mass between the stratosphere and troposphere, *J. Atmos. Sci.*, *47*, 392-395, 1990.
- Hood, L.L., R.D. McPeters, J.P. McCormick, L.E. Flynn, S.M. Hollandsworth, and J.F. Gleason, Altitude dependence of stratospheric ozone trends based on Nimbus 7 SBUV data, *Geophys. Res. Lett.*, *20*, 2667-2670, 1993.
- Hou, A.Y., H.R. Schneider, and M.K.W. Ko, A dynamical explanation for the asymmetry in zonally-averaged column abundances of ozone between northern and southern springs, *J. Atmos. Sci.*, *48*, 547-556, 1991.
- Huang, T.Y.W., and G. Brasseur, The effect of long-term solar variability in a two-dimensional interactive model of the middle atmosphere, *J. Geophys. Res.*, *98*, 20413-20427, 1993.
- Isaksen, I.S.A., B. Rognerud, F. Stordal, M.T. Coffey, and W.G. Mankin, Studies of Arctic stratospheric ozone in a 2-D model including some effects of zonal asymmetries, *Geophys. Res. Lett.*, *17*, 557-560, 1990.
- Jackman, C.H., Energetic particle influences on NO_y and ozone in the middle atmosphere, *Geophysical Monograph* 75, IUGG vol. 15, 131-139, 1993.
- Jackman, C.H., J.E. Frederick, and R.S. Stolarski, Production of odd nitrogen in the stratosphere and mesosphere: An intercomparison of source strengths, *J. Geophys. Res.*, *85*, 7495-7505, 1980.
- Jackman, C.H., A.R. Douglass, P.D. Guthrie, and R.S. Stolarski, The sensitivity of total ozone and ozone perturbation scenarios in a two-dimensional model due to dynamical inputs, *J. Geophys. Res.*, *94*, 9873-9887, 1989.
- Jackman, C.H., A.R. Douglass, R.B. Rood, R.D. McPeters, and P.E. Meade, Effect of solar proton events on the middle atmosphere during the past two solar cycles as computed using a two-dimensional model, *J. Geophys. Res.*, *96*, 7417-7428, 1990.
- Jackman, C.H., A.R. Douglass, S. Chandra, R.S. Stolarski, J.E. Rosenfield, and J.A. Kaye, Impact of interannual variability (1979-1986) of transport and temperature on ozone as computed using a two-dimensional photochemical model, *J. Geophys. Res.*, *96*, 5073-5079, 1991.
- Johnston, H., G. Whitten, and J. Birks, Effect of nuclear explosions on stratospheric nitric oxide and ozone, *J. Geophys. Res.*, *78*, 6107-6135, 1973.
- Johnston, P.V., R.L. McKenzie, J.G. Keys, and W.A. Matthews, Observations of depleted stratospheric NO₂ following the Pinatubo volcanic eruption, *Geophys. Res. Lett.*, *19*, 211-213, 1992.
- Karol, I.L., Y.E. Ozolin, and E.V. Rozanov, Effect of space rocket launches on ozone, *Annales Geophysicae*, *10*, 1810-1814, 1992.
- Kawa, S.R., *et al.*, Photochemical partitioning of the reactive nitrogen and chlorine reservoirs in the high-latitude stratosphere, *J. Geophys. Res.*, *97*, 7905-7923, 1992.
- Kawa, S.R., *et al.*, Interpretation of NO_x/NO_y observations from AASE-II using a model of chemistry along trajectories, *Geophys. Res. Lett.*, *20*, 2507-2510, 1993.
- Kaye, J.A., *et al.*, Spatial and temporal variability of the extent of chemically processed stratospheric air, *Geophys. Res. Lett.*, *18*, 29-32, 1991.
- Kaye, J.A., S.A. Penkett, and F.M. Ormond, eds., *Report on Concentrations, Lifetimes, and Trends of CFCs, Halons, and Related Species*, NASA Reference Publication 1339, 1994.
- Khalil, M.A.K., and R.A. Rasmussen, The global sources of nitrous oxide, *J. Geophys. Res.*, *97*, 14651-14660, 1992.

- Khalil, M.A.K., and R.A. Rasmussen, Decreasing trend of methane: Unpredictability of future concentrations, *Chemosphere*, 26, 803-814, 1993.
- Kiehl, J.T., B.A. Boville, and B.P. Briegleb, Response of a general circulation model to a prescribed Antarctic ozone hole, *Nature*, 332, 501-504, 1988.
- Kinne, S., O.B. Toon, and M.J. Prather, Buffering of stratospheric circulation by changing amounts of tropical ozone: A Pinatubo case study, *Geophys. Res. Lett.*, 19, 1927-1930, 1992.
- Kinnersley, J.S., and R.S. Harwood, An isentropic 2-dimensional model with an interactive parameterization of dynamical and chemical planetary-wave fluxes, *Quart. J. Roy. Meteorol. Soc.*, 119, 1167-1193, 1993.
- Kinnison, D.E., K.E. Grant, P.S. Connell, D.J. Wuebbles, and D.A. Rotman, The chemical radiative effects of the Mt. Pinatubo eruption, *J. Geophys. Res.*, in press, 1994.
- Ko, M.K.W., M.B. McElroy, D.K. Weisenstein, and N.-D. Sze, Lightning: A possible source of stratospheric odd nitrogen, *J. Geophys. Res.*, 91, 5395-5404, 1986.
- Ko, M.K.W., H.R. Schneider, R.-L. Shia, D.K. Weisenstein, and N.-D. Sze, A two-dimensional model with coupled dynamics, radiation, and photochemistry: 1. Simulation of the middle atmosphere, *J. Geophys. Res.*, 98, 20429-20440, 1993.
- Kodera, K., Influence of the stratospheric circulation change on the troposphere in the northern hemisphere winter, in *The Role of the Stratosphere in Global Change*, edited by M.-L. Chanin, Springer-Verlag, 227-243, 1993.
- Kodera, K., M. Chiba, K. Yamazaki, and K. Shiba, A possible influence of the polar night stratospheric jet on the subtropical tropospheric jet, *J. Meteorol. Soc. Japan*, 69, 715-721, 1991.
- Koike, M., et al., Impact of Pinatubo aerosols on the partitioning between NO₂ and HNO₃, *Geophys. Res. Lett.*, 21, 597-600, 1994.
- Kotamarthi, V.R., M.K.W. Ko, D.K. Weisenstein, and N.-D. Sze, The effect of lightning on the concentration of odd nitrogen species in the lower stratosphere: An update, *J. Geophys. Res.*, 99, 8167-8173, 1994.
- Labitzke, K., and M.P. McCormick, Stratospheric temperature increases due to Pinatubo aerosols, *Geophys. Res. Lett.*, 19, 207-210, 1992.
- Lait, L.R., M.R. Schoeberl, and P.A. Newman, Quasi-biennial modulation of the Antarctic ozone depletion, *J. Geophys. Res.*, 94, 11559-11571, 1989.
- Lefèvre, F., G.P. Brasseur, I. Folkins, A.K. Smith, and P. Simon, Chemistry of the 1991-1992 stratospheric winter: Three-dimensional model simulations, *J. Geophys. Res.*, 99, 8183-8195, 1994.
- Legrand, M.R., F. Stordal, I.S.A. Isaksen, and B. Rognerud, A model study of the stratospheric budget of odd nitrogen, including effects of solar cycle variations, *Tellus*, 41B, 413-426, 1989.
- Liu, S.C., M. McFarland, D. Kley, O. Zafirious, and B. Huebert, Tropospheric NO_x and O₃ budgets in the equatorial Pacific, *J. Geophys. Res.*, 88, 1360-1368, 1983.
- Mahlman, J.D., J.P. Pinto, and L.J. Umscheid, Transport, radiative, and dynamical effects of the Antarctic ozone hole: A GFDL "SKYHI" model experiment, *J. Atmos. Sci.*, 51, 489-508, 1994.
- Mankin, M.G., M.T. Coffey, and A. Goldman, Airborne observations of SO₂, HCl, and O₃ in the stratospheric plume of the Pinatubo volcano in July 1991, *Geophys. Res. Lett.*, 19, 179-182, 1992.
- McConnell, J.C., and M.B. McElroy, Odd nitrogen in the atmosphere, *J. Atmos. Sci.*, 30, 1464-1480, 1973.
- McCormick, M.P., R.E. Veiga, and W.P. Chu, Stratospheric ozone profile and total ozone trends derived from the SAGE I and SAGE II data, *Geophys. Res. Lett.*, 19, 269-272, 1992.
- McElroy, M.B., and J.C. McConnell, Nitrous oxide: A natural source of stratospheric NO, *J. Atmos. Sci.*, 28, 1095-1098, 1971.
- McElroy, M.B., and R.J. Salawitch, Changing composition of the global stratosphere, *Science*, 243, 763-770, 1989.
- McElroy, M.B., R.J. Salawitch, and K. Minschwaner, The changing stratosphere, *Planet. Space Sci.*, 40, 373-401, 1992.
- Michelangeli, D.V., M. Allen, and Y.L. Yung, El Chichón volcanic aerosols: Impact of radiative, thermal, and chemical perturbations, *J. Geophys. Res.*, 94, 18429-18443, 1989.

STRATOSPHERIC MODELS

- Mills, M.J., *et al.*, On the relationship between stratospheric aerosols and nitrogen dioxide, *Geophys. Res. Lett.*, 20, 1187-1190, 1993.
- Molina M.J., *et al.*, Physical chemistry of the H₂SO₄/HNO₃/H₂O system: Implications for polar stratospheric clouds, *Science*, 261, 1418-1423, 1993.
- Murphy, D.M., and A.R. Ravishankara, Temperature averages and rates of stratospheric reactions, *Geophys. Res. Lett.*, in press, 1994.
- Natarajan, M., and L.B. Callis, Stratospheric photochemical studies with Atmospheric Trace Molecule Spectroscopy (ATMOS) measurements, *J. Geophys. Res.*, 96, 9361-9370, 1991.
- Newman, P.A., M.R. Schoeberl, R.A. Plumb, and J.E. Rosenfield, Mixing rates calculated from potential vorticity, *J. Geophys. Res.*, 93, 5221-5240, 1988.
- Nicolet, M., On the production of nitric oxide in the stratosphere by cosmic rays in the mesosphere and stratosphere, *Planet. Space Sci.*, 23, 637-649, 1975.
- Nicoli, M.P., and G. Visconti, Impact of coupled perturbations of atmospheric trace gases on earth's climate and ozone, *Pure Appl. Geophys.*, 120, 626-641, 1982.
- Noxon, J.F., Atmospheric nitrogen fixation by lightning, *Geophys. Res. Lett.*, 3, 463-465, 1976.
- Oort, A.H., and H. Liu, Upper-air temperature trends over the globe, 1958-1989, *J. Climate*, 6, 292-307, 1993.
- Park, C., and G.P. Menees, Odd nitrogen production by meteoroids, *J. Geophys. Res.*, 83, 4029-4035, 1978.
- Patten, K.O., Jr., P.S. Connell, D.E. Kinnison, D.J. Wuebbles, T.G. Slanger, and L. Froidevaux, Effect of vibrationally excited oxygen on ozone production in the stratosphere, *J. Geophys. Res.*, 99, 1211-1224, 1994.
- Peter, T., C. Brühl, and P.J. Crutzen, Increase in the PSC formation probability caused by high-flying aircraft, *Geophys. Res. Lett.*, 18, 1465-1468, 1991.
- Pitari, G., Contribution to the ozone trend of heterogeneous reactions of ClONO₂ on the sulfate aerosol layer, *Geophys. Res. Lett.*, 20, 2663-2666, 1993a.
- Pitari, G., A numerical study of the possible perturbation of stratospheric dynamics due to Pinatubo aerosols: Implications for tracer transport, *J. Atmos. Sci.*, 50, 2443-2461, 1993b.
- Pitari, G., S. Palmeri, G. Visconti, and R. Prinn, Ozone response to a CO₂ doubling: Results from a stratospheric circulation model with heterogeneous chemistry, *J. Geophys. Res.*, 97, 5953-5962, 1992.
- Pitari, G., and V. Rizi, An estimate of the chemical and radiative perturbation of stratospheric ozone following the eruption of Mt. Pinatubo, *J. Atmos. Sci.*, 50, 3260-3276, 1993.
- Pitari, G., V. Rizi, L. Ricciardulli, and G. Visconti, High speed civil transport impact: Role of sulfate, nitric acid trihydrate and ice aerosols studied with a two-dimensional model including aerosol physics, *J. Geophys. Res.*, 98, 23141-23164, 1993.
- Planet, W.G., *et al.*, Northern hemisphere total ozone values from 1989-1993 determined with the NOAA-11 Solar Backscatter Ultraviolet (SBUV/2) instrument, *Geophys. Res. Lett.*, 21, 205-208, 1994.
- Plumb, R.A., and M.K.W. Ko, Interrelationships between mixing ratios of long-lived stratospheric constituents, *J. Geophys. Res.*, 97, 10145-10156, 1992.
- Prather, M.J., Catastrophic loss of stratospheric ozone in dense volcanic clouds. *J. Geophys. Res.*, 97, 10187-10191, 1992.
- Prather, M., and A.H. Jaffe, Global impact of the Antarctic ozone hole: Chemical propagation, *J. Geophys. Res.*, 95, 3473-3492, 1990.
- Prather, M.J., M.M. Garcia, A.R. Douglass, C.H. Jackman, M.K.W. Ko, and N.-D. Sze, The space shuttle's impact on the stratosphere, *J. Geophys. Res.*, 95, 18583-18590, 1990a.
- Prather, M., M.M. Garcia, R. Suozzo, and D. Rind, Global impact on the Antarctic ozone hole: Dynamical dilution with a three-dimensional chemical transport model, *J. Geophys. Res.*, 95, 3449-3471, 1990b.
- Prather, M.J., *et al.*, *The Atmospheric Effects of Stratospheric Aircraft: A First Program Report*, NASA Reference Publication 1272, 46-50, January 1992.
- Prather, M.J., and E.E. Remsburg, eds., *The Atmospheric Effects of Stratospheric Aircraft: Report of the 1992 Models and Measurements Workshop*, NASA Reference Publication 1292, Vol. 1, National Aeronautics and Space Administration, Washington, D.C., 1993.

- Ramaswamy, V.M., D. Schwarzkopf, and K.P. Shine, Radiative forcing of climate from halocarbon-induced global stratospheric ozone loss, *Nature*, 355, 810-812, 1992.
- Reinsel, G.C., *et al.*, Statistical analysis of total ozone and stratospheric umkehr data for trends and solar cycle relationship, *J. Geophys. Res.*, 92, 2201-2209, 1987.
- Reinsel, G.C., *et al.*, Seasonal trend analysis of published ground-based and TOMS total ozone data through 1991, *J. Geophys. Res.*, 99, 5449-5464, 1994.
- Rind, D., R. Suozzo, N.K. Balachandran, and M.J. Prather, Climate change and the middle atmosphere. Part I: The doubled CO₂ climate, *J. Atmos. Sci.*, 47, 475-494, 1990.
- Rinsland, C.P., *et al.*, Heterogeneous conversion of N₂O₅ to HNO₃ in the post-Mt. Pinatubo eruption stratosphere, *J. Geophys. Res.*, 99, 8213-8219, 1994.
- Rodriguez J.M., M.K.W. Ko, and N.-D. Sze, The role of heterogeneous conversion of N₂O₅ on sulphate aerosols in global ozone losses, *Nature*, 352, 134, 1991.
- Rodriguez, J.M., M.K.W. Ko, N.-D. Sze, C.E. Heisey, G.K. Yue, and M.P. McCormick, Ozone response to enhanced heterogeneous processing after the eruption of Mt. Pinatubo, *Geophys. Res. Lett.*, 21, 209-212, 1994.
- Rood, R., D.J. Allen, W.E. Baker, D.J. Lamich, and J.A. Kaye, The use of assimilated stratospheric data in constituent transport calculations, *J. Atmos. Sci.*, 46, 687-701, 1989.
- Rood, R.B., *et al.*, Three-dimensional simulations of wintertime ozone variability in the lower stratosphere, *J. Geophys. Res.*, 96, 5055-5071, 1991.
- Rosenfield, J.E., M.R. Schoeberl, and M.A. Geller, A computation of the stratospheric diabatic circulation using an accurate radiative transfer model, *J. Atmos. Sci.*, 44, 859-876, 1987.
- Russell, J.M., III, S. Solomon, L.L. Gordley, E.E. Remsberg, and L.B. Callis, The variability of stratospheric and mesospheric NO₂ in the polar winter night observed by LIMS, *J. Geophys. Res.*, 89, 7267-7275, 1984.
- Sanders, R.W., *et al.*, Visible and near-ultraviolet spectroscopy at McMurdo Station, Antarctica, 9. Observations of OCIO from April to October 1991, *J. Geophys. Res.*, 98, 7219-7228, 1993.
- Schneider, H.R., M.K.W. Ko, and C.A. Peterson, Interannual variations of ozone: Interpretation of 4 years of satellite observations of total ozone, *J. Geophys. Res.*, 96, 2889-2896, 1991.
- Schneider, H.R., M.K.W. Ko, R.-L. Shia, and N.-D. Sze, A two-dimensional model with coupled dynamics, radiative transfer, and photochemistry, 2. Assessment of the response of stratospheric ozone to increased levels of CO₂, N₂O, CH₄, and CFC, *J. Geophys. Res.*, 98, 20441-20449, 1993.
- Schoeberl, M.R., P.K. Bhartia, and E. Hilsenrath, Tropical ozone loss following the eruption of Mt. Pinatubo, *Geophys. Res. Lett.*, 20, 29-32, 1993.
- Slanger, T.G., L.E. Jusinski, G. Black, and G.E. Gadd, A new laboratory source of ozone and its potential atmospheric implications, *Science*, 241, 945-950, 1988.
- Solomon, S., Antarctic ozone: Progress toward a quantitative understanding, *Nature*, 347, 347-354, 1990.
- Solomon, S., P.J. Crutzen, and R.G. Roble, Photochemical coupling between the thermosphere and the lower atmosphere, 1. Odd nitrogen from 50 to 120 km, *J. Geophys. Res.*, 87, 7206-7220, 1982.
- Solomon, S., R.W. Sanders, R.R. Garcia, and J.G. Keys, Increased chlorine dioxide over Antarctica caused by volcanic aerosols from Mt. Pinatubo, *Nature*, 363, 245-248, 1993.
- Solomon, S., R.R. Garcia, and A.R. Ravishankara, On the role of iodine in ozone depletion, *J. Geophys. Res.*, 99, 20491-20500, 1994a.
- Solomon, S., *et al.*, Visible and near-ultraviolet spectroscopy at McMurdo Station, Antarctica 10. Reductions of stratospheric NO₂ due to Pinatubo aerosols, *J. Geophys. Res.*, in press, 1994b.
- Spencer, R.W., and J.R. Christy, Precision lower stratospheric temperature monitoring with the MSU: Technique, validation and results 1979-1991, *J. Climate*, 6, 1194-1204, 1993.
- Stachnik, R.A., J.C. Hardy, J.A. Tarsala, J.W. Waters, and N.R. Erickson, Submillimeterwave heterodyne measurements of stratospheric ClO, HCl, O₃ and HO₂: First results, *Geophys. Res. Lett.*, 19, 1931-1934, 1992.

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- Stolarski, R., R. Bojkov, L. Bishop, C. Zerefos, J. Stachelin, and J. Zawodny, Measured trends in stratospheric ozone, *Science*, 256, 342-349, 1992.
- Strobel, D.F., Odd nitrogen in the mesosphere, *J. Geophys. Res.*, 76, 8384-8393, 1971.
- Sze, N.-D., M.K.W. Ko, D.K. Weisenstein, J.M. Rodriguez, R.S. Stolarski, and M.R. Schoeberl, Antarctic ozone hole: Possible implications for ozone trends in the Southern Hemisphere, *J. Geophys. Res.*, 94, 11521-11528, 1989.
- Tabazadeh, A., and R.P. Turco, Stratospheric chlorine injection by volcanic eruptions: HCl scavenging and implications for ozone, *Science*, 260, 1082-1086, 1993.
- Tie, X., G.P. Brasseur, B. Briegleb, and C. Granier, Two-dimensional simulation of Pinatubo aerosol and its effect on stratospheric ozone, *J. Geophys. Res.*, 99, 20545-20562, 1994.
- Tolbert, M.A., J. Pfaff, I. Jayaweera, and M.J. Prather, Uptake of formaldehyde by sulfuric acid solutions: Impact on stratospheric ozone, *J. Geophys. Res.*, 98, 2957-2962, 1993.
- Toon, O., *et al.*, Heterogeneous reaction probabilities, solubilities and physical state of cold volcanic aerosols, *Science*, 261, 1136-1140, 1993.
- Toumi, R., An evaluation of autocatalytic ozone production from vibrationally excited oxygen in the middle atmosphere, *J. Atmos. Chem.*, 15, 69-77, 1992.
- Toumi, R., A potential new source of OH and odd-nitrogen in the atmosphere, *Geophys. Res. Lett.*, 20, 25-28, 1993.
- Toumi, R., and S. Bekki, The importance of the reactions between OH and ClO for stratospheric ozone, *Geophys. Res. Lett.*, 20, 2447-2450, 1993.
- Toumi, R., B.J. Kerridge, and J.A. Pyle, Highly vibrationally excited oxygen as a potential source of ozone in the upper stratosphere and mesosphere, *Nature*, 351, 217-219, 1991.
- Toumi, R., R.L. Jones, and J.A. Pyle, Direct stratospheric ozone depletion by ClONO₂ photolysis, *Nature*, 365, 37-39, 1993.
- Tuck, A.F., Production of nitrogen oxides by lightning discharges, *Quart. J. Roy. Meteorol. Soc.*, 102, 749-755, 1976.
- Tung, K.K., and H. Yang, Dynamical component of seasonal and year-to-year changes in Antarctic and global ozone, *J. Geophys. Res.*, 93, 12537-12559, 1988.
- Vupputuri, R.K.R., The structure of the natural stratosphere and the impact of chlorofluoromethanes on the ozone layer investigated in a 2-D time dependent model, *Pure Appl. Geophys.*, 117, 448-485, 1978.
- Wallace, L., and W. Livingston, The effect of the Pinatubo cloud on hydrogen chloride and hydrogen fluoride, *Geophys. Res. Lett.*, 19, 1209, 1992.
- Wang, W.-C., Y.-C. Zhuang, and R.D. Bojkov, Climate implications of observed changes in ozone vertical distributions at middle and high latitudes of the northern hemisphere, *Geophys. Res. Lett.*, 20, 1567-1570, 1993.
- Warneck, P., Cosmic radiation as a source of odd nitrogen in the stratosphere, *J. Geophys. Res.*, 77, 6589-6591, 1972.
- Webster, C.R., R.D. May, M. Allen, L. Jaegle, and M.P. McCormick, Balloon profiles of stratospheric NO₂ and HNO₃ for testing the heterogeneous hydrolysis of N₂O₅ on sulfate aerosols, *Geophys. Res. Lett.*, 21, 53-56, 1994.
- Weisenstein, D., M.K.W. Ko, J.M. Rodriguez, and N.-D. Sze, Impact of heterogeneous chemistry on model-calculated ozone change due to high speed civil transport aircraft, *Geophys. Res. Lett.*, 18, 1991-1994, 1991.
- Weisenstein, D., M.K.W. Ko, and N.-D. Sze, The chlorine budget of the present-day atmosphere: A modeling study, *J. Geophys. Res.*, 97, 2547-2559, 1992.
- Weisenstein, D.K., M.K.W. Ko, J.M. Rodriguez, and N.-D. Sze, Effects on stratospheric ozone from high-speed civil transport: Sensitivity to stratospheric aerosol loading, *J. Geophys. Res.*, 98, 23133-23140, 1993.
- Wennberg, P.O., *et al.*, Removal of stratospheric O₃ by free radicals: In situ measurements of OH, HO₂, NO, NO₂, ClO and BrO, *Science*, 266, 398-404, 1994.
- Wilson, J.C., *et al.*, In situ observations of aerosol and chlorine monoxide after the 1991 eruption of Mt. Pinatubo: Effects of reactions on sulfate aerosol, *Science*, 261, 1140-1143, 1993.

- Woodbridge, E.L., *et al.*, Estimates of total organic and inorganic chlorine in the lower stratosphere from in situ measurements during AASE II, *J. Geophys. Res.*, in press, 1994.
- WMO, *Report of the International Ozone Trends Panel: 1988*, World Meteorological Organization Global Ozone Research and Monitoring Project – Report No. 18, Washington, D.C., 1990.
- WMO, *Scientific Assessment of Ozone Depletion: 1991*, World Meteorological Organization Global Ozone Research and Monitoring Project – Report No. 25, Geneva, 1992.
- Yang, H., E. Olaguer, and K.K. Tung, Simulation of the present-day atmospheric ozone, odd nitrogen, chlorine and other species using a coupled 2-D model in isentropic coordinates, *J. Atmos. Sci.*, *48*, 442-471, 1991.
- Zadorozhny, A.M., G.A. Tuchkov, V.N. Kikhtenko, J. Lastovicka, J. Boska, and A. Novak, Nitric oxide and lower ionosphere quantities during solar particle events of October 1989 after rocket and ground-based measurements, *J. Atmos. Terr. Phys.*, *54*, 183-192, 1992.
- Zander, R., M.R. Gunson, J.C. Foster, C.P. Rinsland, and J. Namkung, Stratospheric ClONO₂, HCl and HF concentration profiles derived from Atmospheric Trace Molecule Spectroscopy experiment Space-lab 3 observations: An update, *J. Geophys. Res.*, *95*, 20519-20525, 1990.
- Zerefos, C.S., A.F. Bais, I.C. Ziomas, and R.D. Bojkov, On the relative importance of quasi-biennial oscillation and El Niño/Southern Oscillation in the revised Dobson total ozone records, *J. Geophys. Res.*, *97*, 10135-10144, 1992.