

Two-dimensional simulation of Pinatubo aerosol and its effect on stratospheric ozone

XueXi Tie, Guy P. Brasseur, Bruce Briegleb, and Claire Granier

National Center for Atmospheric Research, Boulder, Colorado

Abstract. This paper presents time-dependent simulations of the response of the stratosphere to the injection into the atmosphere of massive amounts of sulfur during the eruption of Mt. Pinatubo (The Philippines) in June 1991. The study is based on a coupled two-dimensional chemical-dynamical-radiative model to which a microphysical model for sulfate aerosol formation and fate has been added. The study suggests that, during the first year (July 1991 to June 1992) following the volcanic eruption, the observed changes in the ozone amount integrated between 65°S and 65°N were caused primarily by changes in the meridional circulation (associated with heating by the volcanic cloud in the tropics) and in the photolysis rate of molecules such as ozone (associated with backscattering of light by the cloud). During the second year after the eruption, as the aerosol was dispersed at all latitudes and, in particular, reached the polar region, the largest contribution to ozone reduction resulted from the heterogeneous chemical conversion of N_2O_5 and $ClONO_2$ on the surface of the aerosol particles. The conversion of the latter compound, and hence the magnitude of the calculated ozone depletion, is highly dependent on the temperature in the lower stratosphere. Despite the fact that the surface area provided by aerosol particles decreased during the second year following the eruption, the calculated ozone depletion remained significant because the conversion of N_2O_5 is insensitive to the aerosol surface area density for values larger than $1\text{--}10 \mu\text{m}^2/\text{cm}^3$ (depending on latitude). The predicted reduction in ozone at 20 km in March during the third year (July 1993 to June 1994) of the model integration is smaller by a factor of 2 than it was during the second year.

1. Introduction

The suggestion by *Hofmann and Solomon* [1989] that the presence of sulfate particles in the lower stratosphere following the eruption of El Chichón (Mexico) in 1982 could have produced substantial ozone depletion led to much discussion about the importance of heterogeneous reactions above the tropopause at midlatitudes. *Brasseur et al.* [1990] suggested, for example, that with the high abundances of anthropogenic chlorine currently present in the stratosphere, future volcanic eruptions could substantially affect the ozone layer on the global scale. The eruption of Mt. Pinatubo (The Philippines) in June 1991 injected as much as 12–25 MT of sulfur into the stratosphere, according to *Strong and Stowe* [1993], this was 1.6 times as much as from the eruption of El Chichón in 1982. Model calculations [*Prather, 1992; Brasseur and Granier, 1992; D. A. D'Altorio et al., Ozone depletion following the eruption of Pinatubo: Preliminary measurements and model results, personal communication, 1993*] predicted that stratospheric ozone should have been significantly depleted in response to the eruption of Mt. Pinatubo. The mechanism invoked is the heterogeneous conversion of nitrogen oxides into nitric acid on the surface of sulfate aerosol particles,



The corresponding reduction in the abundance of nitrogen oxides leads to an enhancement in the concentration of reactive chlorine ($Cl + ClO + HOCl + 2Cl_2 + 2Cl_2O_2$), as the rate of conversion of ClO into the $ClONO_2$ reservoir is reduced [*Hofmann and Solomon, 1989; Prather, 1992; Brasseur and Granier, 1992*]. An increase in the concentration of OH radical is also predicted as a result of heterogeneous reaction (1) [*Brasseur and Granier, 1992*]. The reaction probability (number of reactions per collision) of reaction (1) is estimated to be independent of temperature and close to 10% [*Hanson and Ravishankara, 1991*]. The heterogeneous conversion of $ClONO_2$,



leads to additional conversion of nitrogen oxides into nitric acid and to the formation of reactive chlorine in the sunlight, where $HOCl$ is rapidly photolyzed. The reaction probability varies strongly with the composition of the aerosol and hence with the ambient temperature and water abundance [*Tolbert et al., 1988; Hanson et al., 1994*]. According to laboratory data, conversion mechanism (2) plays a role only in cold environments, so that it can be ignored at low and midlatitudes but could play a significant role in the polar regions, primarily in winter.

It has also been suggested that the volcanic cloud produced by the eruption of Pinatubo could have affected the rate of scattering of solar radiation in the atmosphere and hence the photodissociation rates and concentrations of several stratospheric compounds [*Fiocco et al., 1978; Mich-*

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elangeli et al., 1989; *Pitari and Rizi*, 1993]. In addition, the absorption of terrestrial radiation and, to a lesser extent, of solar light has led to local warming, mostly in the tropical lower stratosphere [*Labitzke and McCormick*, 1992; *Kinne et al.*, 1992], with probable impact on the atmospheric circulation [*Brasseur and Granier*, 1992; *Schoeberl et al.*, 1993].

Observations made after the eruption of Mt. Pinatubo have revealed perturbations in the chemical composition of the lower stratosphere. *Coffey and Mankin* [1993] reported reductions in the stratospheric NO_x concentration of as much as 70% in the months following the appearance of the volcanic aerosols. Reductions in the NO_2 column abundance of more than 40% were measured at Lauder, New Zealand, by *Johnston et al.* [1992] in October 1991 and were attributed to the presence of volcanic aerosol. During 1992, *Koike et al.* [1993] observed at Moshiri, Japan, a reduction in the NO_2 column abundance of more than 20% compared with the "reference" value (observed column at 45°S in 1990). *Mills et al.* [1993] observed that when aerosol loadings were low, there was a strong anticorrelation between the NO_2 column abundance at Fritz Peak observatory (Colorado) and the amount of stratospheric aerosol near 25–30 km. Little further reduction in NO was observed for higher aerosol loading (saturation effect). Concentrations of HNO_3 measured by the ATMOS (atmospheric trace molecule spectroscopy) instrument during the Atlas I campaign between March 24 and April 2, 1992, were generally higher (a factor of 2 at the equator and 30-km altitude) than those observed by the limb infrared monitor of the stratosphere (LIMS) during the same season in 1979, when the aerosol loading was near background levels [*Rinsland et al.*, 1994]. *Koike et al.* [1994] also reported significant increases in the HNO_3 column amount (10% to 30%) between September 1991 and May 1993 at Lauder, New Zealand. *Fahey et al.* [1993] observed considerable reductions in the NO_x/NO_y ratio and an increase in the ClO/Cl_y ratio with increases in the measured aerosol area density. *Solomon et al.* [1993] found that in 1992, unlike in 1991, chlorine dioxide (OCIO) levels over Antarctica had increased dramatically in April, when polar stratospheric clouds (in which nitrogen oxides and chlorine reservoirs are also converted heterogeneously) were very unlikely to be present.

The global response of ozone to the eruption of Mt. Pinatubo has not yet been well quantified. The annual mean total ozone column abundance measured by the total ozone mapping spectrometer (TOMS) and averaged over 0 to 65°N latitude, which was in the range from 300–306 Dobson between 1983 and 1991, was reduced to 294.5 in 1992 (K. Labitzke, personal communication, 1993). For the period from 3–6 months after the eruption, *Grant et al.* [1992] found a reduction in tropical ozone density of up to 20% between the altitudes of 16 and 29 km. *Hofmann et al.* [1993, 1994] reported an unprecedented ozone decrease in the lower stratosphere (25%) over the United States (Hilo, Hawaii; Boulder, Colorado; and Wallops Island, Virginia) in 1992–1993, although the observed temperatures were within the normal climatological range. The region of low ozone at Boulder, Colorado (12–22 km of altitude), corresponded closely to regions of enhanced sulfate aerosol load. Higher than normal ozone concentrations were observed above 24 km. *Kerr et al.* [1993] note that during the first 4 months of 1993, total ozone over Canada was 11% to 17% below normal and that record low averages were measured during this period at three of the four Canadian midlatitude stations,

where measurements have been made since the 1960s. *Bojkov* [1993] also reported record low ozone column abundance during the northern winters of 1991–1992 and 1992–1993. *Hofmann et al.* [1993] suggested that the unusual ozone depletion observed at the south pole between 14 and 18 km during October 1992 could have been related to the presence of volcanic sulfuric acid droplets trapped inside the polar vortex. *Chandra and Stolarski* [1991] indicated, however, that the apparent decrease of 5%–6% in total ozone reported by TOMS (averaged from 60°N to 60°S) after the eruption of El Chichón was largely associated with the quasi-biennial oscillation of the atmosphere and that at most 2% to 4% of the ozone anomaly observed in the mid-1980s could be attributed to the eruption of the volcano. From an analysis of ozone data measured by the Nimbus 7 TOMS instrument, *Chandra* [1993] reported similar ozone reduction after the eruption of Mt. Pinatubo and stressed that the observed decrease was lower by a factor of 2 to 3 than predicted by the model of *Brasseur and Granier* [1992]. This study, however, is based on less than 1 year of data following the eruption and does not consider observations poleward of 60°N. *Gleason et al.* [1993] and *Herman and Larko* [1994] indicated that the global average total ozone measured by TOMS in 1992 was 2% to 3% lower than in any previous year since 1979 and at least 1.5% lower than would have been predicted by a statistical model that accounts for quasi-biennial oscillation, solar cycle variation, and long-term linear trend. They indicated, however, that the size and timing of the observed ozone decrease in 1992 and 1993 were inconsistent with model predictions [see, e.g., *Brasseur and Granier*, 1992; *Pitari and Rizi*, 1993] and questioned the validity of these models.

The purpose of this paper is to address these discrepancies by analyzing systematically the potential contribution of different factors which could affect the ozone abundance after a large volcanic eruption: change in the atmospheric circulation associated with local heating inside the cloud, change in the photolysis rate associated with scattering of solar light by the sulfate cloud, and chemical effects associated with heterogeneous conversion mechanisms. Our analysis will be based on two-dimensional model simulations. As opposed to previous studies [*Brasseur and Granier*, 1992] performed for steady-state conditions and for specified aerosol loading, the present study is based on a model in which the evolution of aerosol formation and fate and their impact on the dynamics, radiation, and chemistry of the stratosphere are simulated for 2 years following the eruption of Mt. Pinatubo (June 1991 to July 1993).

The model used for the present study will be described briefly in section 2. The calculated distribution and evolution of the aerosol layer will be presented and compared with available observations in section 3. The effect of this volcanic perturbation on the ozone abundance through simulated changes in the dynamics of the atmosphere, the intensity of solar radiation, and the rate of heterogeneous chemical reactions will be discussed in sections 4, 5, and 6, respectively. The major findings will be summarized in section 7.

2. Model Description

The model used in the present study is based on the two-dimensional chemical and dynamical model developed by *Brasseur et al.* [1990] with additions described by *Granier and Brasseur* [1992]. It extends from the Earth's surface to

the mesopause with a vertical resolution of 1 km and from pole to pole with a latitudinal resolution of 5 degrees. Approximately 50 species and 110 chemical and photochemical reactions are taken into account to describe the behavior of the oxygen, hydrogen, nitrogen, chlorine, bromine, fluorine, and sulfur families. Heterogeneous reactions on sulfate aerosol particles are considered in the chemical scheme, but in order to isolate these effects, heterogeneous reactions on polar stratospheric cloud particles are ignored in the present study.

In order to simulate the time evolution and global distribution of stratospheric sulfate aerosols following a volcanic eruption, a representation of the key microphysical processes (heterogeneous nucleation, condensation, coagulation, sedimentation, and washout) affecting stratospheric sulfate aerosol is added to the model. A detailed description of the formulation of these processes is given by *Tie et al.* [1994]. The model is used to simulate the aerosol distribution between July 1991 and June 1994 after the eruption of Mt. Pinatubo, which took place in June 1991. In the calculation, we assume that a total of 13 Tg of sulfur is injected by the Pinatubo eruption into the equatorial lower stratosphere (latitudes of 5°S to 15°N and altitudes of 19 to 26 km) [McCormick and Veiga, 1992; Stowe et al., 1992]. It is also assumed that 90% of the sulfur was injected as gas phase SO₂ and the remaining 10% as sulfate particles. These latter particles are introduced to account for microphysical processes not explicitly treated by the model. For example, homogeneous nucleation (not represented in the model) is believed to have produced a high number of small particles at the early stage following the eruption of Mt. Pinatubo [Deshler et al., 1993; Sheridan et al., 1992; Bekki and Pyle, 1994]. The aerosol area density (square micrometers per cubic centimeter) of sulfate aerosol, mass mixing ratio (parts per million), and size distribution (dn/dr) are calculated and used to estimate the effects of aerosols on solar and longwave radiation and to determine the rate of heterogeneous chemical reactions.

In order to estimate the radiative effects of the volcanic cloud, the aerosol is assumed to be a pure absorber of both solar and longwave (thermal) radiation. The important solar stratospheric radiative effect is due to near-infrared absorption of the incident beam [Kiehl and Briegleb, 1993]. Scattering of longwave radiation is negligible, as the corresponding single particle scattering albedo never exceeds 0.10. To account for the spectral dependence of the absorption, the 18 spectral intervals used by Briegleb [1992a] were employed for the solar spectrum, while the 100 cm⁻¹ spectral resolution of the longwave band model of Briegleb [1992b] was adopted for the terrestrial radiation.

The optical properties are determined from Mie scattering calculations, using the size distributions of aerosols derived from the microphysical model. The indices of refraction data were taken from Palmer and Williams [1975] and are appropriate for an aerosol composition of 75% H₂SO₄ and 25% H₂O by weight. Their dependence on the mass fraction of H₂SO₄ is not strong and so was neglected. The aerosol absorption coefficient (square meters per gram) is given by:

$$\psi = \frac{3}{4} \rho \left(\int Q_a \pi r^2 (dn/dr) dr \right) / \left(\int \pi r^3 (dn/dr) dr \right)$$

where ρ is the sulfate particle mass density, dn/dr is the calculated aerosol size distribution, and Q_a is the absorption

efficiency [see Bohren and Huffman, 1983]. The absorption efficiency was interpolated to the actual effective radius (r_e) of the aerosols, as computed in the model.

The perturbation in the longwave aerosol heating rate is strongly dependent on tropospheric cloudiness, since it is the absorption of upwelling radiation by the aerosol that gives rise to the longwave heating rate perturbation. Ideally, the model should include the zonal and vertical distribution of cloud properties (fraction coverage and longwave emissivity) appropriate for July 1991. In practice, however, detailed and accurate observations are not available. We have therefore assumed the presence of three levels of clouds (fractional coverage of 0.37 at 818 mbar, 0.25 at 520 mbar, and 0.35 at 226 mbar), randomly overlapped with a total fraction coverage of 0.69. The two lowest layers of clouds are assumed to be black in the infrared, while the emissivity of the upper layer is 0.75. With this cloud fractional coverage, the outgoing flux is equal to 247 W/m² in the tropics, a quite acceptable value for outgoing longwave radiation compared with satellite measurements [Barkstrom, 1984; Barkstrom and Smith, 1986; Earth Radiation Budget Experiment Science Team, 1986].

Sulfate particles also have significant effects on the photolysis rates of chemical compounds in the lower stratosphere [Michelangeli et al., 1989; Pitari and Rizi, 1993]. The actinic flux used in the calculation of these photolysis rates is provided by a delta-Eddington solution of the radiative transfer equation [Joseph and Wiscombe, 1976]. In the calculation, the direct solar flux is attenuated by aerosol scattering. The volume backscattering coefficient β [Pitari and Rizi, 1993], accounting for the backscattering by the aerosol layer, is given by

$$\beta(\lambda, z, \varphi) = \frac{3\pi g}{2\lambda} V(z, \varphi)$$

where V is aerosol volume density, expressed by

$$V(z, \varphi) = \int_r n(r, z, \varphi) \frac{4}{3} \pi r^3 dr$$

where $n(r, z, \varphi)$ is the calculated aerosol number density at radius r (r being the radius of aerosol particles), which varies with altitude z and latitude φ ; λ is the wavelength of solar radiation; and g is the Mie scattering efficiency factor, which is approximately equal to 0.8 [Pinnick et al., 1980].

In the model, the reaction probability, γ_1 , for reaction (1) is independent of temperature and is equal to 0.1 [Hanson and Ravishankara, 1991]. The reaction probability, γ_2 , for reaction (2) is, however, very sensitive to the weight percentage of sulfuric acid in the aerosol particles [Tolbert et al., 1988; Hanson and Ravishankara, 1991] and hence varies substantially with temperature and humidity [Steele and Hamill, 1981]. The variation of γ_2 with temperature and water vapor abundance formulated by Hanson et al. [1994] is adopted in the model.

3. Simulation of Pinatubo Aerosol

Figure 1 shows the calculated distributions of the total surface area density of the sulfate aerosol for three periods following the eruption of Mt. Pinatubo. Shortly after the eruption (Figure 1a) (July 1991), the surface aerosol area

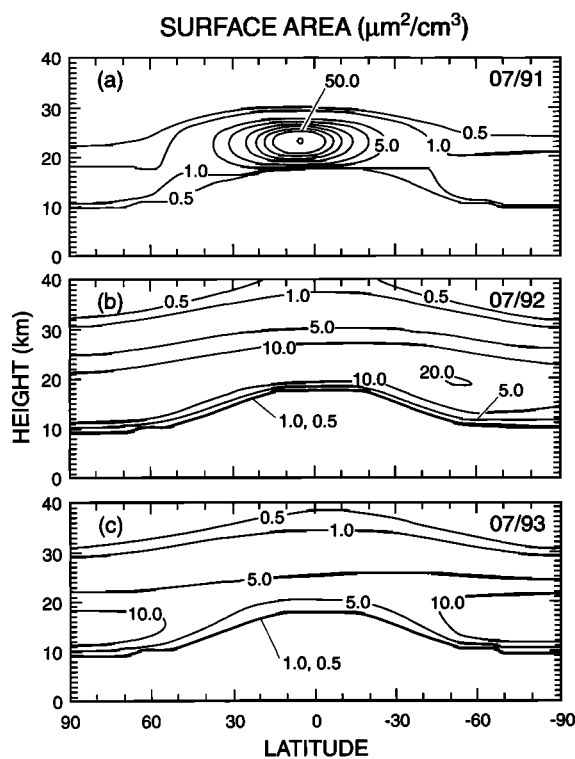


Figure 1. Simulated global distribution of sulfate aerosol surface area density after the eruption of Mt. Pinatubo in (a) July 1991, (b) July 1992, and (c) July 1993.

density has reached a maximum value of $75 \mu\text{m}^2/\text{cm}^3$ in the tropical lower stratosphere and is about 2 orders of magnitude above the values representative of background conditions [World Meteorological Organization, 1992]. The rapid increase in the aerosol load indicates that a large fraction of the gas phase SO_2 injected during the eruption has condensed on the surface of aerosol particles. The highest surface area is found in the tropical region, in agreement with observations [McCormick and Veiga, 1992; Grant *et al.*, 1992, 1994].

One year after the eruption (Figure 1b) (July 1992), the volcanic aerosols have been dispersed by transport processes, suggesting, as shown earlier by three-dimensional model calculations, that the time constant required for the transport of aerosols from the tropics to the polar regions is approximately 6–12 months [Boville *et al.*, 1991]. At this time, the total surface area in the lower stratosphere is of the order of $10 \mu\text{m}^2/\text{cm}^3$ at all latitudes.

Two years after the eruption (Figure 1c) (July 1993), the total surface area of aerosol is reduced to 5.0, 5.0–10.0, and $10.0 \mu\text{m}^2/\text{cm}^3$ in the tropics, at midlatitudes, and in the polar regions, respectively. This decrease in the aerosol load is more rapid in the tropics than at higher latitudes because of rapid meridional mixing of the volcanic particles. Another potential reason for this difference with latitude is that strong upward motion in the tropics transports aerosol particles towards higher levels (above 40 km), where the warmer temperature causes substantial evaporation of sulfate aerosols. In the polar regions, however, the maximum aerosol load is located in the lower stratosphere (approximately 5 km lower than in the tropics), where the air is denser and

vertical displacements of parcels of air are smaller than in the tropics. In these regions, gravitational sedimentation therefore plays a major role in transporting aerosol particles down to lower levels and into the troposphere. For aerosol particles with radii of the order of $1 \mu\text{m}$, the time constant for sedimentation is more than 1 year [Kasten, 1968]. Thus the residence time of aerosols in the polar regions is considerably longer than it is in the tropics.

Figure 2 shows a comparison between the calculated aerosol surface area density and the observed aerosol extinction by satellite (ISAMS) reported by Lambert *et al.* [1993]. Although the two quantities are different, they are related [Jager and Hofmann, 1991]. They suggest that the model is realistic in different respects: (1) in October 1991 (4 months after the eruption), the largest amount of aerosol is located in the tropics and midlatitudes between 20 and 30 km of altitude; (2) in January 1992 (7 months after the eruption), the aerosol maximum located in the tropical lower stratosphere has decreased by approximately 50% from its value in October 1991 and at the same time the aerosols are transported towards higher latitudes; and (3) in July 1992 (13 months after the eruption), the aerosols in the tropics represent only 20% of their value in October 1991. The comparison also shows disagreements between the observations and the calculations; the most striking of them is that the latitudinal gradient associated with the model calculations is significantly smaller than suggested by the observations (see also the aerosol cross sections reported by Trepte and Hitchman [1992]). A likely explanation for this discrepancy is that the model overestimates the meridional transport associated with mixing processes in the lower stratosphere. A similar feature has also been reported for the calculation of the ^{14}C distribution (see Jackman *et al.* [1989]). Because the two-dimensional model does not reproduce correctly the “dynamical barrier” near the subtropical jet and in the vicinity of the polar vortex, the aerosol spread too rapidly towards high latitudes, while observations suggest that aerosols reach the polar regions only after the final warming, when the polar vortex breaks down. Note also that the model does not simulate the quasi-biennial oscillation (QBO) of the atmosphere, which is known to have had an impact on the meridional transport of aerosol after the eruption of Mt. Pinatubo [Hitchman *et al.*, 1994]. The observation includes high-altitude clouds, while the model ignores polar stratospheric clouds. The presence of polar stratospheric clouds (PSCs) in Antarctica is, for example, visible in July 1992.

Yue *et al.* [1992] reported that in January 1992 (7 months after the eruption) the maximum aerosol surface area density was approximately $30 \mu\text{m}^2/\text{cm}^3$ in the tropical lower stratosphere, in agreement with the calculated value. A slight decrease in the surface area (from $27 \mu\text{m}^2/\text{cm}^3$ in January 1992 to $15 \mu\text{m}^2/\text{cm}^3$ in July 1992) was reported by Deshler *et al.* [1993] at Laramie, Wyoming (41°N), in fair agreement (see Figure 3) with the model prediction (peak surface area of $30 \mu\text{m}^2/\text{cm}^3$ in January 1992 and of $15\text{--}20 \mu\text{m}^2/\text{cm}^3$ in July 1992 at 45°N). This translates into a modeled e-folding time for the surface area of 1.4 years, which is consistent with the value observed after the eruption of El Chichón [Hofmann and Solomon, 1989]. Note, however, that after July 1992, the decay in the surface area at Laramie was interrupted for several months, which is inconsistent with model predictions. Bekki and Pyle [1994] have suggested that the differ-

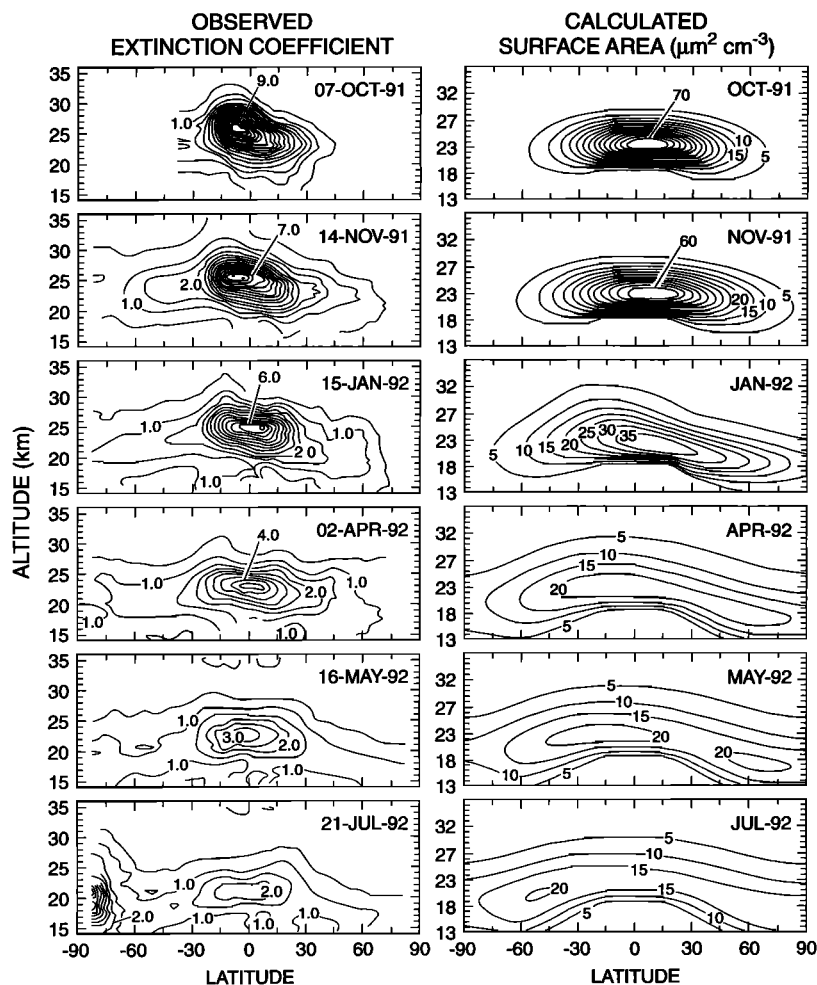


Figure 2. Measured aerosol extinction coefficient [Lambert *et al.*, 1993] and simulated aerosol surface area density after the eruption of Mt. Pinatubo between July 1991 and July 1992.

ence in the evolution of the clouds after the eruptions of El Chichón and Mt. Pinatubo could be due to much higher levels of nucleation in the initial Pinatubo cloud and hence to differences in the rate of condensation, coagulation, and sedimentation. Both calculations and observations show that the aerosol abundance decreases rapidly with increasing altitude. For example, the total surface area of the order of 1 to 2 $\mu\text{m}^2/\text{cm}^3$ observed between 30 and 35 km is well reproduced by the model.

Figure 3 shows the time evolution of the aerosol surface area density calculated as a function of height from July 1991 to June 1994 at 65°N, 45°N, the equator, 45°S, and 65°S. At 65°N (Figure 3a), the surface area reaches a maximum of 20 $\mu\text{m}^2/\text{cm}^3$ and decays after 2 years, with a time constant of approximately 20 months. At 45°N (Figure 3b), the surface area starts to increase substantially 2 months after the eruption. It reaches a value of 20 to 25 $\mu\text{m}^2/\text{cm}^3$ in the altitude range of 15 to 20 km, which remains fairly constant between 11 months and 21 months after the eruption. During this period of time, transport, microphysical growth, and microphysical loss seem to have reached a balance at this location. This steady behavior has also been observed by Deshler *et al.* [1993] at Laramie, Wyoming (41°N). Two years after the eruption, the aerosol surface area starts to

decrease, with an average decay time (e^{-1}) of approximately 15 months.

At the equator (Figure 3c), the aerosol surface area density increases rapidly and reaches 50 $\mu\text{m}^2/\text{cm}^3$ at 23 km. Later, the aerosol surface area density decreases. The average decay time is, in this case, of the order of 10 months, which is slightly longer than the observed value of 8 months reported by Grant *et al.* [1994]. The faster decay of aerosol in the tropics is due mainly to the vigorous Hadley cell and the dispersion of aerosol toward higher latitudes.

At 45°S (Figure 3d), the maximum surface area of 20 $\mu\text{m}^2/\text{cm}^3$ is reached 12 months after the eruption. At 65°S (Figure 3e), the evolution of the aerosol cloud is similar to that at 45°N except that the maximum aerosol area (20 $\mu\text{m}^2/\text{cm}^3$) appears 15 months after the eruption, i.e., approximately 7–8 months later than at 65°N. One of the reasons for the late maximum is that planetary wave activity is weaker in the southern hemisphere than in the northern hemisphere and hence meridional transport is slower. A key issue is also the timing of the eruption relative to the seasonal cycle, because the horizontal mixing is larger in winter than in summer. We also note that at a 20-km altitude, the aerosol does not start to increase significantly until 6 months after the eruption, so that, in the model, the effect of

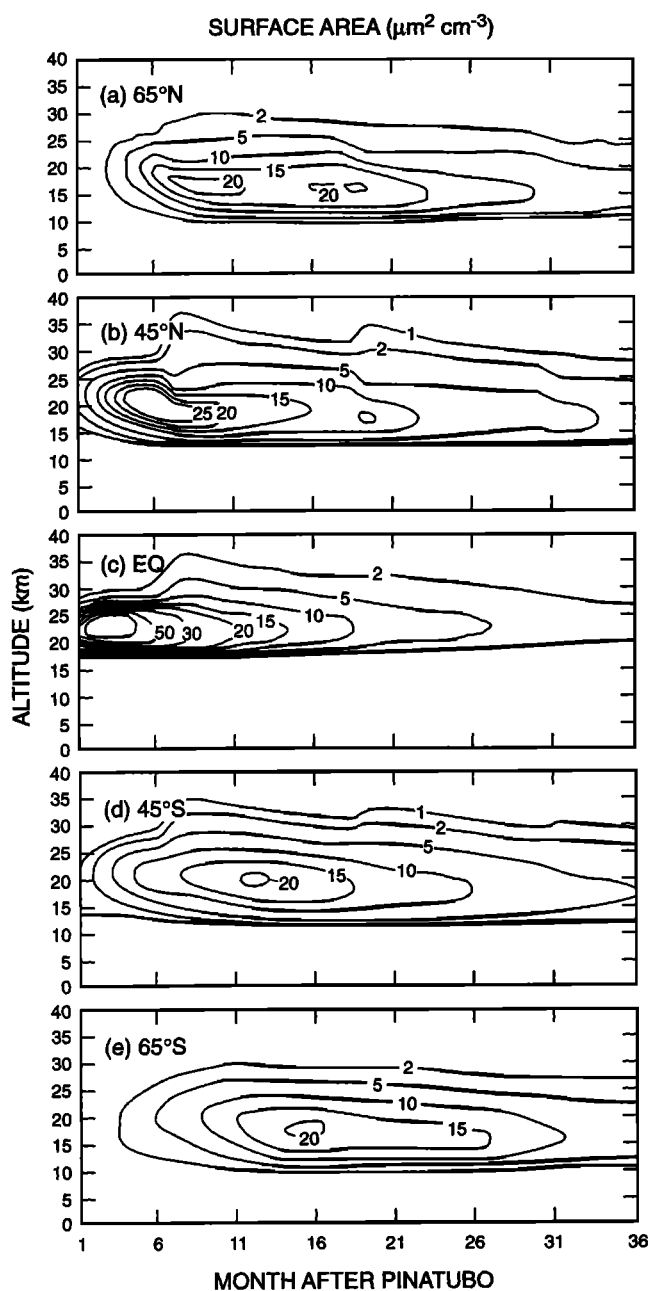


Figure 3. Simulated evolution of sulfate aerosol surface area density after the eruption of Mt. Pinatubo as function of height at 65°N, 45°N, equator (EQ), 45°S, and 65°S.

volcanic aerosol on Antarctic ozone occurs approximately 6 months later than in the Arctic.

Figure 4 shows a comparison between the observed and calculated evolution of the aerosol surface area at midlatitude in the northern hemisphere. The observations (Figure 4a) reported by D. A. D'Altorio et al. (personal communication, 1993) were made in Italy at 41°N between August 1991 and January 1992. Both observations and calculations show that the aerosol surface area reaches a maximum near 20 km, 5–6 months after the eruption. However, the calculated maximum ($25 \mu\text{m}^2/\text{cm}^3$) is slightly higher than the observed one ($20 \mu\text{m}^2/\text{cm}^3$). In addition, the secondary maximum ($10 \mu\text{m}^2/\text{cm}^3$) seen in the data 3–4 months after

the eruption is not produced in the calculation. This may be because zonally averaged models do not treat explicitly the perturbations associated with the presence of large scale waves.

In summary, the calculated evolution and distribution of the aerosol surface areas are in reasonable agreement with the observations and therefore applicable for studying volcanic aerosol perturbations on the atmosphere after the eruption of Mt. Pinatubo.

4. Effects of Volcanic Aerosols on Stratospheric Ozone

The presence of enhanced aerosol load in the stratosphere is expected to perturb the radiative, dynamical, and chemical fields in the atmosphere, including the abundance of ozone. Several competing mechanisms have to be considered, including (1) the local heating of air masses inside the volcanic cloud and the associated changes in the meridional circulation, (2) the absorption and backscattering of photolytic (solar) radiation, and (3) enhanced heterogeneous chemical reactions on the surface of the sulfate aerosols. The radiative contribution of these three effects to changes in the ozone concentration is discussed in the following sections. An additional effect, which is ignored in the present study but could have affected the radiative balance and ozone

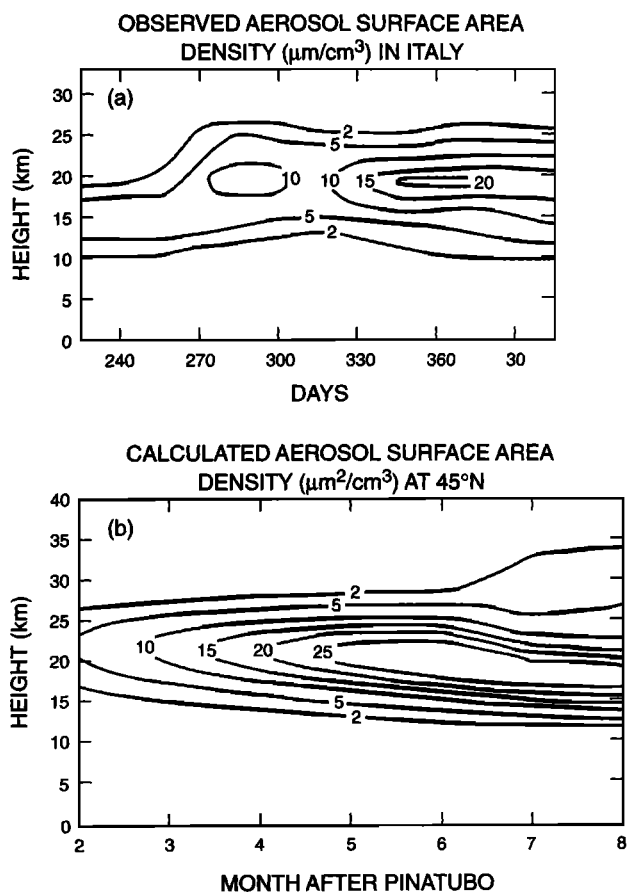


Figure 4. Comparison of measured (D. A. D'Altorio et al., personal communication, 1993) and calculated time evolution of sulfate aerosol surface area density after the eruption of Mt. Pinatubo in midlatitude of the northern hemisphere.

budget during the first month following the eruption of Mt. Pinatubo, is the absorption of solar radiation by the SO_2 cloud and the production of ozone in the tropics by gas phase processes involving the photolysis of SO_2 followed by the reaction between SO and O_2 [Crutzen and Schmailzl, 1983; Bekki *et al.*, 1993]. These effects are believed to become negligible a few weeks after the eruption because SO_2 is rapidly converted into sulfates.

4.1. Heating Effect

The absorption of terrestrial (longwave) and solar (shortwave) radiation by the volcanic cloud produces a local heating which is expected to perturb the circulation of the atmosphere. Approximately 2 months after the eruption, the volcanic cloud located in the tropics was relatively dense, and according to the model, the peak concentration of sulfate mass (130 parts per billion by mass) was located near the pressure surface of 30 mb (approximately 25 km). The different components of the heating rate by the cloud are represented as a function of pressure in Figure 5. Clearly, the largest contribution (up to 0.22 K/d) is provided by the absorption of terrestrial radiation. The absorption of solar radiation leads to a heating rate which never exceeds 0.08 K/d. This value is reduced to 0.06 K/d when the effect of scattering by the particles is taken into account. Backscattering of shortwave radiation produces a slight heating (less than 0.025 K/d) above the volcanic cloud. The contribution of scattering to the total heating rate is relatively small (less than 10% of the peak value) and has therefore been ignored in the assessment of ozone changes due to heating effects.

The time evolution of the perturbation temperature at 20 km is shown in Figure 6 (top) as a function of latitude during

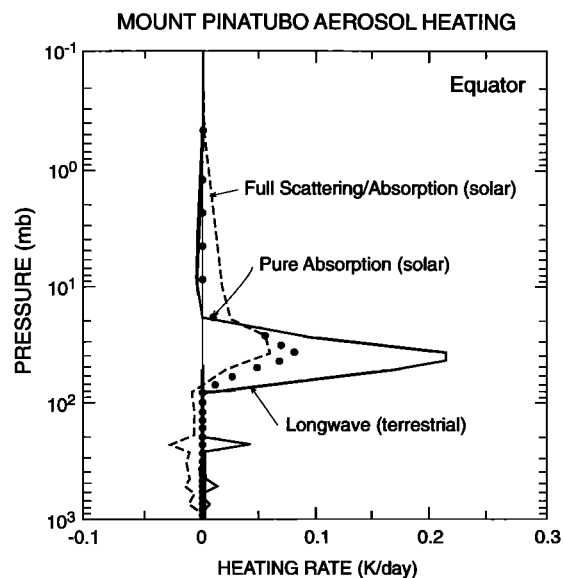


Figure 5. Perturbations in the radiative heating rate due to aerosol, about 1 month after eruption, for a total aerosol mass loading of 0.0438 g/m^2 and a peak concentration of 130 parts per billion by mass around 30 mb. Solid line, longwave perturbation; solid circles, solar perturbation with pure absorption for the incident beam; dashed line, combined effect with scattering and absorption. Typical tropical profiles for temperature and specific humidity, with three levels of clouds in the troposphere and a solar zenith angle of 60° .

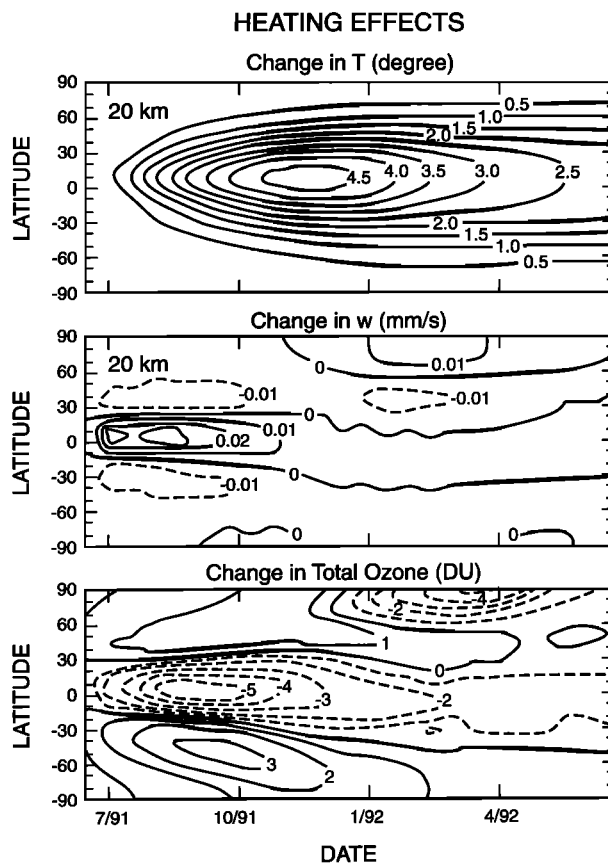


Figure 6. Calculated perturbation temperature (degrees Kelvin) and vertical velocity at 20 km of altitude, and ozone column abundance (DU (Dobson units)) as a function of time due to aerosol heating after the eruption of Pinatubo.

a period of 1 year following the eruption. The largest perturbation is found in the tropics, with a maximum (4.5 K) occurring between 5 and 6 months after the injection of SO_2 into the stratosphere. The change in the vertical velocity, shown in Figure 6 (center), is largest during the first 5 months, with ascending motions between 10°S and 20°N and descending motions at midlatitudes of both hemispheres relative to the background circulation. The perturbed vertical velocity of the order of 0.01 mm/s (with a maximum of 0.03 mm/s at the equator) is small compared with background velocities of approximately 0.25 mm/s. The changes in the ozone column abundance predicted (Figure 6, bottom) during the few months following the eruption and resulting from these dynamical perturbations are characterized by a reduction of approximately 5 Dobson units (DU) (approximately 2%) near the equator and an increase of 2–3 DU at midlatitudes in both hemispheres. During the first 4 months following the eruption, the temperature at the equator increases by approximately 1 K/month, in agreement with observations. The temperature perturbation, however, seems to fade out faster in the observation than in the calculation (see Figure 7a). This overestimation is believed to be associated with aerosol uncertainties in the calculation of the radiation effects of aerosols. These include the approximation of a purely absorbing aerosol, the error in the particle size distribution, and assumption made for the tropospheric cloudiness. The total uncertainty in the net

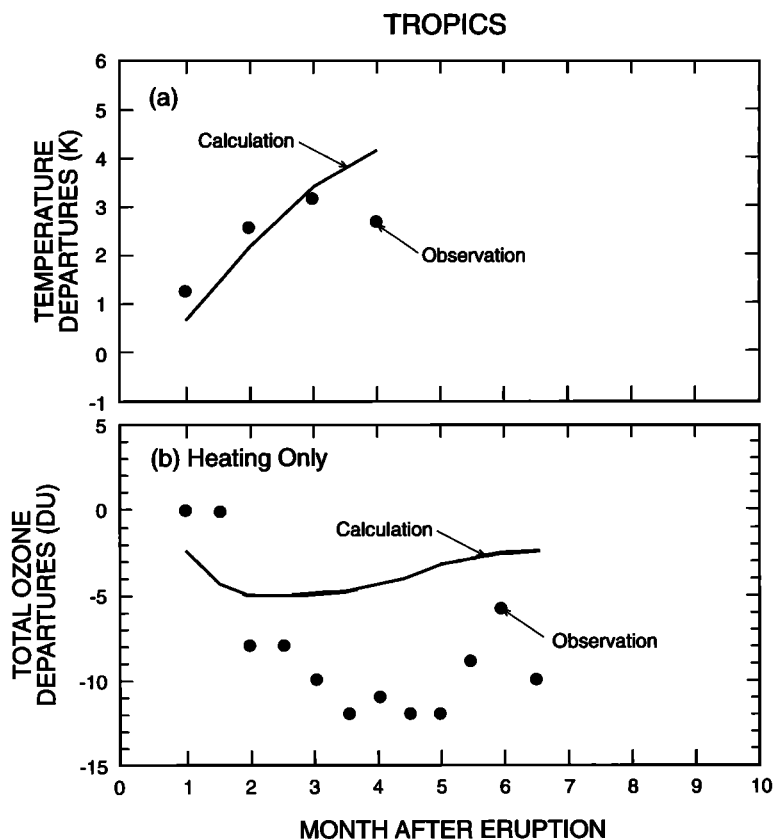


Figure 7. Comparison of measured [Labitzke and McCormick, 1992] and calculated changes (a) in the tropical temperature and (b) in total ozone concentration at the equator (DU) after the eruption of Mt. Pinatubo.

heating rate calculation is approximately 20%. Note that although the calculation overestimates the increase in temperature, the simulated perturbation in the ozone column due to the radiative effect of aerosol is smaller by a factor of 2 than that reported by Schoeberl *et al.* [1993] (see Figure 7b). A possible explanation for this discrepancy is that the perturbed circulation calculated by the model is unrealistically weak. This is consistent with the fact that, in the model, the aerosol cloud spreads too rapidly: Since the circulation is forced by the meridional gradient in the net heating rate (rather than the heating rate itself), the dynamical response should be too weak and consequently the temperature response should be too high. Perhaps other factors, such as a photolysis effect, play an important role in the tropical ozone perturbation.

4.2. Photolysis Effect

The presence of a relatively dense aerosol cloud after the eruption of Mt. Pinatubo leads to absorption and backscattering of solar radiation, especially in the tropics. As a result, the photolysis rate of all atmospheric molecules was reduced below the cloud, and for molecules such as ozone which are photolyzed at sufficiently long wavelengths (e.g., >300 nm), the photolysis rate was enhanced above it. Figures 8a and 8b show the percentage change in the photodissociation frequency of molecular oxygen and ozone, respectively. The radiative impact of the volcanic cloud on the production of O_3 (by O_2 photolysis) is insignificant since its absolute value below 20 km is extremely small. The increase in the photol-

ysis of O_3 , which converts more ozone molecules into oxygen atoms near 25–30 km of altitude, is responsible for a reduction in the ozone column abundance, which is of the same order as the reduction caused by dynamical perturbations (see Figure 8c). When these two effects are added, the calculated reduction in the ozone column at the equator reaches 10 DU 3–4 months after the eruption and is relatively close to the TOMS observed depletion reported by Schoeberl *et al.* [1993]. It is, however, smaller than the ozone decreases determined between August and November 1991 from electrochemical concentration cell (ECC) sonde data and Stratospheric Aerosol and Gas Experiment (SAGE II) climatology [Grant *et al.*, 1994].

4.3. Effects of Heterogeneous Chemistry

As already found by Brasseur and Granier [1992], the effect of heterogeneous chemistry on the ozone abundance is relatively small during the first months following the eruption of Mt. Pinatubo. As time evolves, however, the volcanic cloud is dispersed and (see Figure 9a) the surface area density at mid- and high latitudes increases progressively, while it begins to decrease in the tropics 3–4 months after the eruption. A major consequence of the presence of sulfate aerosols in the lower stratosphere is that nitrogen oxides are converted into nitric acid (reaction 1), but as the photolysis frequency decreases significantly with increasing latitude, the net efficiency of NO_x to HNO_3 conversion is largest at high latitudes and during the winter season, when solar zenith angles are high [Hofmann and Solomon, 1989; So-

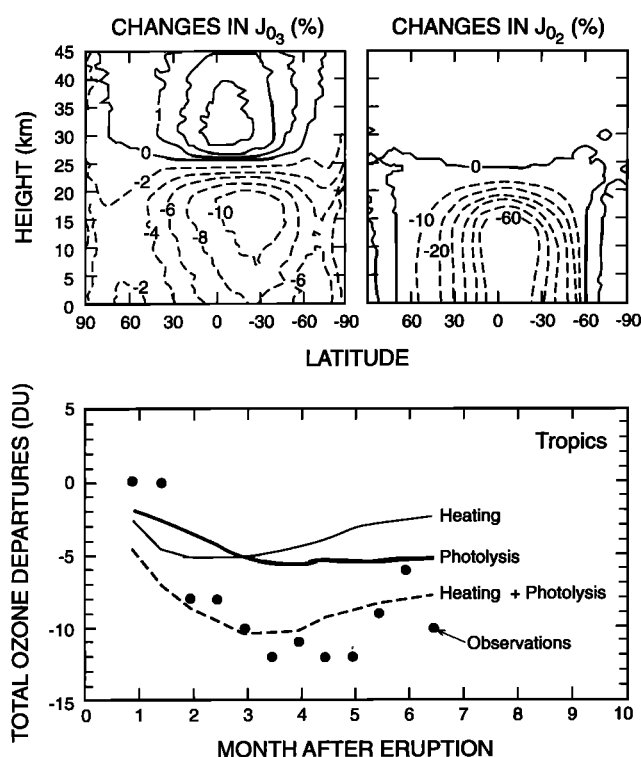


Figure 8. Relative changes (percent) as a function of latitude and height [October 1992] in the photolysis frequency of (a) ozone and (b) molecular oxygen, and (c) changes in total ozone (Dobson units) in the tropics due to the radiative effects of sulfate aerosol during 6 months after the eruption of Mt. Pinatubo.

lomon et al., 1993]. The largest enhancements in ClO concentrations and depletion in ozone are therefore expected to be found in winter near the terminator. This conclusion is

reinforced by the fact that the conversion of ClONO₂ into active chlorine by reaction 2 is most rapid in cold air masses [Tolbert *et al.*, 1988; Hanson and Ravishankara, 1991; Toon *et al.*, 1993] and therefore is maximized in the same regions and at the same time of the year. The accommodation coefficient of reaction 2 remains, however, uncertain, so that two cases have been considered. In the first of them (case A), only reaction 1 is taken into consideration, while in the second case (case B), both reactions are taken into account.

Figures 9a–9d show for the northern hemisphere (0°–90°N) at 20 km of altitude the evolution of the surface area density provided by volcanic sulfate aerosols, the reduction in the NO₂ concentration in response to the volcanic perturbation, the corresponding increase in the ClO concentration, and the percentage change in the ozone density, respectively, during the first year following the eruption. In this simulation (not including the radiative perturbation) the only heterogeneous reaction involved is the conversion of N₂O₅ on aerosol surface (case A). NO₂ is depleted at midlatitudes by as much as a factor of 2 (300 parts per trillion by volume [pptv]) in late summer. A 50% reduction (150 pptv) is predicted in the tropics. At the same time ClO is enhanced by as much as 16 pptv at high latitude (near the terminator) in winter. In relative terms (not shown), the increase in ClO concentration is of the order of 50% from the equator to 75°N in December and from the equator to 45°N in April and is less further north. It is of the order of 20% near the terminator. For case A, the model predicts a 4% reduction in the 20-km altitude ozone density at 60°N–75°N in late winter to early spring. In summer, 10 months after the eruption, an enhancement in the ozone concentration is found at latitudes higher than 45°N.

The evolution of the same quantities for the second year following the eruption of Mt. Pinatubo (case A) is shown in Figure 10. During this period, the surface area density at 20 km is decreasing with time at all latitudes except north of 60°N, where a slight increase is still visible until January

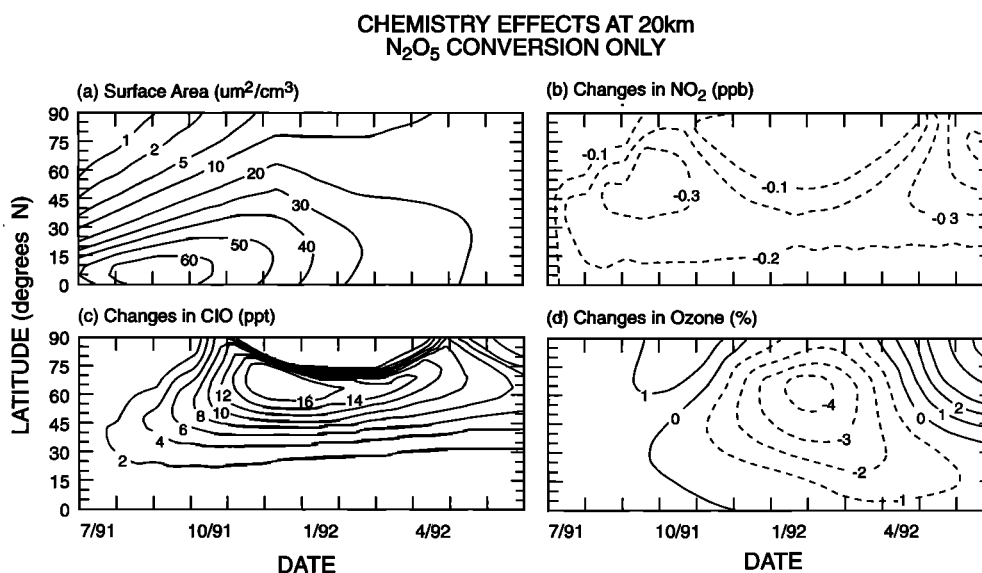


Figure 9. Calculated changes in (a) the aerosol surface area density, (b) the NO₂ concentration, (c) the ClO concentration, and (d) the O₃ concentration at 20 km of altitude in the northern hemisphere due to the effects of the chemical heterogeneous reaction during the first year following the eruption of Mt. Pinatubo (July 1991 to June 1992).

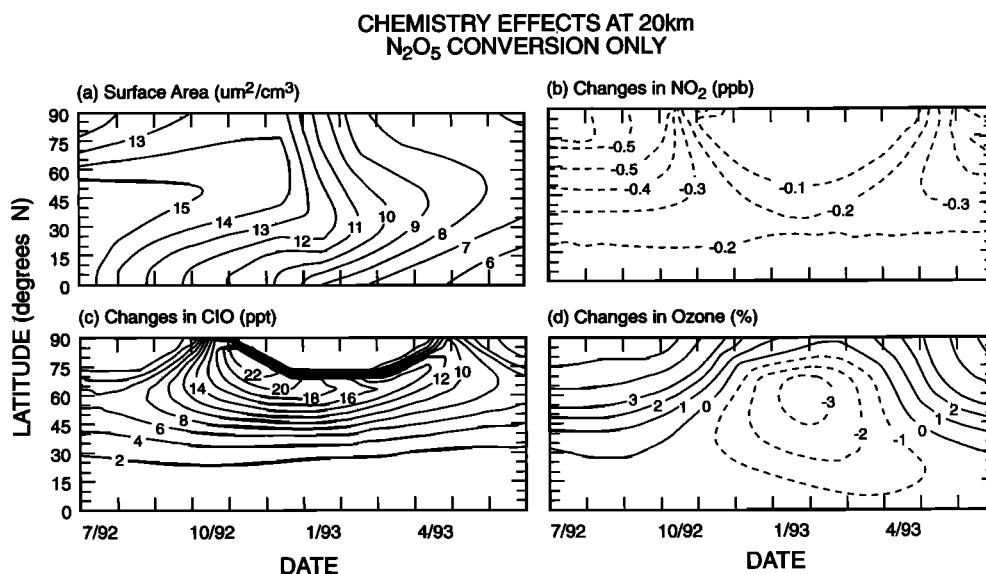


Figure 10. Same as Figure 9 but for the second year after the eruption of Mt. Pinatubo (July 1992 to June 1993).

1993. The magnitude of the calculated reduction in NO₂ and in the calculated increase in ClO during this second year is quantitatively similar to that during the first year, in spite of the reduction in the surface area density of the volcanic aerosols. This is attributed to a “saturation effect,” which is discussed in section 4.6 (see also Prather [1992] and Fahey *et al.* [1993]). Note that the maximum reduction in the ozone concentration at 20 km (in March 1993) is now of the order of 3%, while at the same time the aerosol surface area at this height is of the order of 10 $\mu\text{m}^2/\text{cm}^3$.

Figures 11, 12, and 13 show the time evolution for three consecutive years of the surface area density and the

changes in NO₂, ClO, and ozone concentrations at 20 km in the northern hemisphere when the effects of both reactions (1) and (2) are taken into account (case B). As indicated earlier, the rate at which ClONO₂ is converted into active chlorine is highly dependent on the chemical composition of the aerosol and hence on the temperature and water abundance in the lower stratosphere. Because, especially at high latitudes, the temperature calculated by the model in the range from 10 to 20 km is several degrees K lower than the observed (climatological) temperatures, and consequently the accommodation coefficient for reaction (2) used in the model could be as much as a factor of 20 higher than in

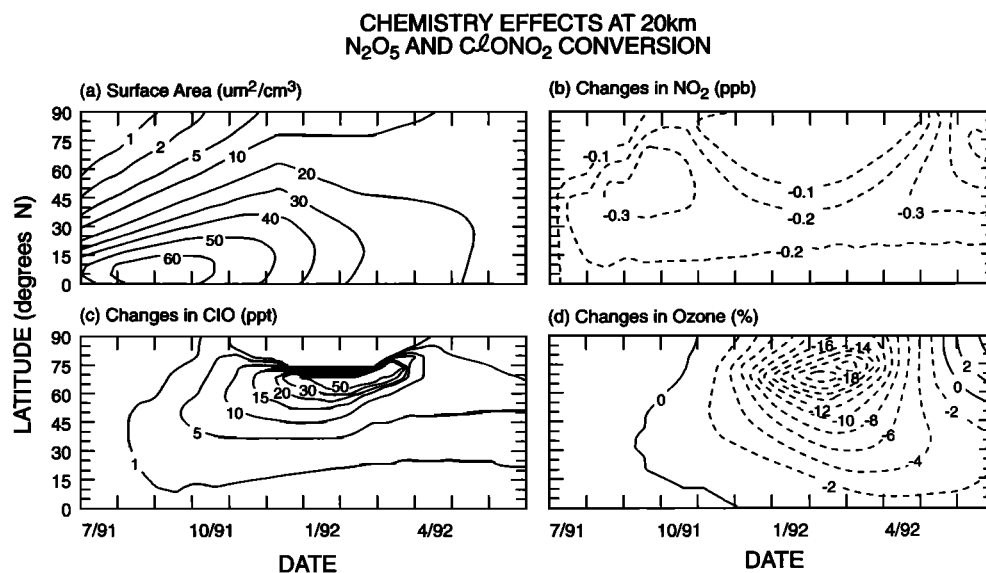


Figure 11. Calculated changes in (a) the aerosol surface area density, (b) the NO₂ concentration, (c) the ClO concentration, and (d) the O₃ concentration at 20 km in the northern hemisphere due to the effects of chemical heterogeneous reactions (1) and (2) during the first year following the eruption of Mt. Pinatubo (July 1991 to June 1992). Reaction coefficient 2 is calculated by using the observed (climatological) temperature [Randel, 1992].

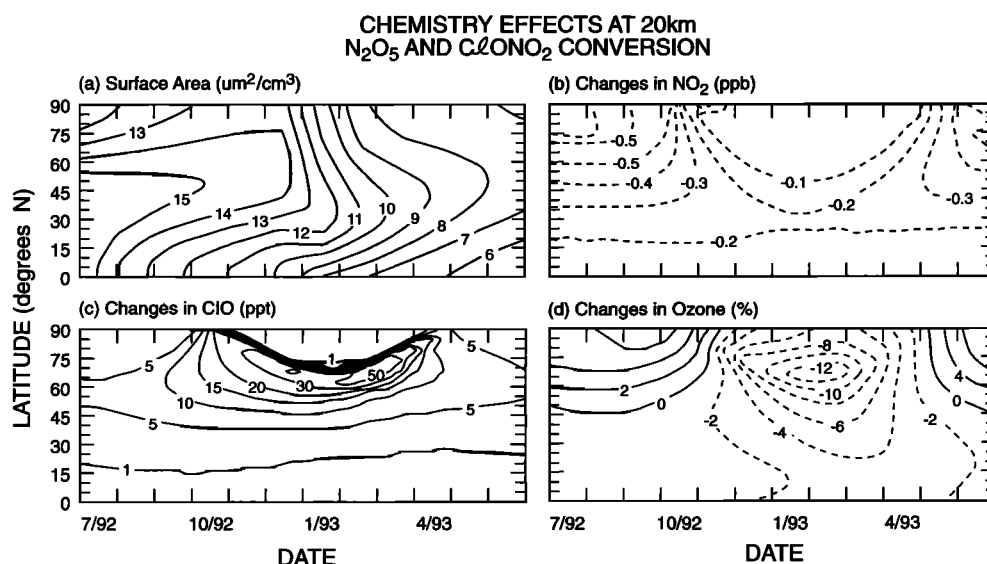


Figure 12. Same as Figure 11 but for the second year after the eruption of Mt. Pinatubo (July 1992 to June 1993).

reality, we have chosen to estimate the value of $\gamma_2(T, H_2O)$ from climatological values of the temperature [Randel, 1992]. As will be shown later, the use of this assumption significantly affects the calculated changes in the abundances of chemical compounds, including stratospheric ozone. Under the adopted conditions, the reduction in NO_2 is very similar to the results obtained in case A, but the enhancement in the ClO mixing ratio, which, in case A, reached a maximum of 16 pptv in January 1992 near the terminator, reaches in case B a maximum of more than 50 pptv in March 1992. The maximum reduction in the 20-km ozone concentration (also in March) is 18% and is predicted to occur near the terminator (solar zenith angle effects on the photolysis of nitric acid). This value is larger by a factor of 4 than in case A. A comparable reduction (maximum of 12% at 65°N in March 1993) is predicted for the second year of the model simulation (see Figure 12). When the model simulation is

extended over a third year (Figure 13), the predicted reduction in the ozone density reaches a maximum of 6% in February 1994 in spite of the fact that the aerosol surface area has decreased to approximately $5 \mu m^2/cm^3$. Thus in early 1994, the reduction in the ozone density at 20 km associated with the eruption of Mt. Pinatubo in 1991 should remain significant and only a factor of 3 smaller than in early 1992. Note that as in case A, an increase in the 20-km ozone is predicted at high latitudes each year during the summer season.

In order to assess the altitude dependence of the changes in the key chemical variables discussed above, Figure 14a depicts the evolution versus height of the aerosol surface area density at 60°N during the first year following the eruption. Although the volcanic perturbation between July and November 1991 remains localized primarily between 10 and 26 km, it extends to higher altitudes as time evolves and

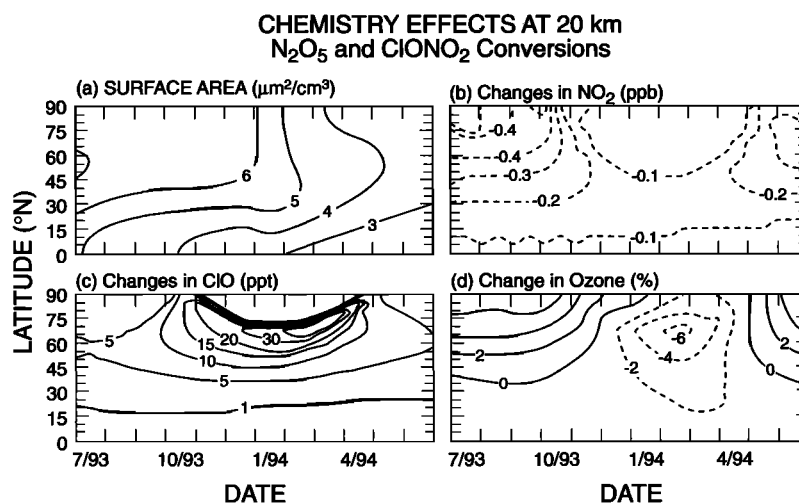


Figure 13. Same as Figure 11 but for the third year after the eruption of Mt. Pinatubo (July 1993 to June 1994).

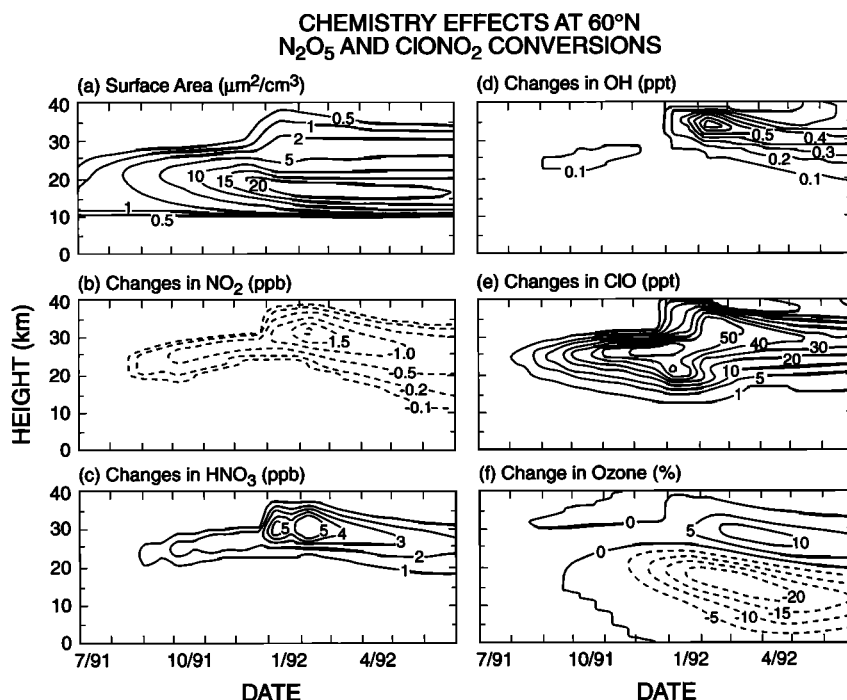
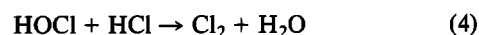
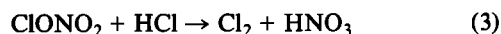


Figure 14. Calculated changes in (a) the aerosol surface area density, (b) the NO₂ concentration, (c) the HNO₃ concentration, (d) the OH concentration, (e) the ClO concentration, and (f) the O₃ concentration at 60°N between 0 and 40 km of altitude due to the effects of chemical heterogeneous reactions (1) and (2) during the first year following the eruption of Mt. Pinatubo (July 1991 to June 1992). Reaction coefficient 2 is calculated by using climatological temperature [Randel, 1992].

reaches 37 km in January 1992. Afterwards, as aerosols coagulate and sediment, a slow descent of the stratospheric aerosol layer occurs, and above approximately 20 km of altitude, the surface area density decreases with time. Reductions in the NO₂ concentration at 60°N (Figure 14b) follow the patterns associated with the evolution of the aerosol layer, with the largest values occurring at 30 ± 5 km of altitude. A significant increase in the nitric acid mixing ratio is predicted between 20 and 35 km, reaching values as high as 5 parts per billion by volume (ppbv) in January and February (Figure 14c). The major role played by liquid aerosols above 30 km in determining the abundance of HNO₃ in the polar winter at high latitudes was recently pointed out by Garcia and Solomon [1994] and is confirmed by the present study for volcanic conditions. Significant change is also predicted for the OH concentration above 25 km (Figure 14d). The largest absolute increase in ClO (see Figure 14e) at 60°N latitude (case B) occurs in January 1992, with values reaching 80 pptv at 25–30 km. A time-altitude cross section at 70°N would show a maximum ClO increase of 120 pptv in February. The change in the ozone density at 60°N (Figure 14f) is characterized by an increase at altitudes higher than approximately 25 km (due to a reduction in the efficiency of the NO_x catalytic destruction of O₃) and by a decrease at altitudes below this level (where the increase in the concentration of OH and ClO enhances the overall destruction rate of O₃). The ozone change is consistent with the observation reported by Hofmann *et al.* [1993]. The relative local changes in the ozone density at 60°N slightly exceed 20% (case B) when climatological temperatures are used for the calculation of the accommodation coefficient for

reaction (2). Similar features are simulated during the second year following the eruption (Figures 15a–15f).

Laboratory studies [Hanson and Ravishankara, 1991] have shown that HCl could dissolve in aerosol droplets and that the reactions



should be considered potential mechanisms for the conversion of chlorine reservoirs (e.g., HCl and ClONO₂) into active chlorine. Uptake of OH and HO₂ onto sulfuric acid particles seems to be an important process [Gershenson *et al.*, 1987; Mozurkewich *et al.*, 1987; Hanson *et al.*, 1992], but the impact of these reactions for Mt. Pinatubo aerosols seems to be insignificant [Hanson *et al.*, 1994]. To account for the possibility of accelerated conversion of chlorine reactions when HCl is dissolved in sulfate-water aerosol particles, we have added reaction (3) to our chemical scheme with an accommodation coefficient derived from Table 4 in Hanson *et al.* [1994]. This accommodation coefficient increases dramatically with decreasing H₂SO₄ weight percentage in the aerosol and hence with decreasing temperature. According to Hanson *et al.* [1994], it could reach 5 × 10⁻³, 3 × 10⁻², and 9 × 10⁻² for H₂SO₄ weight percentages of 55%, 50%, and 45%, respectively. Where included in the model, reaction (3) does not produce any dramatic changes in the response in the northern hemisphere to the eruption of Mt. Pinatubo (when the climatological temperature is used in the quantification of heterogeneous processes). However, in

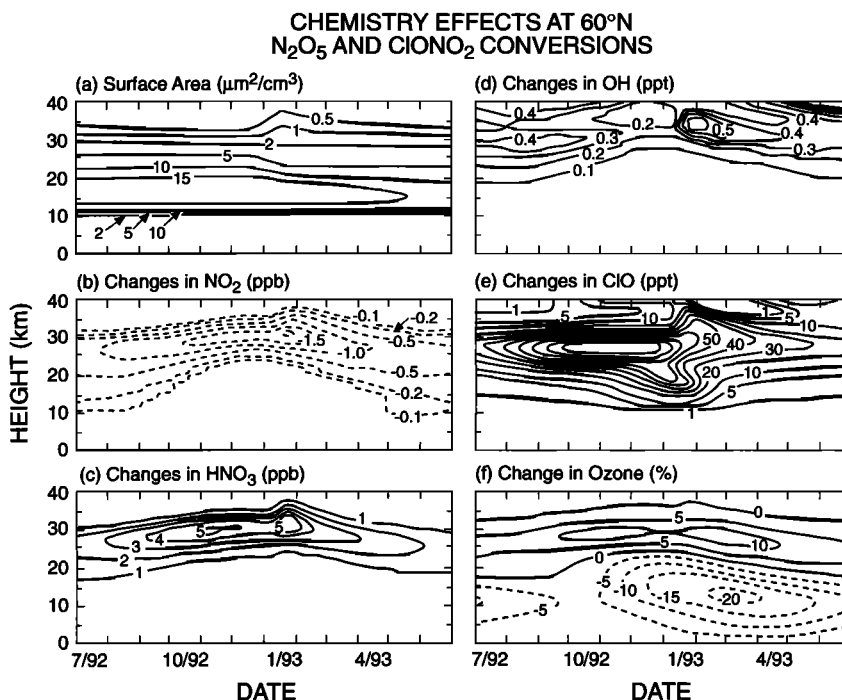


Figure 15. Same as Figure 14 but for the second year after the eruption of Mt. Pinatubo (July 1992 to June 1993).

the southern hemisphere, when the polar winter temperature is approximately 10 K lower than in the opposite hemisphere, chlorine activation is increased dramatically south of 60°S in September and October and high levels of ClO (above 500 pptv; see Figure 16) are produced at the edge of the polar night region. It is therefore likely that significant amounts of chlorine could be activated on sulfate aerosol

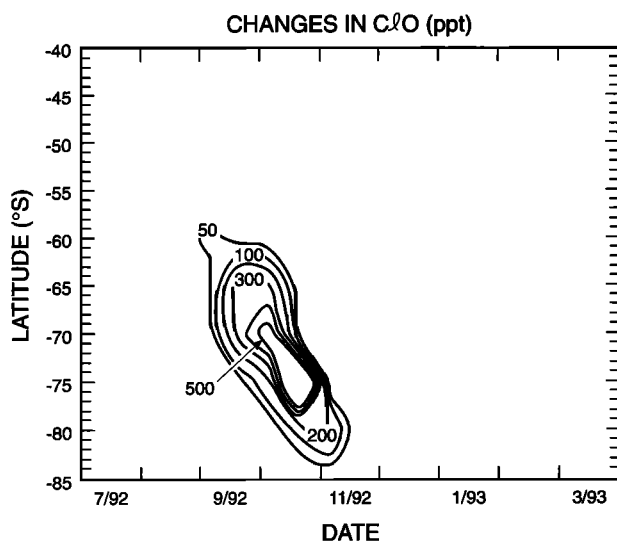


Figure 16. Enhancement in the concentration of ClO (parts per trillion by volume) in the southern hemisphere in response to the presence of Pinatubo aerosols in the stratosphere. The dilution of HCl inside sulfate aerosol droplets is taken into account. Reaction (3) plays a significant role in cold polar regions and produces the large ClO concentration in September and October near the terminator.

particles just prior to the formation of polar stratospheric clouds. The dramatic chlorine activation under cold conditions was already noted by *Hanson et al.* [1994]. This effect should be most pronounced during postvolcanic periods but should also occur for background conditions. Heterogeneous processes at temperatures near 200 K, corresponding to the transition between liquid aerosol particles and nitric acid trihydrate (NAT), are not well understood and need to be elucidated in order to understand the causes of ozone depletion at high latitudes. It is likely that at temperatures near the threshold for NAT formation or if supersaturation prevails, aerosols could be as efficient in converting ClONO₂ as polar stratospheric clouds, especially under volcanic conditions.

4.4. Overall Effects on Ozone

In order to quantify the relative importance of the radiative, dynamical, and chemical effects leading to ozone changes on a nearly global scale, we have integrated between 65°S and 65°N the amount of ozone calculated by the model and have derived for 3 years following the eruption of Mt. Pinatubo its relative departure from the values in a model simulation in which the aerosol level is representative of background conditions (see Figure 17). When only the radiative effects are taken into account (scattering of solar light and absorption of terrestrial radiation by volcanic aerosols as well as the resulting changes in the atmospheric circulation), the global reduction in total ozone reaches 1.3% during the first year following the eruption and gradually decreases during the second year. When only the chemical effects associated with heterogeneous concentration mechanisms are considered, a slight increase (approximately 0.5%) is predicted during the first year (July 1991 to May 1992) and a significant decrease is calculated during the second year,

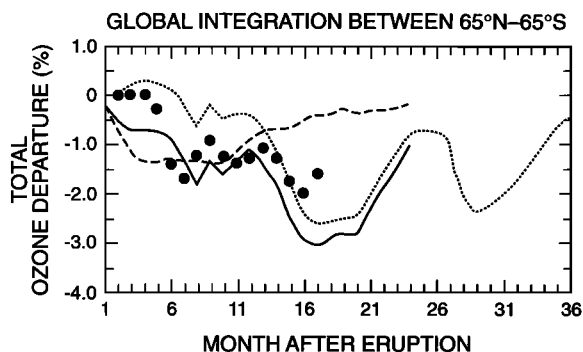


Figure 17. Comparison between observed [Gleason *et al.*, 1993] and calculated changes in global ozone amount (latitudinal weighted integration between 65°S and 65°N) after the eruption of Mt. Pinatubo. Reaction coefficient 2 is calculated by using climatological temperature [Randel, 1992]. The contribution of chemical and radiative effects is shown.

with a maximum of 2% in October 1992. Finally, when all processes are considered simultaneously, an intermediate ozone response is found, in good agreement with the ozone depletion reported by Gleason *et al.* [1993]. During the first year, the reduction in the integrated ozone column abundance is thus related primarily to radiative effects, while during the second year the calculated depletion is associated with heterogeneous chemistry. This conclusion is consistent with the finding [Gleason *et al.*, 1993] that ozone reduction in the northern hemisphere was larger during the 1992–1993 winter than 1 year earlier, even though the global aerosol load had become smaller.

Finally, Figure 18 shows the calculated change in the ozone column abundance in the tropics and in the northern hemisphere during 3 years following the eruption of Mt. Pinatubo. Values in the southern hemisphere are not shown since they are severely affected by heterogeneous processes inside polar stratospheric clouds, an effect that is not considered explicitly in the present study. The predicted changes are compared with values deduced from TOMS observations after removal of QBO effects (W. J. Randel and F. Wu, manuscript in preparation, 1994). The model reproduces remarkably well the general features deduced from satellite observations. It predicts, for example, the reduction in total ozone observed near the equator and simulates within 25% the ozone changes observed at high latitudes during the two springs following the volcanic eruption. Some discrepancies are also noticeable (e.g., the overestimation by the model of the ozone reduction between 10°N and 40°N from July to September 1991), but such differences are to be expected because of the model formulation and simplifications in the transport and chemical schemes.

Our calculations show that the key parameter is not the globally integrated aerosol load nor the value of the surface area density (since saturation occurs for relatively small surface area density; see section 4.6), but the latitude at which the aerosols are present. It took several months before large amounts of aerosol were transported into polar regions, where their chemical effects become substantial. The major cause for this latitudinal effect is the slow photolysis rate of nitric acid in a region where the solar zenith angle is generally high [Hofmann and Solomon, 1989; Solomon *et al.*, 1993] and hence the high level of “denoxification” (low

NO_x/NO_y concentration ratio) in this region of the atmosphere, maintaining high concentrations of ClO. Another important factor affecting the calculated ozone depletion is the temperature at which reaction (2) occurs. As indicated earlier, in the model calculations reported above, the accommodation coefficient (reaction probability) for the ClONO_2 conversion on aerosols was derived by using climatological temperatures. The calculation was redone (case C) by using the temperature derived by the model itself. The difference between the calculated and climatological temperature in March is shown in Figure 19 as a function of latitude and height. In spite of the fact that the temperature differences do not exceed 10 K except in the polar regions, the ozone reductions calculated in the two cases are substantially different, as shown by Figure 20. This figure depicts the departure of the total ozone burden (integrated from 65°S to 65°N) from its value derived in the absence of volcanic eruption. The results refer to the second year following the eruption. When the accommodation coefficient γ_2 is derived from calculated temperatures, the ozone reduction is at least a factor 2 or 3 larger than if the climatological temperatures are adopted. The agreement between calculated and observed ozone changes during the second year of the model integration is best for case B. The changes in the ClO and O_3 concentrations at 20 km of altitude in response to the Pinatubo aerosols are shown in Figure 21 for a case in which the calculated temperature is used to estimate the accommo-

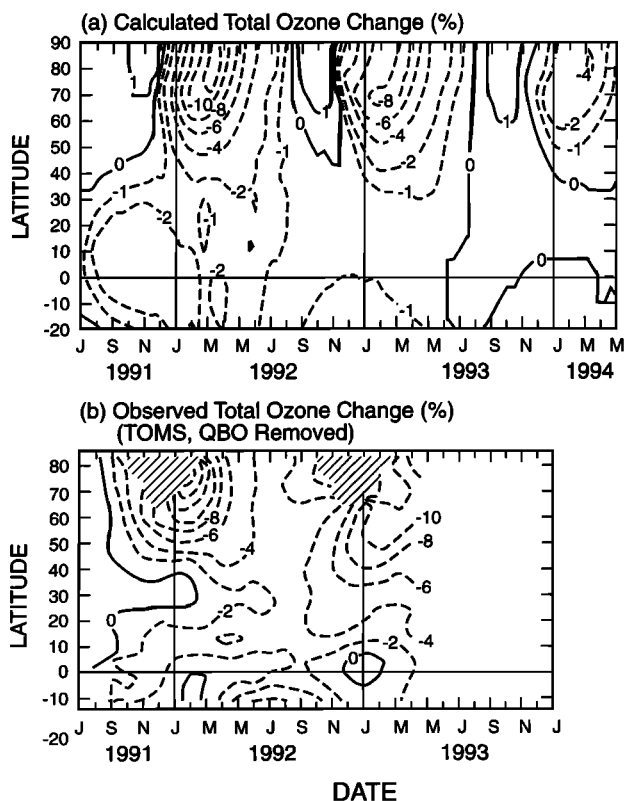


Figure 18. Comparison between observed (TOMS reported by W. J. Randel and F. Wu (manuscript in preparation, 1994)) and calculated changes in total ozone in northern hemisphere and tropics after the eruption of Mt. Pinatubo. The QBO effect is removed from observation. The calculation includes both radiative and chemical effects.

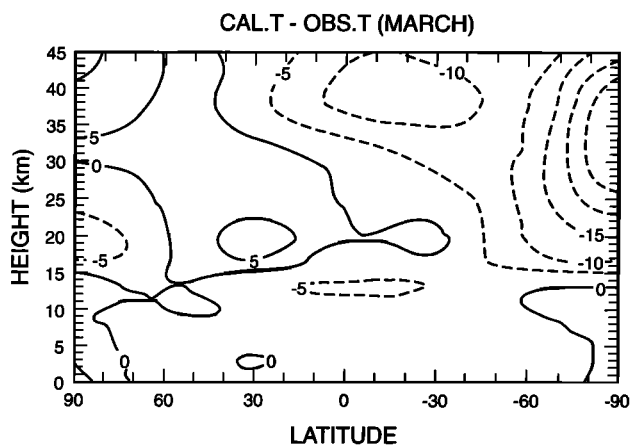


Figure 19. Difference (degrees Kelvin) between calculated and climatological temperatures [Randel, 1992] for March conditions. The dashed and solid lines represent calculated temperatures below and above observed temperatures, respectively.

dation coefficient of reaction (2). The perturbations are significantly larger than those shown in Figure 12.

4.5. Saturation Effects

The chemical response of the atmosphere to large volcanic eruptions remains similar for 2 to 3 years despite a substantial decrease with time in the aerosol load, because the rate-limiting step in the conversion of nitrogen oxides into nitric acid is not provided by reaction (1) but by reaction (3) in the following sequence: $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$ (reaction (3)), $\text{NO}_3 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$ (reaction (4)), and $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ (aerosol) $\rightarrow 2 \text{HNO}_3$ (reaction (1)). Figure 22, which shows the changes in the concentrations of NO_2 , HNO_3 , and ClO with aerosol surface area density at 25 km during February, suggests that in the tropics (Figure 22a), saturation is achieved for surface areas of $10 \mu\text{m}^2/\text{cm}^3$, while at high latitudes (Figure 22c), the same situation is

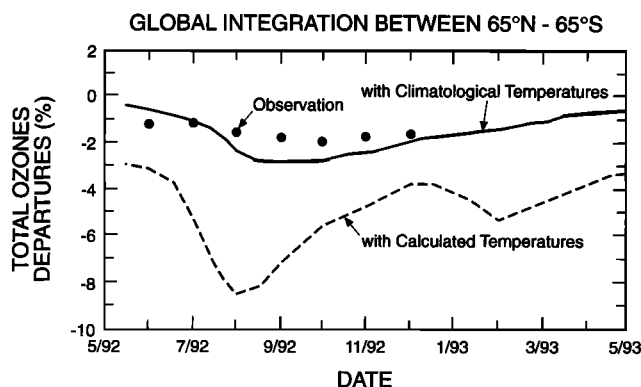


Figure 20. Observed [Gleason *et al.*, 1993] and calculated changes in global ozone (latitudinal weighted integration between 65°S and 65°N) between May 1992 and April 1993. The dashed line represents the calculated ozone depletion in which calculated temperatures are used to calculate the accommodation coefficient of reaction (2). The solid line represents the calculated ozone depletion when the observed (climatological) temperature [Randel, 1992] is used to calculate the accommodation coefficient.

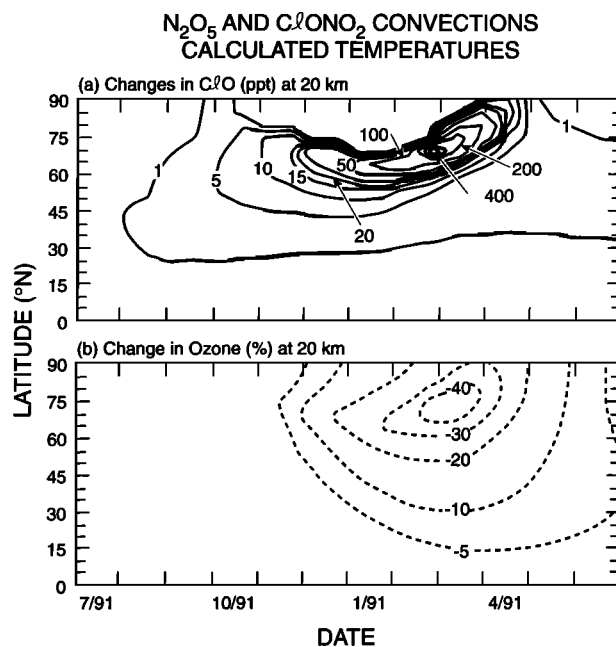


Figure 21. Calculated changes in (a) ClO concentrations and (b) O_3 concentrations at 20 km in the northern hemisphere due to the effects of chemical heterogeneous reactions (1) and (2) during the second year following the eruption of Mt. Pinatubo (July 1992 to June 1993). In this case, the accommodation coefficient for reaction (2) is calculated by using the temperature calculated by the model.

reached for much smaller areas ($1 \mu\text{m}^2/\text{cm}^3$) if the only heterogeneous conversion mechanism taken into account is reaction (1). If, however, both heterogeneous reactions (1) and (2) are included in the model calculation, the situation remains approximately the same at low and midlatitudes but is substantially modified at high latitudes. Figure 22c shows that in the case of ClO , the concentration continues to increase with surface area density for values higher than $10 \mu\text{m}^2/\text{cm}^3$. This result provides another example of the importance of the temperature-dependent conversion of ClONO_2 at high latitudes. Note that the saturation effect of NO_x species manifests itself in the NO_x/NO_y concentration ratio. This ratio, calculated as a function of the aerosol surface area density at 20 km of altitude, 45°N and equinox conditions (Figure 23), compares well with the values provided by Fahey *et al.* [1993] from their measurements in different air masses.

5. Summary and Conclusions

We have used a two-dimensional chemical-dynamical-radiation model of the middle atmosphere, coupled to a microphysical model of aerosol formation and fate, to simulate as a function of time the evolution of chemical compounds, including ozone, in the lower stratosphere. The advantage of such model is that it provides a quantitative estimate of the various dynamical, radiative, and chemical processes responsible for perturbations in the ozone layer in response to a volcanic perturbation. The microphysical model [Tie *et al.*, 1994] produces a distribution of the aerosol surface area density which is in relatively good agreement with available data. The heterogeneous conversion of N_2O_5

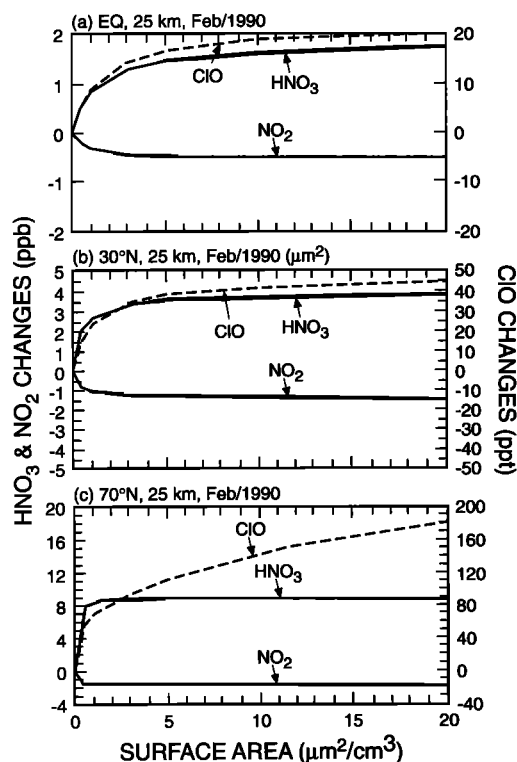


Figure 22. Calculated changes in HNO_3 , ClO , and NO_2 concentrations with increasing aerosol surface area density with (a and b) only heterogeneous chemical reaction 1 taken into account and (c) heterogeneous reactions (1) and (2) included in the model. The results are shown for 25 km at the equator (a) and at 30°N (b) and 70°N (c) (conditions representative of February 1990).

into HNO_3 on the surface of these sulfate aerosols appears to play an important role at midlatitudes, while the conversion of ClONO_2 , with a temperature-dependent rate, plays a key role at high latitudes in winter. In our standard simulations, the maximum reduction in the ozone concentration at 20 km is four times larger when the two heterogeneous reactions are taken into account than when only the N_2O_5 conversion is included in the model. The predicted reduction in the ozone concentration at 20 km is significantly higher

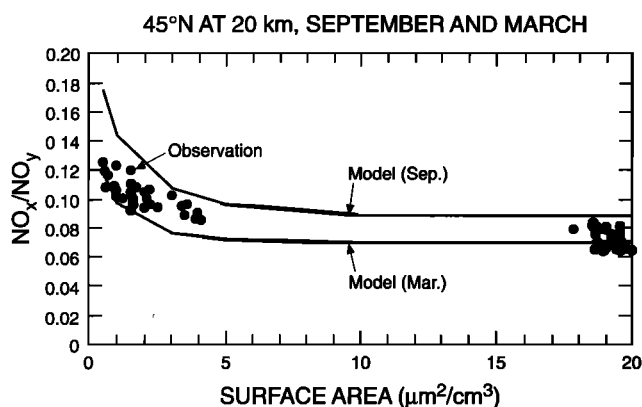


Figure 23. Observed [Fahey et al., 1993] and calculated NO_x/NO_y concentration ratio shown as a function of increasing sulfate aerosol area (equinox).

when the accommodation coefficient for reaction (2) is derived with the calculated temperature rather than the climatological (observed) one. Thus the magnitude of the ozone response to volcanic perturbations is highly dependent on the atmospheric temperature, so that the difference in the ozone decrease at high latitudes between two consecutive years may be due to a result of interannual variations in the temperature.

The model also suggests that, during the first year following the eruption, the observed ozone depletion is due primarily to dynamical and radiative effects which are predominant when the volcanic cloud is dense. As the aerosols reach polar regions several months after the eruption, the chemical effects tend to become dominant. The chemical effects are most efficient at high latitudes, where the photolysis of nitric acid (producing NO_x) is slow and the temperature is low, allowing heterogeneous conversion of ClONO_2 into active chlorine (ClO). The magnitude of the ozone depletion does not increase indefinitely with the aerosol burden (aerosol surface area density); it is saturated rapidly when the surface becomes larger than a few square micrometers per cubic centimeter. For large volcanic eruptions, the depletion of ozone is more sensitive to the level of chlorine in the atmosphere (amount of chlorofluorocarbons released) than to the amount of volcanic material injected into the stratosphere. The time period over which the atmosphere is perturbed increases, however, with the burden of SO_2 having reached the stratosphere.

It should be realized that, because of the limitations associated with two-dimensional models, especially with regard to their ability to simulate meridional transport, the results presented and discussed here should be regarded largely as qualitative rather than fully quantitative. The purpose was to explain some of the recent observations and provide some insight concerning the respective role of dynamics versus chemistry leading to the ozone reduction observed after the eruption of Mt. Pinatubo in June 1991. The model clearly suggests, like other similar studies [Pitari and Rizi, 1993; Bekki and Pyle, 1994], that the observed ozone decrease between 1991 and late 1993 was related to the eruption of Mt. Pinatubo.

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G. P. Brasseur, B. Briegleb, C. Granier, and X. Tie, National Center for Atmospheric Research, Atmospheric Chemistry Division, P.O. Box 3000, Boulder, CO 80307.

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