Model study of polar stratospheric clouds and their effect on stratospheric ozone
2. Model results

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Abstract. We use the detailed microphysical/chemical/dynamical two-dimensional model described in part I [*De Rudder et al.*, this issue] to study the effect of heterogeneous reactions occurring on the surface of polar stratospheric clouds (PSCs) on stratospheric ozone. The calculations show that the heterogeneous reactions occurring on the surface of PSCs are the likely causes of the ozone decrease observed from 1980 to 1990 in both Antarctica and the Arctic. The calculation shows that the dense sulfate aerosol cloud produced by the eruption of Mount Pinatubo (in the Philippines, 1991) has enhanced the formation rate of type I PSCs in the Arctic and the Antarctic. In the calculation, the concentration and surface area of type I PSCs are enhanced. The effect on the ozone depletion in the Antarctic is, however, limited due to fact that the conversion from $ClONO_2$ to ClO on PSCs is almost "saturated" under no-volcanic conditions. For the potential ozone depletion, the enlargement in the area covered by PSCs may therefore be more important than the increase in PSC density. The calculation also shows that, in the future, the density of PSCs in the Arctic could be enhanced owing to the potential emission of water vapor and nitrogen species by high altitude aircraft. The increase in PSC density could lead to a maximum of ozone depletion of 10% at the northern high latitudes in winter.

1. Introduction

Mother-of-pearl clouds have been observed in the cold polar vortex of the Antarctic since the 19th century [*Stanford and Davis*, 1974]. However, it is only since the discovery of the ozone hole in the early 1980's [*Farman et al.*, 1985] that the importance of these polar stratospheric clouds (PSC) for the chemistry of the lower polar stratosphere has been emphasized [*Solomon et al.*, 1986; *McElroy et al.*, 1986; *Solomon*, 1990]. It is now commonly accepted that PSC particles provide important sites for heterogeneous reactions to occur. These reactions contribute to the depletion of ozone by activating chlorine and, at the same time, by converting nitrogen oxides into nitric acid [*Fahey et al.*, 1989]. Models which are developed to simulate the fate of stratospheric ozone must include a representation of heterogeneous reactions on the surface of PSC particles and of sulfate aerosols. Earlier models [e.g., *Granier and Brasseur*, 1992] assumed that, as soon as the temperature drops below given temperature thresholds, the conversion of chlorine reservoirs into reactive chlorine is quasi- instantaneous, and large quantities of ozone are subsequently destroyed. More sophisticated approaches require that microphysical processes (nucleation, condensation, evaporation, and sedimentation) be explicitly simulated by the model, and that the particle surface area and sedimentation properties be accurately calculated. A microphysical model for sulfate aerosols has already been coupled to our two-dimensional chemical/transport model [*Tie et al.*, 1994a] to assess, for example, the impact of volcanic eruptions on the ozone layer [*Tie et al.*, 1994a,b].

In part I of this paper (*De Rudder et al.*, this issue), we have shown that our 2-D model, which accounts with some detail for microphysical processes, represents reasonably well the global distribution of type I and type II PSC (PSC I and PSC II) particles. In this paper, we will assess the impact of polar stratospheric clouds on ozone and other chemical species. We will also examine the effect of aerosols produced by the Mount Pinatubo eruption on the formation of PSCs. Finally, the effects of NO_x injected by the engines of a projected fleet of high speed civil transport (HSCT) on the formation of PSCs and stratospheric ozone will be estimated.

2. Model Results

2.1. Heterogeneous Reactions on the Surface of PSC Particles

Heterogeneous reaction $ClONO_2 + HCl(psc)$ converts inorganic chlorine reservoirs ($ClONO_2$ and HCl) into less stable chlorine

compounds (HOCl and Cl_2). The photolysis of HOCl and Cl_2 then leads to the formation of reactive chlorine radicals (Cl and ClO) [*Solomon et al.*, 1986; *Solomon*, 1990]. During the formation of PSCs, condensation processes convert a large amount of HNO_3 and H_2O vapor into a liquid or solid (ice) phase. Gravitational sedimentation which affects mainly PSC II particles leads to a permanent loss of HNO_3 (denitrification) and H_2O (dehydation) in the polar lower stratosphere. [*Fahey et al.*, 1989; *Kelly et al.*, 1989; *Salawitch et al.*, 1989; *Toon et al.*, 1990; *Kondo et al.*, 1990; *Kelly et al.*, 1990]. The reduction in the HNO_3 abundance reduces the concentration of NO_2, which leads to an increase in the ClO concentration due to the reduction in the $ClO+NO_2$ pathway. The dramatic increase in the ClO concentration resulting from chlorine activation and denitrification leads to the depletion of ozone inside the isolated polar vortex [*Solomon, et al.*, 1986; *Anderson et al.*, 1989a,b; *Solomon*, 1990]. The ozone destruction rate associated with PSC chemistry can be expressed by [*Solomon*, 1990]

$$(dO_3/dt) = -k_1[ClO][ClO] - k_2[ClO][BrO]$$

where k_1 and k_2 are the rate constants of the rate limiting reactions (ClO+ClO and ClO+BrO), and t is time. It must be kept in mind that the maximum ClO concentration is coincident with the maximum ozone loss rate, but not necessarily with the minimum ozone concentration.

Figure 1 presents the vertical distributions of ozone and ClO concentration calculated by the model, as well as of the surface areas provided by PSC I and PSC II particles. The results are shown at 80°S for selected dates from August 10 to December 8. The distri-
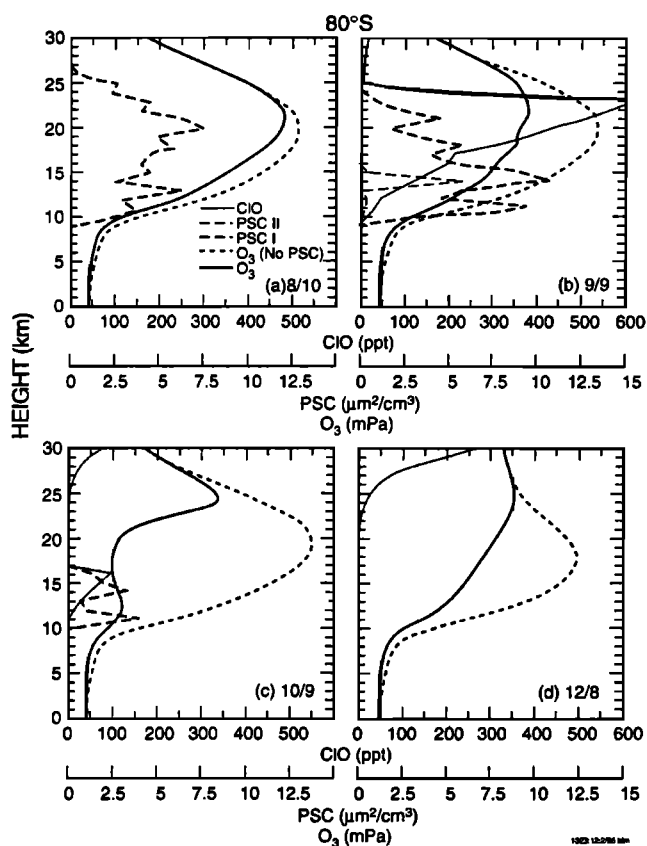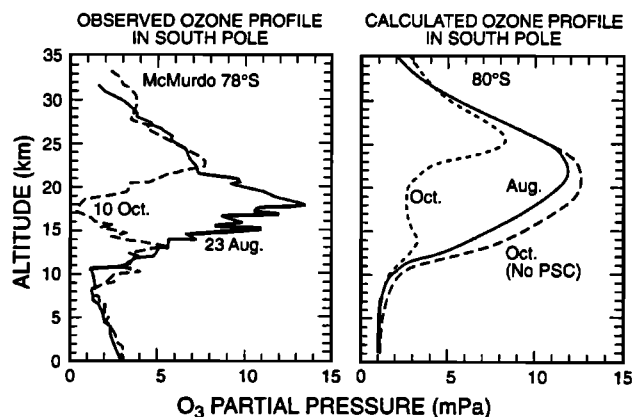

Figure 2. Comparison between calculated and observed [*Johnson et al.*, 1992] ozone vertical profiles at the south pole in August and October.

butions of ozone are shown from calculations with and without PSC chemistry. In Antarctica (80°S), PSC I have already formed by early August (Figure 1a). Since there is no sunlight at this time (polar night), the concentration of ClO (and BrO) remains very small, and no significant ozone depletion is found. In early September (Figure 1b), sunlight reaches higher latitudes, while the temperature remains cold enough to maintain the presence of PSCs (I and II). The concentration of ClO is dramatically higher than in August, and ozone starts to be destroyed between 10- and 25-km altitude. The maximum decrease in the ozone concentration is found at 20 km. In early October, as described in Part I, PSCs start to evaporate between 15- and 25-km, and only a very small amount of particles remains present in the 10- and 15-km altitude range. During September, the ClO concentration reaches a maximum of 600 ppt, which leads to a maximum ozone depletion of 80% at 20 km. The calculated maximum ClO concentration is smaller than the observed noon values (800 to 1200 ppt) reported by *Anderson et al.* [1989a] and *Brune* [1990]. It should be remembered, however, that the model provides a zonally averaged ClO concentration, which is always smaller than the noon values. In early December (Figure 1d), after the breakdown of the polar vortex, ozone depletion at 80°S gradually decreases through mixing of ozone-rich air from the Midlatitude, but the ozone remains depleted by approximately 50% at 17 km. Figure 2, which shows a comparison between the calculated ozone partial pressure and that observed at McMurdo (78°S) [*Johnson et al.*, 1992], suggests no impact of PSCs on ozone during August; the calculated ozone maximum is equal to 13 mPa at 18 km, and is thus similar to the observed maximum of 12 mPa at 17 km. In October, a dramatic ozone depletion is seen between 12- and 23-km in the observation as well as in the model. The calculated ozone minimum is about 2.5 mPa at 20 km, and is thus higher than the ozone minimum of 1.0 mPa observed at 17 km. It can be noticed that, without PSC chemistry, no ozone depletion would have taken place.

Figure 3 shows the latitudinal distribution of ozone, ClO, and PSCs at 20 km in the southern hemisphere with and without PSC chemistry for four specific dates. In July (Figure 3a), the Antarctic temperature is sufficiently cold for PSCs I to be formed within the polar vortex. The surface area of PSC I particles is 15 $\mu m^2/cm^3$ at 85°S and decreases to 5 $\mu m^2/cm^3$ at 70°S. Because there is no sunlight (polar night), the ClO concentration is very small, and no ozone depletion is found. In late August (Figure 3b), however, with PSC I surface areas similar to those found in July and sunlight
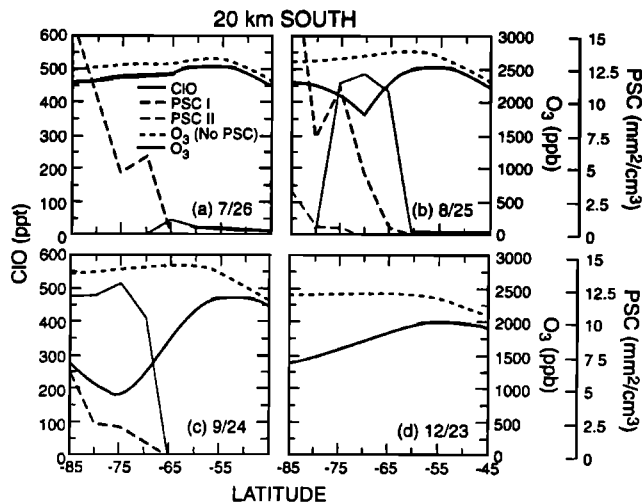

Figure 1. Calculated surface area ($\mu m^2/cm^3$) for PSCs, ozone (mPa), and ClO (ppt) vertical profiles at 80°S in winter-spring (August 10, September 9, October 9, and December 8).

Figure 3. Calculated surface area of PSCs ($\mu\,m^2/cm^3$), ozone (ppb), and ClO (ppt) latitudinal distributions at 20 km in the southern hemisphere on (a) July 26, on (b) August 25, on (c) September 24, and on (d) December 23.

reaching most of Antarctica (except 85°S), the ClO concentration increases dramatically with a maximum value of 500 ppt at 70°S. Ozone is reduced. The results are consistent with the calculation made by Danilin and McConnell (1994). In late September, even though the PSC I surface area starts to decrease, the ClO concentration maintains its high value between 70°S and 85°S because more sunlight reaches the polar region. Consequently, ozone depletion remains significant. Relative to the calculation without PSC chemistry, the depletion is approximately 65% at 75°S. In late December (Figure 3d), ozone concentrations at high latitudes increase substantially as a result of the rapid influx of ozone-rich air from lower latitudes as the polar stratospheric vortex breaks down (see the analysis by Newman [1986]). At midlatitude (45°N), the depletion of ozone is small during springtime, but reaches about 8% in December. The analysis of observations shows similar results [Hartman et al., 1989]. One should emphasize, however, that 2-D models are not expected to simulate accurately the breakup of the polar vortex, nor the dilution of polar air masses.

Figure 4 shows comparisons between calculations and observations in September at high latitude in the southern hemisphere. Both calculations and observations suggest strong anticorrelation between the concentrations of ClO and O3 at 70°S. It can be noticed, however, that the calculated ozone gradient at 60°S is smaller than that observed one, which indicates that the barrier of the winter polar vortex is somewhat weaker in the calculation than in the observation. The smaller effective barrier may be attributed either to the fact that the parameterization of planetary waves is more diffusive, or to the low latitudinal resolution of the model (5° in latitude). The observation suggests significant ozone changes within 1° of latitude (e.g., from 67°S to 68°S), which can not be resolved in the model calculation.

In the northern hemisphere, no PSC II are calculated in the Arctic. Thus, no significant sedimentation occurs. The surface area of type I PSCs is approximately 5 times less than in Antarctica [De Rudder, et al., this issue]. More important, PSC I in the Arctic exist only over a relatively short period of time (mostly in January). Because sunlight can not reach the polar region in January, ozone depletion occurs near the edge of the polar vortex, where PSCs I are produced in the model as a result of the temperature wave. The calculated simulation of latitudinal (17 km) and altitudinal (65°N) dis-

tributions of PSCs I surface area, as well as of ClO, and O3 concentrations are shown in Figure 5 and 6.

The calculation shows that, on January 27, PSC I are formed at 17 km between 65°N and 85°N. ClO concentrations increase to 250 ppt at 70°N, but remain low at 80°N (polar night), which is consistent with the observations made during the Airborne Arctic Stratospheric Expedition (AASE), as reported by Tuck et al. [1989]. On February 11, PSCs I have disappeared, while the concentration of ozone has decreased by a maximum of 30% at 70°N owing to the earlier formation of ClO. Because the ClO concentration does not increase at high latitudes polarward of 70°N, the decrease of ozone north of 70°N is due to polarward mixing of poor-ozone air from 70°N. Between 70°N and the region outside of the polar vortex (<60°N), the mixing is slow (relatively low K_{yy} values), and the ozone depletion is quite small. After February, the depleted ozone recovers due to the transport of ozone-rich air from outside of the vortex, but the area with depleted ozone (approximately 20%) still remains between 70°N and 85°N.

Figure 6 shows the distributions with altitude of PSC I, ozone, and ClO in the Arctic at 65°N. During a short time period (late January, Figure 6a), type I PSC are produced and ClO concentrations increase (400 ppt at 20 km). We notice that, at 15 km, larger surface areas of PSC I (5 $\mu\,m^2/cm^3$) lead to a smaller increase in the ClO
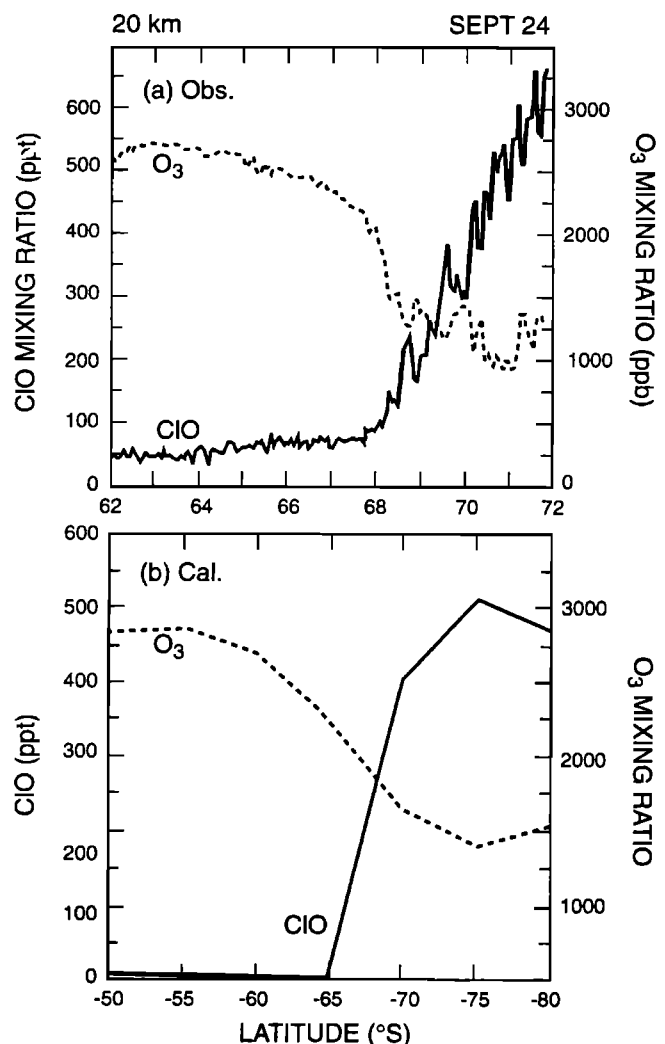

Figure 4. Comparison between calculated and observed [Anderson et al., 1989b] ozone and ClO latitudinal distributions at approximately 20 km in September.
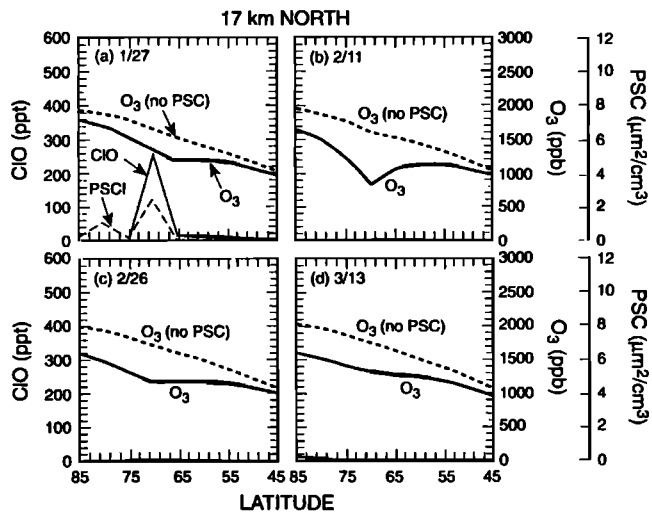
Figure 5. Same as Figure 3 except for at 17 km in the northern hemisphere.

density (70 ppt), while at 19 km, smaller surface areas of PSC I (2 $\mu m^2/cm^3$) lead to a larger increase in the ClO concentration (400 ppt). The explanation is that $ClONO_2$ and HCl concentrations as well as the sunlight intensity are much higher at 19 km than at 15 km. On February 11, PSC I disappear, and ClO concentrations return to their original low values. Ozone concentrations rebound back after February 26.

Figure 7a illustrates the importance of PSC processes for the global column ozone distribution. Including PSC chemistry decreases ozone from mid-latitude to the polar regions with a maximum ozone reduction in Antarctic spring. Significant differences between Arctic and Antarctic ozone reduction can be seen. First, in the Arctic, the ozone reduction (10%) is considerably less than in Antarctica during spring (40%). Second, the maximum decrease in ozone is located at 70°N in the Arctic, while it is near the pole in the southern hemisphere. Third, the maximum depletion in the Arctic is in late winter, while it is in early spring in Antarctica. All these aspects are relatively similar to the observations reported by *Stolarski et al.* [1991, 1992], which is an indication that the PSC chemistry is responsible for most of the observed ozone decrease in the polar regions of both hemispheres. Figure 7b shows an estimate by the model of ozone trends between 1980 and 1990.

2.2 Phase changes of HNO_3 and Denitrification effect

An important impact of PSCs on the lower stratosphere is that these clouds convert substantial amounts of gaseous HNO_3 and H_2O into the liquid phase or the solid phase (ice). The sedimentation velocity for PSC I particles is about 1 km/month, while that for PSC II particles is about 10 km/month (for typical particle sizes [*Kasten*, 1968]). Thus removal through sedimentation becomes significant only if PSC II are present. The sedimentation process transports PSC particles from the lower stratosphere into the upper troposphere. The loss of HNO_3 (and therefore NO_x) from the stratosphere is called denitrification, and the resulting changes in NO_x concentrations in the lower stratosphere affect ClO and ozone concentrations [*Fahey et al.*, 1989]. Besides the permanent loss of HNO_3 due to sedimentation processes, HNO_3 decreases temporarily owing to the condensation process during the formation of PSC I. However, gas phase HNO_3 reappears when PSC particles

evaporate [*De Rudder et al.*, this issue]. If PSC I is exposed to sunlight, this temporary decrease of HNO_3 has an impact on the ClO and ozone concentration.

The vertical distribution of gas phase HNO_3 can be changed significantly as a result of these condensation and evaporation processes. For example, if PSCs first form at 20 km, sediment and evaporate at 15 km, a net downward transport of HNO_3 takes place. (For simplification, this transport is referred to as Sedimentation Transport of HNO_3. Since PSC II is not easily produced in the Arctic, the discussion will focus on these processes as they occur in Antarctica.

Figure 8a shows the changes in HNO_3 and H_2O along with the calculated vertical distributions of PSC I and PSC II at 80°S. After the formation of type I PSCs (July 26), the abundances of gas phase HNO_3 and H_2O start to decrease. The largest decrease calculated for HNO_3 is about 0.04 mPa (7 ppb) between 15 and 20 km, which is consistent with the observation [*Santee et al.*, 1995]. After formation of PSC II in late August (Figure 8b), the decrease of H_2O becomes evident. The maximum decrease of H_2O represents approximately 15 mPa at 15 km (1.2 ppm). As a result of sedimentation, there is a noticeable increase of HNO_3 and H_2O in the upper troposphere. In late October (Figure 8c), PSCs evaporate, and HNO_3 and H_2O rapidly recover in the lower stratosphere. The HNO_3 concentration, however, has decreased at 20 km and increased at 12 km, which suggests that sedimentation transport of HNO_3 takes place. In December, approximately 2 months after the evaporation of PSCs, HNO_3 and H_2O concentrations are still reduced by 0.01 mPa at 20 km (1.7 ppb) and 3 mPa at 15 km (0.2 ppm), respectively. This decrease represents approximately the amount of HNO_3 and H_2O that has been removed as a result of denitrification and dehydration in the lower stratosphere.

To understand whether the decrease in HNO_3 during the formation of PSCs has impacts on stratospheric ozone, the temporal vari-
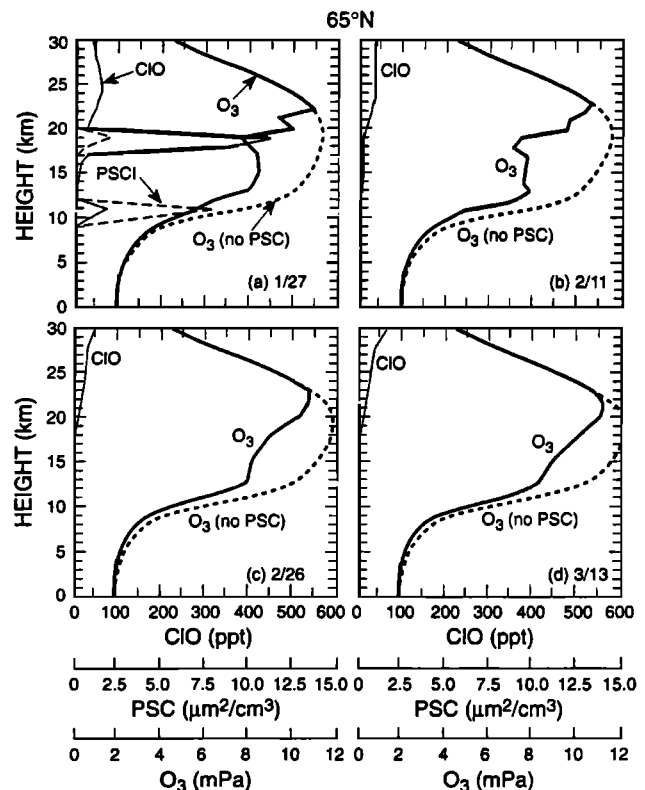

Figure 6. Same as Figure 1 except for 65°N.

(a) CHANGES IN COLUMN O$_3$ (%) DUE TO PSC

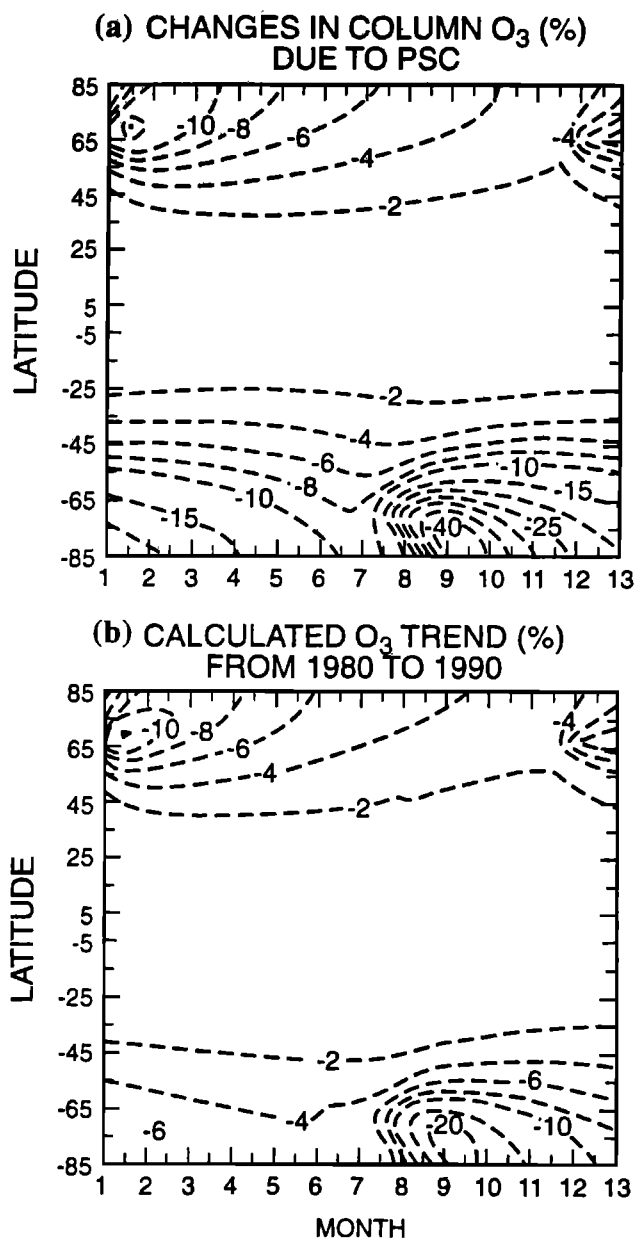## (b) CALCULATED O$_3$ TREND (%) FROM 1980 TO 1990

MONTH

Figure 7. (a) Calculated changes in the total ozone (percent) when PSC processes are taken into account. (b) Calculated ozone trends (percent) from 1980 to 1990 when accounting for the PSC microphysics and related heterogeneous reactions.

ations of PSCs, ClO, O$_3$, HNO$_3$, and H$_2$O have been analyzed at 20 km and at 80°S and 70°S. At 80°S (Figure 9b), a large amount of PSC I particles is formed between early June and late August, leading to a large decrease in the HNO$_3$ abundance. However, without sunlight (polar night), the concentration of ClO remains very low, and no ozone depletion occurs. The large decrease in gas phase HNO$_3$ has thus no significant effect on the Antarctic ozone depletion. During September, sunlight is present, and only a small amount of PSC I particles remain present (surface area of 2 μ m^2/ cm^3 in late September, in contrast to 10 μ m^2/cm^3 in early August). HNO$_3$ recovers and its concentration even slightly increases as a result of the conversions of N$_2$O$_5$ into HNO$_3$ and of ClONO$_2$ into HNO$_3$. Meanwhile, the concentration of ClO increases dramatically (500 ppt) and produces a large depletion of ozone. Thus the increase in the ClO concentration is mainly due to reactions

ClONO$_2$+H$_2$O(s) and ClONO$_2$+HCl(s) and is not significantly connected to the decrease in gas phase HNO$_3$ during the formation of PSCs.

At 70°S (Figure 9a), however, sunlight is already present in late July, which is approximately a month earlier than at 80°S. Therefore during August, large amounts PSCs I are exposed to sunlight. Thus, increase in ClO is large even if the decrease in HNO$_3$ is limited (4 ppb). The PSC-induced decrease in NO$_x$ prohibits the reformation of ClONO$_2$, so that ClO concentrations remain elevated during several weeks.

2.3. Effect of Pinatubo Aerosols on the Formation of PSCs

After the eruption of Mount Pinatubo (Philippines, 1991), the sulfate aerosol load increased as a consequence of the injection of sulfur gases (mostly SO$_2$) in the stratosphere. A model of the atmosphere including microphysical processes [*Tie et al.*, 1994a] suggests that the aerosol surface area in the tropics increased by as much as a factor of 100 after the eruption, which is consistent with the observations [*Deshler et al.*, 1993; *McCormick* and *Veiga*, 1992; *Yue et al.*, 1992]. The model results also suggest that the amount of large sulfate aerosol particles remained high in the polar region 2 years after the eruption (see Figure 10). As the nucleation rate increases strongly as a function of cloud condensation nuclei (CCN) radius, the enhancement in the number density of large aerosol particles after the eruption tends to accelerate the nucleation rate, and hence the number of PSC particles. To examine this question, the aerosol size distribution used in the calculation presented in section 2 is replaced by a size distribution typical of the post-Pinatubo situation, while other conditions remain identical. In a
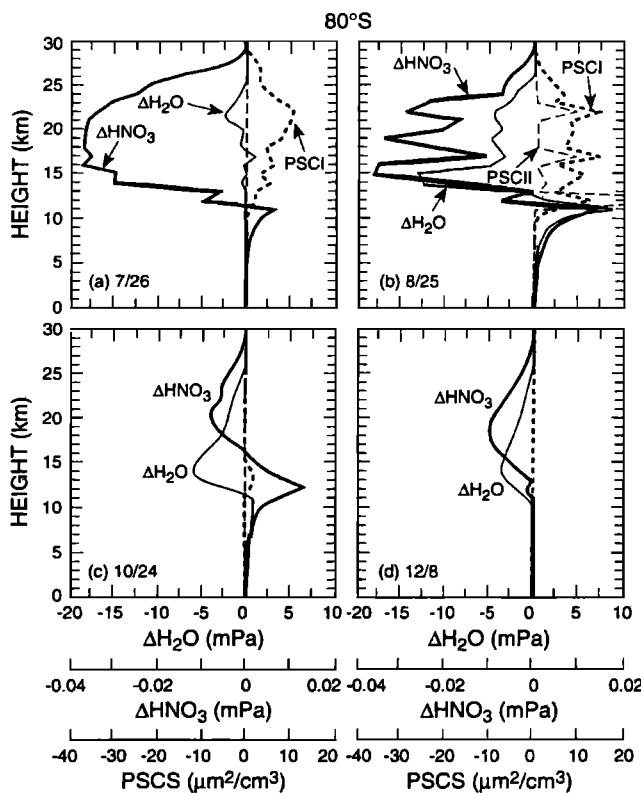
80°S

Figure 8. Calculated surface area of PSCs (μ m^2/cm^3), changes in HNO$_3$ (mPa), and H$_2$O (mPa) vertical distributions at 80°S on (a) July 26, (b) August 25, (c) October 24, and (d) December 8.
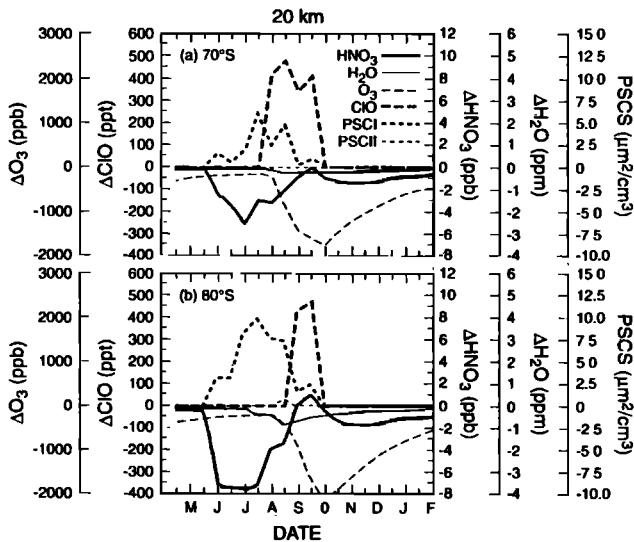
Figure 9. Evolution at 70°S and 80°S, and 20-km altitude of the PSC (type I and type II) surface area, and of the changes in the H_2O (ppm), HNO_3 (ppb), ClO (ppt), and O_3 (ppb) mixing ratio, from March to February.

previous paper, the direct impact of heterogeneous reactions on sulfate aerosol particles after the eruption of Pinatubo was studied [*Tie et al.*, 1994b], and this effect is not further discussed here.

Figure 11 shows the increase in the PSC I surface area in the southern hemisphere caused by the presence of Pinatubo aerosol particles. The solid line corresponds to a surface area of 3 $\mu m^2/$
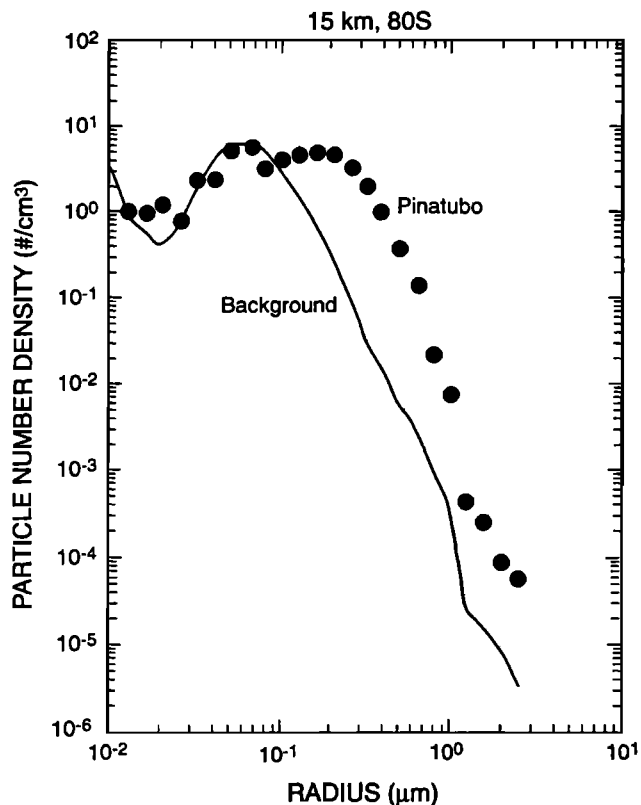

Figure 10. Sulfate aerosol size distributions calculated at 15 km and 80°S for background (solid line) and for volcanic conditions (dots). Volcanic conditions are representative of the aerosol burden produced by the eruption of Pinatubo and is averaged between June 1991 and May 1993.
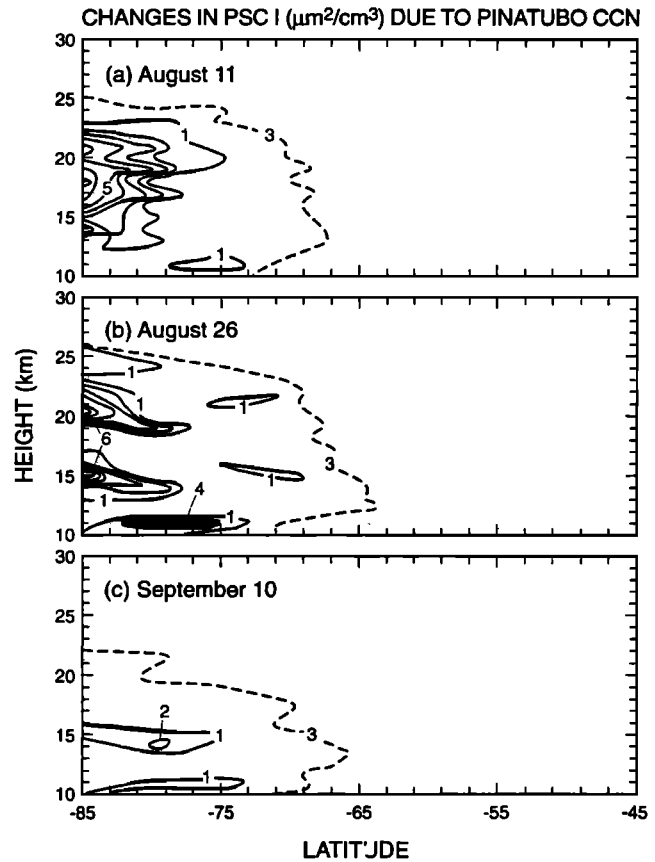

Figure 11. Calculated changes of surface area of PSC I ($\mu m^2/cm^3$) due to the increase of sulfate aerosol particles after the eruption of Pinatubo in the southern hemisphere during winter and earlier spring.

cm^3, representing a typical pre-eruption condition. The maximum increase in the surface area is about 5 $\mu m^2/cm^3$ over Antarctica at 17 km in the middle of August in 1992 after the eruption of Pinatubo. In the northern hemisphere, the PSC I surface area also increases (Figure 12). The maximum increase in January (1 $\mu m^2/cm^3$) is smaller than that in the southern hemisphere in August. As the same climatological temperature distribution was used in the two calculations (background CCN and volcanic CCN), the calculated changes in the surface area of PSC I result from changes in their density. The region in which PSCs are formed is unchanged. Additional perturbations could result from temperature and other dynamical variations associated with the volcanic eruption.

Figure 13 shows the percent difference in the total ozone distribution when the two calculations are compared. Overall, when the impact of the Pinatubo eruption on the PSC formation is taken into account, ozone decreases to the north of 40°N. The maximum decrease is found in the northern hemisphere, but is limited to only 0.5% to 2%. This result raises two interesting questions: First, although the increase of the surface area PSCs I is largest in the southern hemisphere (see Figures 11 and 12), the ozone decrease is most pronounced in the northern hemisphere. Second, the maximum increase in the PSC I surface is about 40%, while the decrease in the ozone abundance is insignificant (1-2%). Figure 14 shows the $ClONO_2$ distribution in the run with the background CCN. After the formation of PSC, $ClONO_2$ has been largely depleted, with the largest decrease located in the southern hemisphere. With enhanced PSC surface areas caused by the volcanic eruption, very little addi-
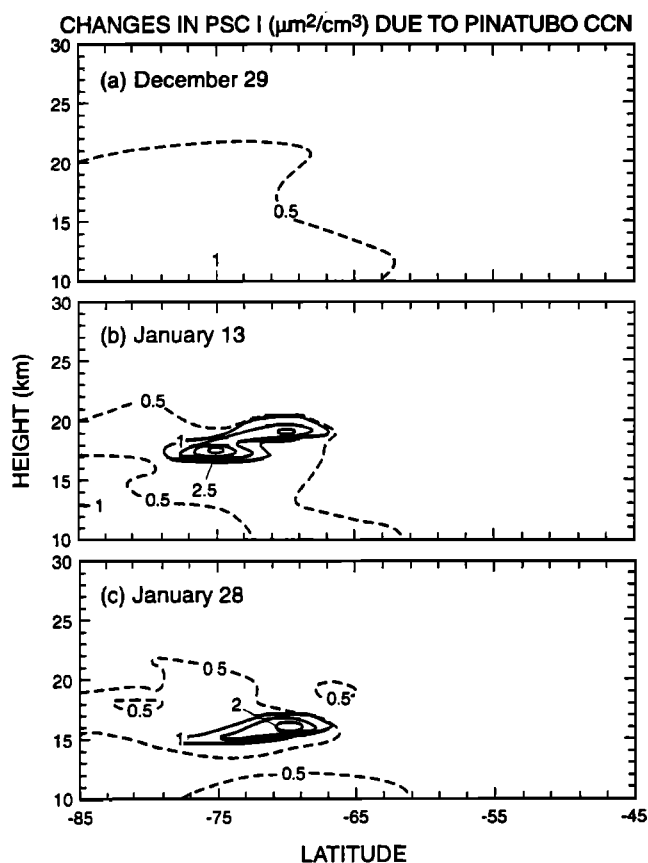
CHANGES IN PSC I (μm²/cm³) DUE TO PINATUBO CCN

Figure 12. Same as Figure 11, except for the northern hemisphere.

tional $ClONO_2$ is converted into ClO. The depletion for $ClONO_2$ is already almost "saturated" with the existence of PSCs produced with background CCN. Thus the effect on ozone is small. In addition, since the "saturation" of $ClONO_2$ conversion is less pronounced in the northern hemisphere, the impact of the Pinatubo

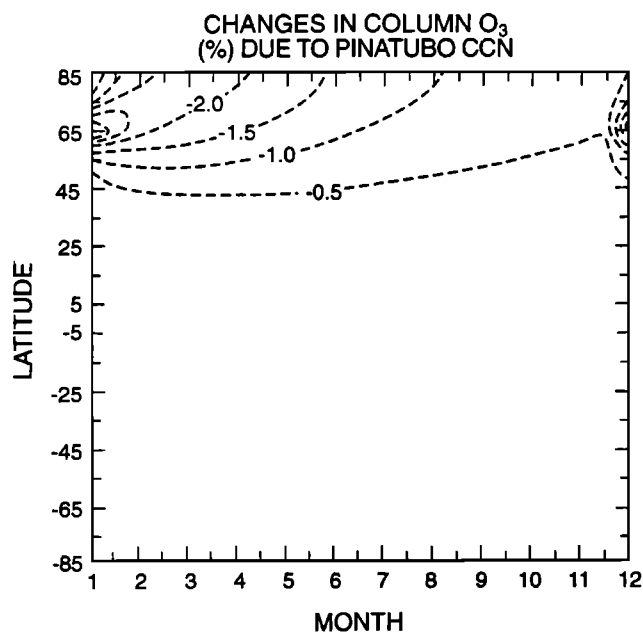## CHANGES IN COLUMN O₃ (%) DUE TO PINATUBO CCN

Figure 13. Calculated changes of total ozone distributions due to the increase in PSC surface area produced by sulfate aerosol particles after the eruption of Pinatubo.
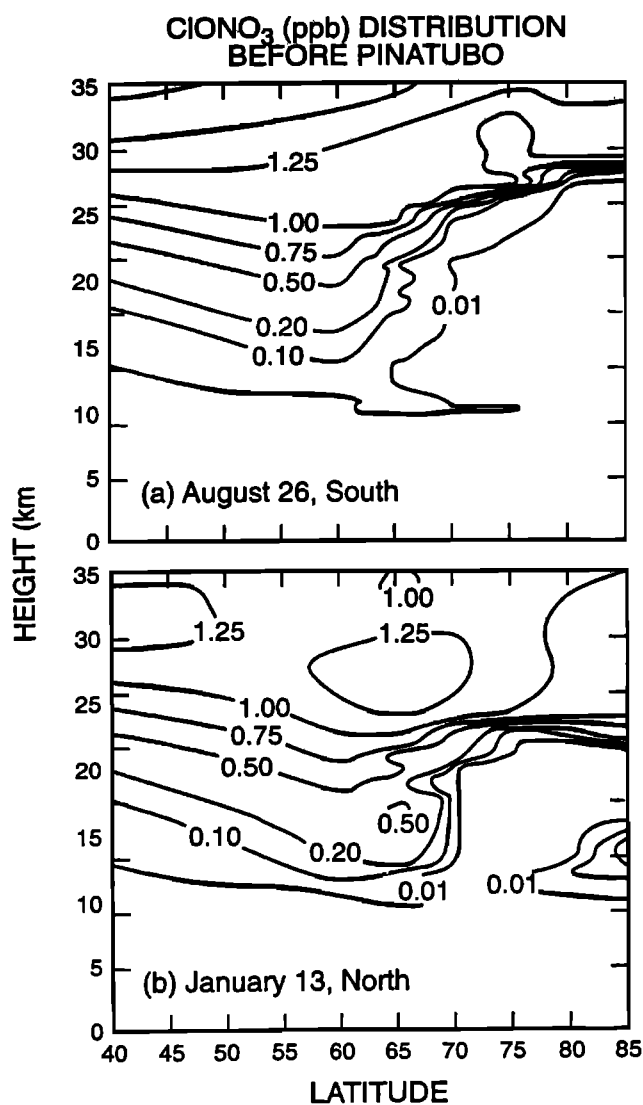
ClONO₃ (ppb) DISTRIBUTION BEFORE PINATUBO

Figure 14. Meridional distribution of $ClONO_2$ calculated poleward of $40°$ with background sulfate aerosol in winter for the (a) southern and the (b) northern hemispheres.

eruption on ozone through PSC effects is larger. This sensitivity test did not account for the possibility of enhanced occurrence of PSCs (more locations). This latter effect may be more important for ozone than the increase in PSC densities at a given location.

2.4. Effect of Injection of NO$_x$ From HSCT

Recently, several countries have proposed to develop a fleet of high speed civil transport (HSCT), which will fly in the stratosphere at supersonic speed. This projected fleet would inject into the lower stratosphere a significant amount of NO_x, leading to a potential destruction of stratospheric ozone. Several studies [*Weisenstein et al.*, 1991; *NASA*, 1992, 1993; *Bekki and Pyle*, 1993; *Tie et al.*, 1994c] suggest that the enhanced NO_x due to HSCT could lead to a column ozone depletion of 2-5% at high latitudes in the northern hemisphere, but these estimates do not account for the impact of injected NO_x on the formation of PSC I. In this section, we examine this particular effect and we assess its impact on the changes of PSCs and on stratospheric ozone, in response to the injection of NO_x from HSCT. The distribution of the emitted materials from
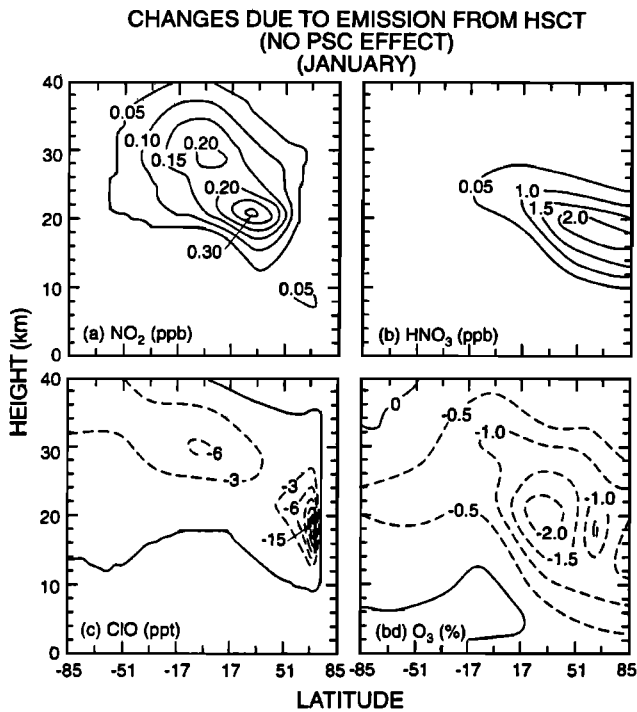
Figure 15. Changes in NO_2 (ppb), HNO_3 (ppb), ClO (ppt), and O_3 (percent) calculated in January in response to the emission from HSCT without accounting for the microphysics of PSC formation.

HSCT is adopted from the *NASA* [1992], assuming an emission index for NO_x of 15 g/kg of fuel as NO_2, and a Mach number of 2.4. The heterogeneous chemical reactions on sulfate aerosols are included in this assessment.

Figure 15 shows for January the changes in the abundances of NO_2, HNO_3, ClO, and O_3 due to NO_x emissions from HSCT, when
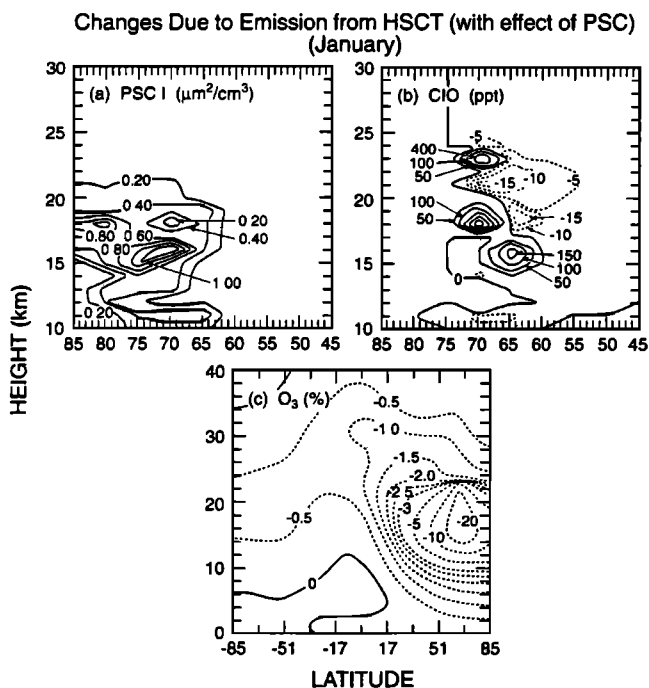

Figure 16. Changes in the surface area of PSC I ($\mu m^2/cm^3$), ClO (ppt), and O_3 (percent) calculated in January in response to the emission from HSCT with PSC microphysics taken into account.

impact on the formation of PSCs is ignored. In this case, the O_3 concentration decreases by a maximum of 2% ($40°N$, 20 km). The ClO concentration decreases at high latitudes in the lower stratosphere due to a faster conversion of ClO with NO_2 into $ClONO_2$. The HNO_3 concentration increases by 2 ppb at middle and high latitudes in the lower stratosphere, with potentially important impacts on the formation of type I PSCs.

When the same calculation is repeated, but with coupled PSCs (see Figure 16), the injection of NO_x enhances the surface area of PSC I by a maximum of 1.2 $\mu m^2/cm^3$ (15 km, 70-75°N). As a result, heterogeneous reactions become more efficient and ClO concentrations increase by 200 to 400 ppt (15 to 23 km, 70°N). The related ozone decrease reaches a maximum of 20% in the lower stratosphere at 60°N. *Considine et al.* [1994] used a method in which the formation of PSC particles are is calculated as a function of the probability distribution of temperature for a mean radius of the particles. Their formulation leads to lower PSC surface area densities, and hence to a smaller effect on ozone of NO_x released from supersonic aircraft.

Figure 17 shows the changes in column ozone in the two cases (with and without microphysical processes associated with PSCs). In both cases, the maximum ozone decrease produced by the HSCT emissions is located at high latitudes in the northern hemisphere, but at different seasons. When the PSC microphysics is ignored, the maximum ozone decrease of 3% is found in August and September. When PSC microphysics is taken into account, the maximum ozone
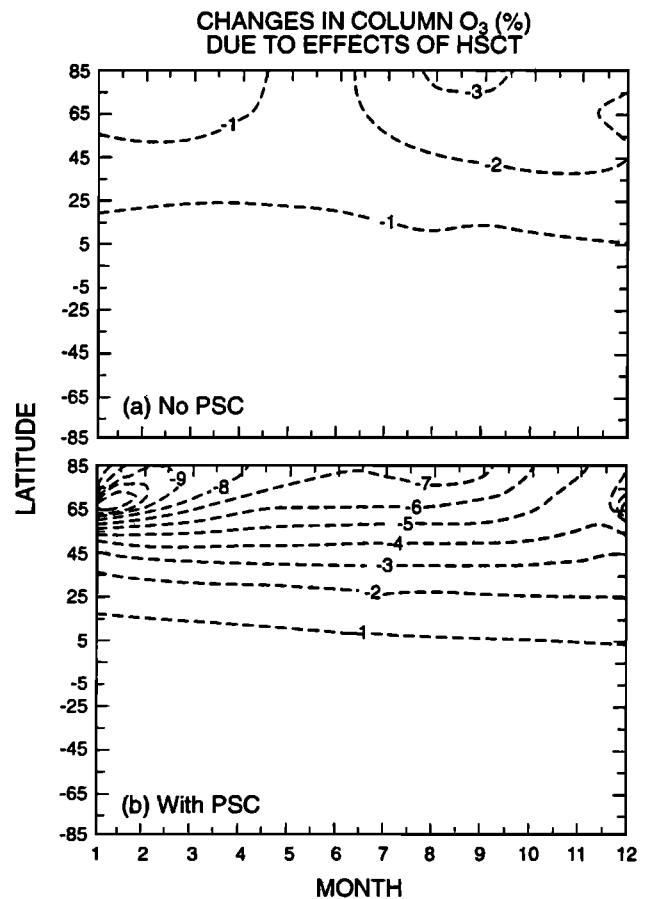

Figure 17. Changes in ozone column (percent) calculated in response to the emission of NO_x from HSCT (a) without accounting for PSC microphysics and (b) with PSC microphysics taken into account.

decrease of 10% is produced in January and February. This seasonal shift results from the fact that, in the first case, ozone is depleted primarily by an NO_x catalytic cycle (which is most efficient in the summertime), while, in the latter case, it is a ClO_x catalytic cycle which plays the major role. The large decrease in ozone calculated with microphysics taken into account suggests that the enhanced formation of PSCs due to the injection of NO_x from HSCT could potentially produce a significant perturbation in stratospheric ozone.

3. Summary and Conclusions

The heterogeneous conversion of $ClONO_2$ into ClO under sunlight conditions plays an important role in the destruction of ozone in both polar regions (Antarctic spring and northern high latitudes (around 70°N) in late winter). The calculation reproduces well the development of the springtime ozone hole over Antarctica. The largest ozone depletion starts in September and reaches a maximum in October (polar sunrise). The maximum ozone depletion is located at the top of the PSC layer (20 km), where the Cl_x concentration is highest. In the Arctic, the ozone depletion due to PSCs is much smaller because of the shorter occurrence period and the smaller surface area available for chemical conversions.

The calculation also simulates the large HNO_3 decrease (7 ppb in August) in Antarctica occurring during the formation of PSCs in winter owing to phase conversion and sedimentation. The decrease in the HNO_3 concentration (also NO_x) has little effect on ozone depletion at 80°S because the large decrease in HNO_3 exists only in the polar night, when the ClO concentration is very small. However, as sunlight returns earlier (in late July) at 70°S, the large decrease of HNO_3 enhances ClO concentrations. The depletion in NO_2 prohibits the reformation of inactive chlorine reservoir ($ClONO_2$), so that the ozone depletion could be larger. PSC II plays an important role as they sediment and transport the large PSC particles into the troposphere. The sedimentation process results in a HNO_3 and H_2O decrease after the evaporation of PSCs. The reduction is about 2 ppb for HNO_3 and 200 ppb for H_2O in the lower stratosphere during December, producing effective "denitrification" and "dehydration".

PSC processes have important effects on the ozone trend from 1980 to 1990 in both northern and southern hemispheres. The calculation reproduces the ozone trend observed in the southern hemisphere and shows the importance of the "dilution" effect for the mid - latitude ozone trends. The calculation also represents the observed ozone trend at high latitudes in the northern hemisphere, but fails to reproduce the (secondary) maximum ozone depletion observed at midlatitudes in the northern hemisphere. This may indicate that some additional chemistry processes leading to ozone destruction could play an important role [Solomon et al., 1994].

The formation of PSCs is significantly affected by the injection of NO_x from HSCT at high latitudes in the northern hemisphere. As a result, the ClO concentrations increase significantly, leading to an enhanced decrease in the column ozone in the northern hemisphere. The model suggests that the perturbation in PSCs caused by the injection of NO_x from HSCT could produce a significant effect on stratospheric ozone.

In summary, we have shown that, when used in a coupled mode, a microphysical model for PSC formation and a global atmospheric model provide a powerful tool for studying the effects of heterogeneous chemical reactions on the chemical composition of the lower stratosphere if the variations in temperature associated with planetary waves are properly taken into account. A three-dimensional global model would improve the calculation, since such models are

more adequate to treat dynamical mixing between the polar vortex and mid - latitudes. These models are, however, computationally very expensive, especially if they include an explicit formulation of PSC microphysics.

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