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Five years of NO_2 vertical column measurements at Faraday (65°S): Evidence for the hydrolysis of $BrONO_2$ on Pinatubo aerosols

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Abstract. Summertime measurements of NO_2 vertical column amounts over a 5 year period from May 1990 until February 1995 from Faraday Base, Antarctica, show a marked reduction following the arrival of the Mount Pinatubo volcanic aerosol in December 1991. Model calculations show that this reduction can be explained by $BrONO_2$ and N_2O_5 hydrolysis on the volcanically enhanced aerosol, with the former dominating. Given the measurement and model uncertainties and lack of any treatment the effects of the quasi-biennial oscillation, the reduction in NO_2 is consistent with a $BrONO_2$ sticking coefficient gamma of 0.4. However, the best agreement between the model and the measurements occurs using a gamma of 0.2. Over the time span of the measurements the known increases in chlorine and bromine loadings have an effect of less than 2% on midsummer NO_2 columns. With background aerosols, summertime ozone catalytic losses are dominated by the HO_x cycle between 12 and 18 km and by the NO_x cycle at greater altitudes. With heavy aerosol loading, HO_x is the primary loss cycle from 12 to 22 km. The total ozone loss increases by 38% at 16 km as a result of heavy aerosol loading.

Introduction

Nitrogen dioxide, NO_2, plays an important role in stratospheric ozone chemistry. Only with reduced concentrations of NO_2 can chlorine and bromine catalytic reactions effectively destroy large quantities of ozone in polar regions [*Solomon*, 1990], leading to the formation of the Antarctic ozone hole and to losses in the northern hemisphere. In summer, however, the catalytic loss of odd oxygen O_x (O_3 + O) between 12 and 30 km is dominated by the NO_x (NO and NO_2) and HO_x (OH and HO_2) cycles. Below 15 km the bromine related catalytic cycle is important and at altitudes above about 30 km the chlorine related cycle replaces the HO_x cycle to become the second most important cycle in ozone loss.

NO_2 column amounts have been measured by ground-based UV visible spectrometers since the work of *Brewer et al.* [1973] and *Noxon* [1975]. The British Antarctic Survey installed a spectrometer of the design "Système d'Analyse par Observations Zénithales" (SAOZ) in March 1990 at Faraday in Antarctica (65.25°S, 64.26°W), which has been making continuous measurements of line-of-sight column NO_2 amounts [*Lee et al.*, 1994] and ozone. In this work we present SAOZ measurements of NO_2 from May 1990 to January 1995. This spans the period before and after the eruption of Mount Pinatubo in June 1991, which increased the surface area of the stratospheric sulfate aerosol layer over Antarctica in December 1991 by a factor of up to 100 [*Hofmann and Oltmans*, 1993].

The primary focus of this study is the assessment of the importance of heterogeneous reactions on sulfate aerosols during summertime immediately following the Pinatubo eruption. This time series is also used to assess the effect of increases in chlorine and bromine loading on NO_2 column amounts and the effect of bromine loading on NO_2 column amounts Finally the effect of heavy volcanic aerosol loading on the profile of the various catalytic O_3 loss cycles is investigated.

Photochemistry of NO_x

Current thinking is that in the very low stratosphere (below ≈ 22 km), away from the very cold temperatures when polar stratospheric clouds may form, NO_2 has the effect of moderating HO_x and halogen-related O_3 loss [*World Meteorological Organization*, 1994]. For example, in order for ClO to reach large concentrations, NO_2 concentrations must be suppressed as NO_2 reacts with ClO to form the stable chlorine reservoir $ClONO_2$. Similarly, NO_2 reacts with OH to form the stable molecule HNO_3.

At higher altitudes, NO_2 participates in an O_3 loss cycle [*Crutzen*, 1970] via

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (1)$$

$$NO_2 + O \rightarrow NO + O_2. \quad (2)$$

Thus measurements of NO_2 column amounts provide important constraints on our understanding of the ozone photochemical balance. The partitioning between reactive and reservoir nitrogen is

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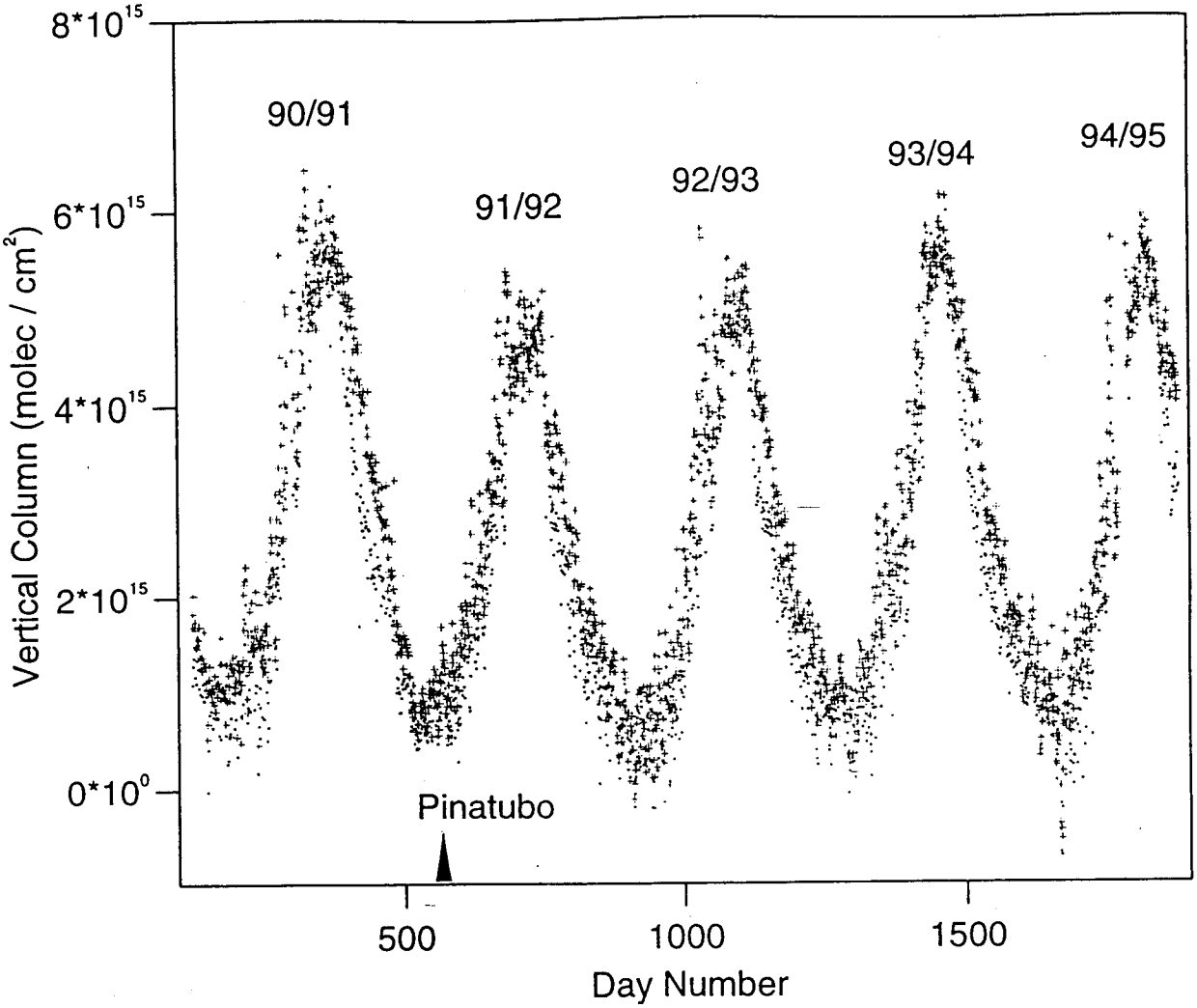

Figure 1. NO_2 vertical column amounts measured by the SAOZ at Faraday during morning (solid circles) and evening (crosses) twilight. These are weighted averages between 85° and 91° solar zenith angles, the weights being the inverse square due to the residuals in the least squares fit to the spectrum. The evening measurements are largest in spring and fall, when morning and evening twilight are well separated.

controlled in part by NO_3, which is an intermediary between NO_2 and N_2O_5: during the dark, NO_3 concentrations build up which may allow significant quantities of N_2O_5 to form. In daylight, N_2O_5 is photolyzed with a time constant of hours and is responsible for the diurnal changes (morning to evening) seen in NO_2 (see, e.g., Figure 1). The reaction of N_2O_5 with water on sulfate aerosols occurs at the same rate at all temperatures [*Jet Propulsion Laboratory,* 1994],

$$N_2O_5 + H_2O \text{ (aerosol)} \rightarrow 2HNO_3. \quad (3)$$

However, *Hanson and Ravishankara* [1995] showed that hydrolysis of $BrONO_2$ on sulfate aerosols can also occur, which indirectly converts NO_x to the less reactive HNO_3. It also produces HOBr, which is readily photolyzed to Br + OH, both of which destroy ozone. Unlike the hydrolysis of N_2O_5, $BrONO_2$ hydrolysis is not thought to saturate even under heavy volcanic aerosol loading [*Lary et al.,* 1996].

Experimental Description

The SAOZ instrument [*Pommereau and Goutail,* 1988] has a resolution of 1.2 nm at full width at half maximum and uses an uncooled 512 element photodiode array. Spectra were recorded from 290 to 600 nm at various intervals throughout the day, with continuous recording at twilight. Spectra for the entire data set were analyzed by fitting laboratory cross sections of the constituents to the ratio of the observed spectrum to a single reference spectrum [*Sarkissian,* 1992]. The fits were carried out after filtering the ratio and the cross sections with a high-pass filter in wavelength to remove sensitivity to aerosol (the commonly used differential spectroscopy method [*Syed and Harrison,* 1980]) and with different low-pass filters for each constituent to reduce the correlation between constituents. Fits were obtained in separate wavelength intervals for each constituent, NO_2 being derived from the wavelength interval 405 to 498 nm. The wavelength calibration of each spectrum was determined from the spectrum itself by fitting absorption features in the solar spectrum.

The results of the analysis are the measured line-of-sight amounts (minus the amount in the reference spectrum), the statistical errors in each amount, and the air mass factors (AMFs) which convert line-of-sight amounts to vertical columns. The AMFs were precalculated by *Sarkissian* [1992] using the formalism of *Solomon et al.* [1987]. A reference spectrum, free from tropospheric NO_2 as are all spectra at Faraday, was used, taken at noon local October 17, 1991. The vertical column amount in the reference spectrum was assumed to be the average of the reference

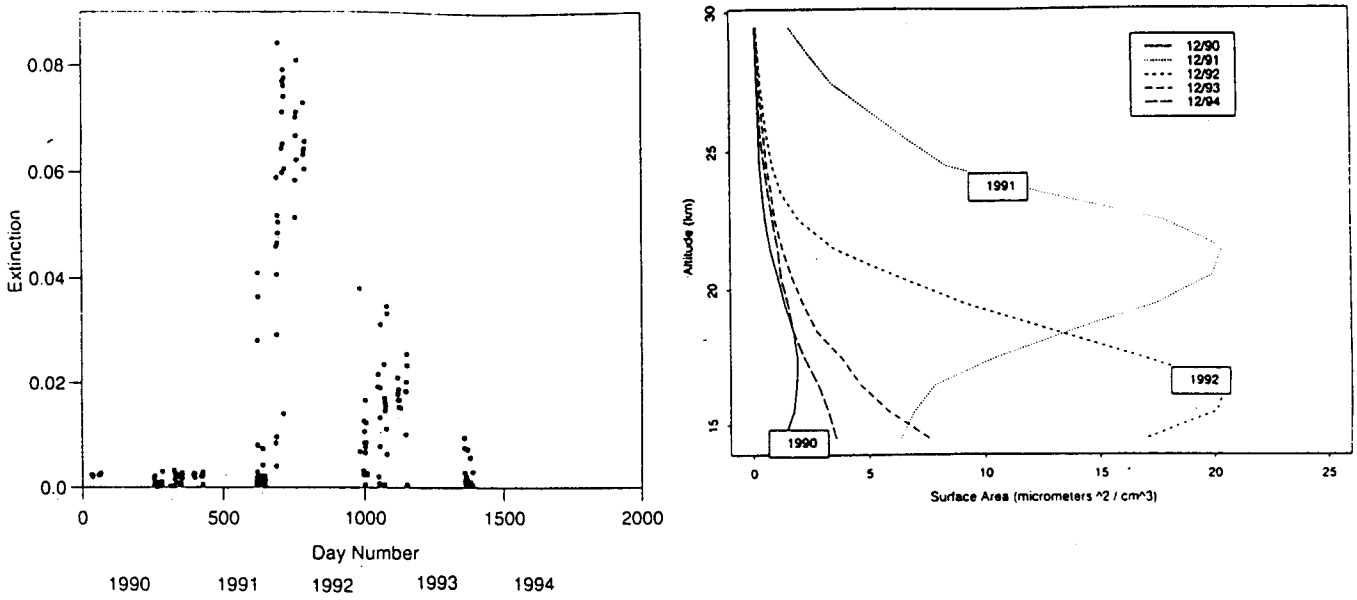

Figure 2. Aerosol extinction at 60°S at 525 nm integrated from 16 to 25 km measured by (left) SAGE II and (right) aerosol surface area profiles for December 1990, 1991, 1992, 1993, and 1994.

day's morning and evening vertical columns [*McKenzie and Johnston*, 1983]. This amount was added to the measured line-of-sight column amount to give the total line-of-sight column. The NO_2 morning and evening vertical column amounts are the error-weighted average of the vertical column amounts for solar zenith angles (SZAs) between 85° and 91°. The standard error of these averages is less than 0.1×10^{15} molecules cm^{-2} in summer, which therefore represents the random error of the measured vertical columns.

Results and Ancillary Data

Five years of NO_2 vertical column amounts obtained from Faraday are shown in Figure 1. The basic features are summer maxima and winter minima, neither showing significant diurnal variation. A significant morning to evening difference appears in the spring and autumn.

A qualitative explanation of this behavior is as follows: NO_2 columns are strongly affected by the length of daylight and, to a lesser extent, by stratospheric temperatures. The small winter column amounts are the result of gas phase reactions converting NO_2 into N_2O_5, heterogeneous reactions converting N_2O_5 and $ClONO_2$ into HNO_3, and possible denitrification (sedimentation of HNO_3 particles leading to reduced NO_y). In summer months the lifetime of HNO_3 is reduced by photolysis and reaction with OH, both releasing NO_2. The near-continuous sunlight in midsummer inhibits the formation of N_2O_5, thus reducing the diurnal variation. In winter there is almost no daylight to photolyze N_2O_5, which similarly reduces the diurnal variation.

Superimposed on this pattern are significant year-to-year differences and considerable short-term variability. The most notable feature is the abrupt reduction in midsummer values following the December 1991 arrival at high southern latitudes of aerosol from the Mount Pinatubo eruption on June 15, 1991 (see Figure 2 (left)). There is a gradual recovery in midsummer NO_2 column amounts in the following years. This feature is discussed below. Day-to-day variability is also present in the data. This variability is real as it is larger than the random error of the measurement. Based on our analysis of potential vorticity data at 475 K from the United Kingdom Meteorology Office, it is the result of dynamical changes as air from different latitudes moves over Faraday. As might be expected, this variability is greatest in the spring when the NO_2 latitudinal gradient and the latitude excursions of air parcels are largest.

Integrated aerosol extinction at 525 nm from Stratospheric Aerosol and Gas Experiment II (SAGE II), zonally averaged over 60°S ± 5°, are shown in Figure 2 (left) and midsummer aerosol surface area profiles in Figure 2 (right) [*Thomason et al.*, 1997]. The estimated uncertainty in the aerosol surface area is 20-30% (Larry Thomason, private communication, 1996). A dramatic increase in the integrated aerosol extinction is seen after day 600 following the eruption of Mount Pinatubo on day 521. The volcanic eruption resulted in a maximum aerosol extinction integrated from 16 to 25 km of 0.08, near December 15, 1991 (day 714).

The NO_2 AMFs have not been corrected for the optical properties of the aerosol even for the period of heaviest aerosol loading. The presence of a stratospheric aerosol layer of total optical depth 0.1 centered at 22.5 km has less than 5% effect on NO_2 AMFs at a SZA of 91° and less at smaller SZAs [*Perliski and Solomon*, 1993]. Single-scattering calculations using the code of *Sarkissian* [1992] limit the change in NO_2 AMFs due to the heaviest observed aerosol loading to less than 3% at 91° and less at smaller SZAs. The effect is small because the peak altitude of the NO_2 concentration profile, unlike ozone, is above the maximum of the aerosol surface area profile. As this work averages data from 85° to 91°, the effect of the heaviest aerosol loading will be even less than at 91°.

Comparison of Measurements and Model Predictions

A column model [*Fish and Burton*, 1997] was used to test the sensitivity of the observed NO_2 vertical column amounts to changes in aerosol loading, chlorine and bromine concentrations, and atmospheric temperatures. Stratospheric temperatures were obtained from the European Centre for Medium-Range Weather Forecasts assimilations. The aerosol surface area profile in the model was the monthly averaged zonal means at 60° from SAGE II for December 1990, 1991, 1992, 1993, and 1994 [*Thomason et al.*,

Table 1. Calculations of the Influence of Mount Pinatubo Aerosol on Summer Solstice, NO_2 Vertical Columns

	Full Chemistry		No $BrONO_2$ Hydrolysis	
	Morning	Evening	Morning	Evening
1990	5.47	5.54	5.63	5.70
1991	4.34	4.44	5.14	5.22
1992	4.64	4.74	5.25	5.34
1993	5.16	5.24	5.44	5.52
1994	5.33	5.41	5.54	5.61

NO_2 column amounts ($\times 10^{15}$ molecules / cm^{-2}), 65°, 1990 chlorine and bromine levels, gamma=0.4.

1997]. Initial concentrations of the source gases were taken from the Cambridge two-dimensional model [*Chipperfield et al.*, 1996]. Br_y was initialized at 2 parts per trillion by volume (pptv) at 12 km, increasing linearly with altitude to 21 pptv at 24 km, and constant to 40 km [*Fish et al.*, 1995]. In order to eliminate the dependence on initialization, the model was run for 10 days for each date. This was found to be sufficient to partition the reactive nitrogen species with no further significant changes if the model was run for a longer period. While a box model would not be satisfactory for winter, it suffices for midsummer where the dynamical and chemical conditions are not as variable as in winter.

Two integrations were performed, one with full chemistry and the second assuming no $BrONO_2$ nydrolysis. A sticking coefficient, gamma (γ), of 0.4 was used for the full chemistry case, consistent with the gamma of $0.4^{+0.6}_{-0.2}$ measured by *Hanson and Ravishankara* [1995]. Results from these integrations are shown in Table 1.

A small diurnal variation is seen in the model (Table 1) despite the continuous daylight at summer solstice at this latitude because sufficient NO_3 still persists to form N_2O_5 which is then photolyzed. Significant reductions in midsummer NO_2 column amounts are colocated to maximum aerosol loadings, amounting to $\approx 1.1 \times 10^{15}$ molecules cm^{-2} NO_2, due primarily to $BrONO_2$ hydrolysis in the model. The calculated reduction in NO_2 column amounts following the arrival of the Mount Pinatubo aerosol shown in Table 1 is comparable to that reported by *Solomon et al.* [1994] (a 20% reduction in midsummer NO_2 column amounts at 75°S in 1992). However, that work did not include the effects of $BrONO_2$ hydrolysis, invoking the assertion that air made excursions to lower latitudes where there would be sufficient darkness for more N_2O_5 production.

The subsequent hydrolysis of N_2O_5 to HNO_3 would then lead to lower NO_2 abundances. An important conclusion of this work is that the dominant denoxification process is $BrONO_2$ hydrolysis and that air parcel excursions need not be invoked. Indeed, if the air parcels made excursions to lower latitudes, significantly smaller NO_2 column amounts would have been predicted by the model.

Figure 3 shows a comparison between the measured midsummer morning NO_2 column amounts at Faraday and the calculated amounts with various values of gamma for $BrONO_2$ hydrolysis. These data are an average of the 10 days nearest the solstice with

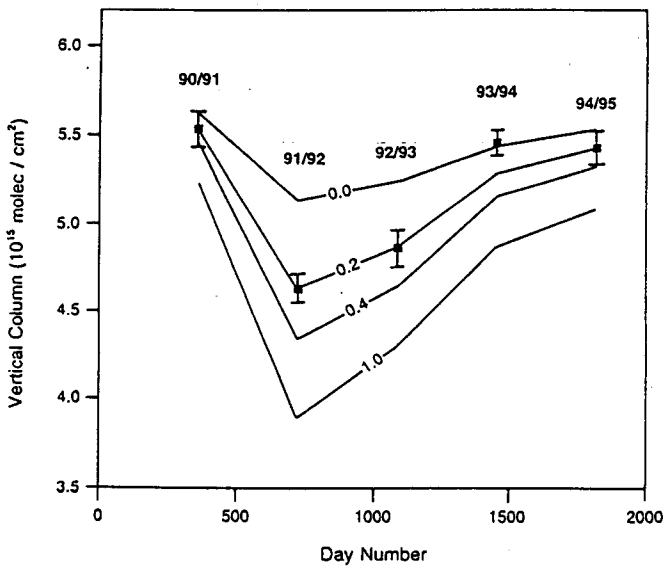

Figure 3. Comparison between the measured midsummer morning NO_2 vertical column amounts for Faraday and calculations using various values of gamma for $BrONO_2$ hydrolysis. Measured values are the mean of 10 days around solstice, and error bars are ± 1 σ.

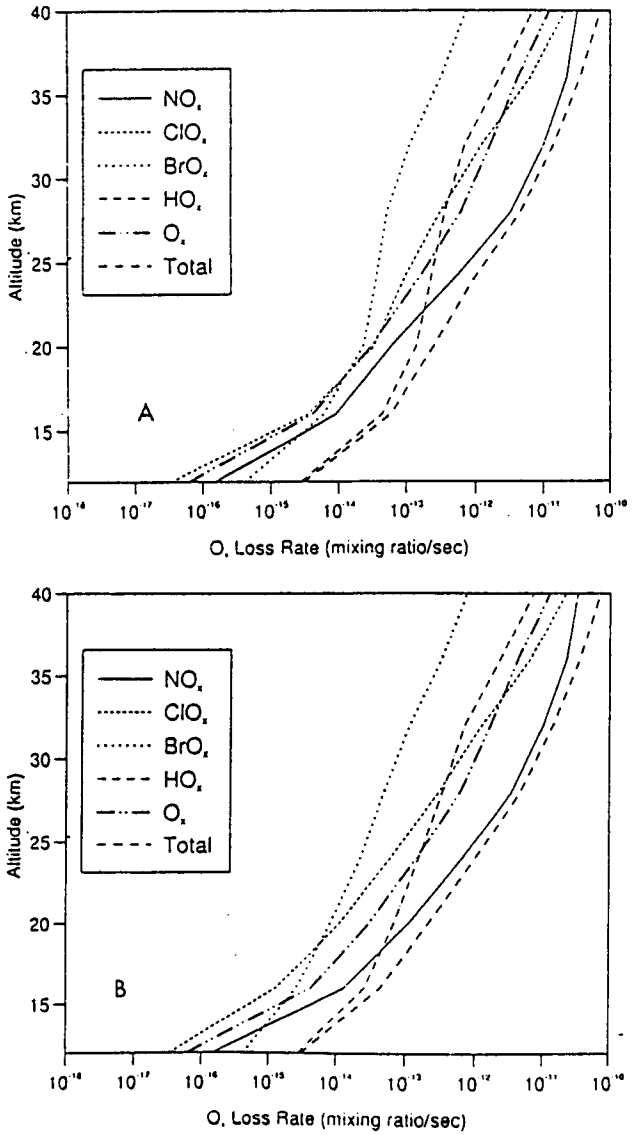

Figure 4. Calculated 24-hour averaged O_x loss rates (mixing ratio/s) for (a) volcanic and (b) background sulfate aerosol loading. The sticking coefficient gamma for $BrONO_2$ hydrolysis was 0.4 for Figures 4, 5, and 6. With background aerosol loading the HO_x cycle is the most important below 18 km with the NO_x cycle taking precedence between 18 and 40 km. Under heavy aerosol loading the HO_x cycle dominates up to 22 km.

Table 2. Calculations on the Effects of Varying Chlorine and Bromine Loading on Summer Solstice NO_2 Vertical Column Amounts

	1990 Halogens		Time-Varying Halogens*		Low Halogens+	
	Morning	Evening	Morning	Evening	Morning	Evening
1990	5.47	5.54	5.47	5.54	5.89	5.92
1991	4.34	4.44	4.32	4.42	5.24	5.31
1992	4.64	4.74	4.60	4.70	5.40	5.47
1993	5.16	5.24	5.11	5.19	5.67	5.76
1994	5.33	5.41	5.27	5.34	5.79	5.8

*Chlorine and bromine loadings increasing from 1990 values at 3% and 2% per year, respectively.

+Chlorine and bromine loadings at 25% of 1990 values.

NO_2 column amounts ($\times 10^{15}$ molecule / cm^2), full chemistry, 65°S.

the error bars ± 1 σ. With no $BrONO_2$ hydrolysis the model underestimates the measured reduction in midsummer NO_2 column amounts. The inclusion of $BrONO_2$ hydrolysis with a gamma value of 0.4 improves the comparison, but now the model tends to overestimate the decline in column amounts. The best agreement between the measurements and the model is with a gamma value of 0.2. Since this work was done and submitted for publication, new laboratory measurements of *Hanson et al.* [1996] have shown that $BrONO_2$ hydrolysis is temperature dependent. At the fairly high summertime temperatures (230 to 240 K) at 20-25 km above Faraday the reaction should indeed proceed with a gamma value of approximately 0.2.

The same ozone profile, output from the two-dimensional model, was used in the model throughout. To test whether the measured decrease in NO_2 column amounts for December 1991 compared to December 1990 might have been due to changes in ozone profile as the result of the Mount Pinatubo volcanic eruption instead of $BrONO_2$ hydrolysis, SAGE II ozone profiles for these 2 months were obtained and used for model initialization (Larry Thomason, private communication, 1996). The December 1991 ozone profile information was only available down to 26 km because of the heavy aerosol loading. At this altitude the December 1991 ozone was 10% lower than in December 1990. We have therefore assumed a 10% loss below 26 km and lesser losses above 26 km in December 1991. Two model integrations were performed with all other initializations including aerosol loadings identical.

The integrations resulted in morning and evening NO_2 column amounts 2.4% larger in December 1991 than in December 1990. This is due to less ozone at all altitudes in December 1991 resulting in less conversion of NO_2 to N_2O_5 and hence more NO_2. These calculations demonstrate that the measured 16% decrease in December 1991 summertime NO_2 column amounts compared with December 1990 cannot be explained by the observed SAGE II changes in ozone profile.

Although there is no ozone profile information below 26 km in December 1991, in January and February 1992 the total ozone measured by the Dobson at Faraday increased by 3% relative to the same months in 1991, 1993, 1994 and 1995 (A. E. Jones and J. D. Shanklin, private communication, 1996). It is not clear whether this was due to Pinatubo aerosol; nevertheless, the increase occurred. If instead of a 10% ozone loss below 26 km the model is run with a 3% ozone increase at all altitudes and all other conditions the same, the decrease in NO_2 column amounts in December 1991 was 0.5% for the morning and 1% for the evening compared with December 1990. This decrease is far smaller than the measured 16% decrease in NO_2 column amounts, again arguing against

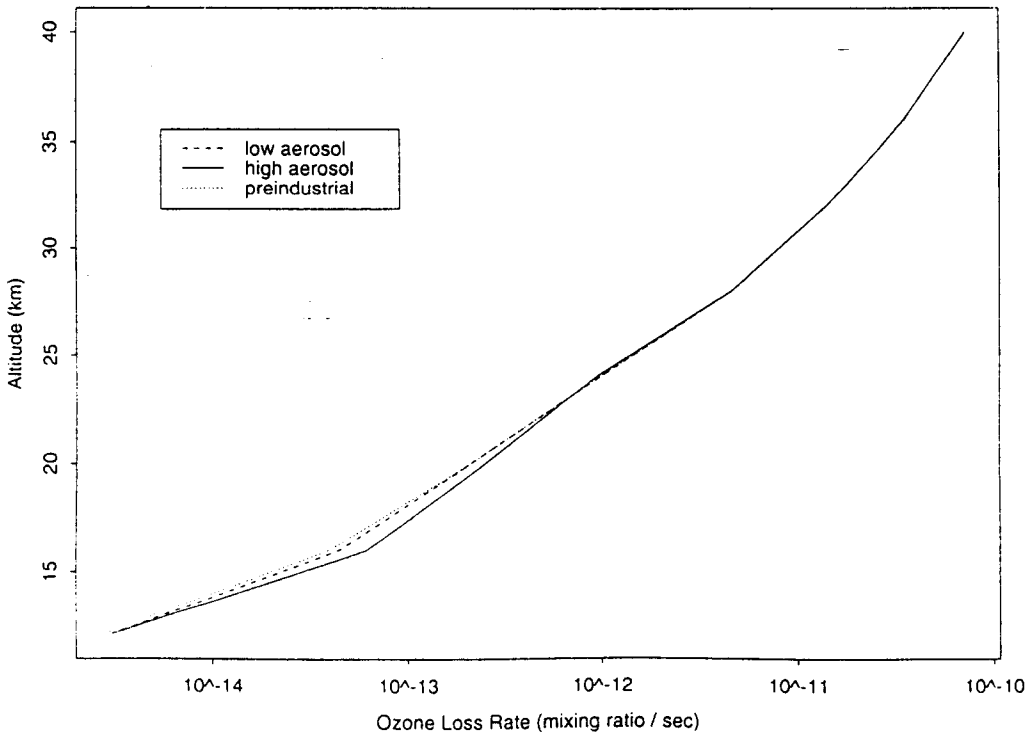

Figure 5. Total O_x loss rate profiles for $BrONO_2$ hydrolysis gamma of 0.4 for 1990 Br_y and Cl_y levels with 1990 low aerosol loading (dashed), 1991 high aerosols loading (solid), and 25% Br_y and Cl_y (preindustrial) with 1990 low aerosol loading (dotted). The total O_x loss for high aerosol loading is 38% greater at 16 km compared to losses with background aerosol. The total midsummer O_x loss profile appears not to be very sensitive to the Br_y and Cl_y loadings.

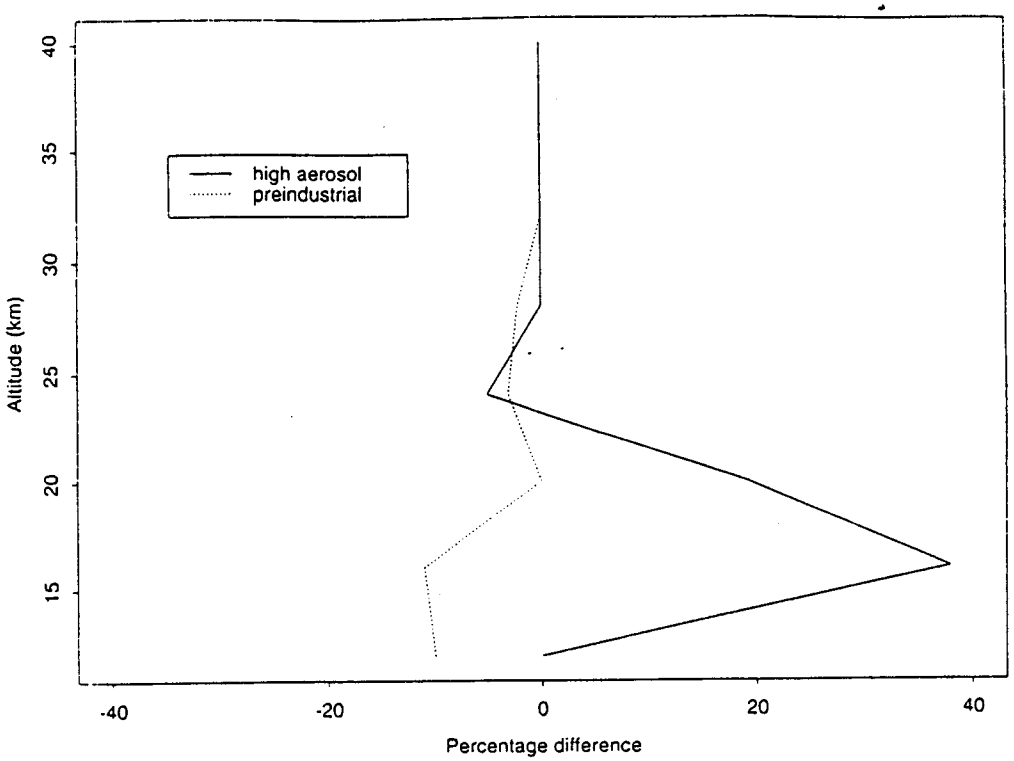

Figure 6. Percentage difference in total O_x loss rates for $BrONO_2$ hydrolysis gamma of 0.4 between low aerosol loading and high aerosol loading (solid), background aerosols with 25% Br_y and Cl_y (preindustrial) 1990 levels (dotted).

changes in ozone being the major cause of the large reduction in NO_2 column amounts.

The ozone data available for December 1991 are not good and not consistent between the SAGE II and the Dobson. The SAGE II data had large uncertainties, and it was necessary to extrapolate below 26 km. These two measurements appear to be the best data available. We have determined that the sensitivity of NO_2 column amounts to two different ozone profiles is significantly less than the measured decrease in NO_2 column amounts.

Given the importance of $BrONO_2$ hydrolysis, a sensitivity test of known and assumed rates of halogen changes to NO_2 column amounts was performed, shown in Table 2. These calculations show that significantly reduced NO_2 concentrations are to be expected in periods of large volcanic loading with present-day bromine (Br_y) and chlorine (Cl_y) loading. The effect of the increasing halogen levels on modeled NO_2 columns for the various aerosol loadings is less than 2% in any summer from 1990 to 1994. For a low halogen (Br_y and Cl_y) loading of 25% current levels, NO_2 column amounts would have been much less sensitive to the volcanic aerosol layer.

The calculated ozone loss rates due to the various catalytic cycles are shown for midsummer with December 1991 Pinatubo aerosol profiles in Figure 4 (a) and for December 1990 background aerosol in Figure 4 (b), which may be compared to those given by *Garcia and Solomon* [1994]. With background aerosols, HO_x is the most important catalytic cycle from 12 to 18 km above which NO_x takes over primary importance. With the volcanic aerosol the HO_x cycle dominates up to 22 km before the NO_x cycle becomes the most important. Thus in addition to reducing midsummer NO_x concentrations, heavy aerosol loading makes HO_x the most important O_3 loss cycle between 12 and 22 km. The total ozone loss for high aerosol loading is 38% greater at 16 km compared with the losses with background aerosols (Figures 5 and 6).

To further assess the importance of present-day industrial Br_y and Cl_y levels on ozone abundances, ozone catalytic loss rates were calculated with background aerosol loading and low halogens (25% 1990 levels) Br_y and Cl_y (Figure 5). Figure 5 shows the total midsummer ozone loss profiles for 1990 low aerosol loading, 1991 high aerosol loading, and low-halogen Br_y and Cl_y with low aerosol loading. The predicted total midsummer ozone loss profile increases by 38% at 16 km due to high aerosol loading. However, with background aerosol loading the total midsummer ozone loss profile appears not to be very sensitive to Br_y and Cl_y loadings (Figures 5 and 6), as halogen-related ozone loss is compensated for by reduced ozone loss due to nitrogen oxides.

Conclusions

Model calculations show that the measured reduction in midsummer maxima of NO_2 column amounts at 65°S following the eruption of Mount Pinatubo can be explained by $BrONO_2$ and N_2O_5 hydrolysis on the volcanic aerosol layer, with the former dominating. The best agreement between the measurements and the model predictions of NO_2 column amounts was with the $BrONO_2$ hydrolysis gamma equal to 0.2. But since there are the unknown effects of the quasi-biennial oscillation and year-to-year variability in NO_2 column amounts, using this data alone it is not possible to rule out a gamma of 0.4. The effect of the increasing halogen levels on modeled NO_2 column amounts for the various aerosol loadings was less than 2% in any summer from 1990 to 1994. With low halogen concentrations (25% current levels), NO_2 column amounts would be less sensitive to increased aerosol loading. Under conditions of enhanced volcanic aerosol loading, the HO_x catalytic O_3 loss cycle dominates between 12 and 22 km, above which the NO_x cycle becomes the most important. With the background aerosol the HO_x is the major loss cycle only up to 18 km. The predicted total midsummer ozone loss profile increases by 38% at 16 km due to high aerosols but is not very sensitive to the Br_y and Cl_y loadings when aerosol loadings are small.

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