MODULATIONS OF STRATOSPHERIC OZONE BY VOLCANIC ERUPTIONS

Christian Blanchette and John C. McConnell

York University, Dept. of Earth and Atmospheric Sciences
4700 Keele St., Downsview, Ontario, Canada, M3J 1P3.

ABSTRACT

We have used a time series of aerosol surface based on the measurements of Hofmann (1990) to investigate the modulation of total column ozone caused by the perturbation to gas phase chemistry by the reaction N_2O_5(gas) + H_2O(aero) $\rightarrow$ $2HNO_3$(gas) on the surface of stratospheric aerosols. We have tested a range of values for its reaction probability, $\gamma = 0.02$, 0.13 and 0.26 which we compared to unperturbed homogeneous chemistry. Our analysis spans a period from Jan. 1974 to Oct. 1994. The results suggest that if lower values of γ are the norm then we would expect larger ozone losses for highly enhanced aerosol content than for larger values of γ. The ozone layer is more sensitive to the magnitude of the reaction probability under background conditions than during volcanically active periods. For most conditions, the conversion of NO_2 to HNO_3 is *saturated* for reaction probability in the range of laboratory measurements, but is only *absolutely saturated* following major volcanic eruptions when the heterogeneous loss dominates the losses of N_2O_5. The ozone loss due to this heterogeneous reaction increases with the increasing chlorine load. Total ozone losses calculated are comparable to ozone losses reported from TOMS and Dobson data.

The appearance of massive ozone depletion over Antarctica has prompted a great interest in heterogeneous chemistry on polar stratospheric clouds (PSCs). More recently, it has become apparent that heterogeneous reactions may also be playing an important role in ozone destruction outside of the polar regions (Hofmann and Solomon, 1989; Brasseur et al., 1990; Pitari et al., 1991; Rodriguez et al., 1991). The ozone destruction from heterogeneous reactions is related to the availability of aerosol surface which is modulated by potent volcanic eruptions which penetrate the stratosphere.

In this study, we evaluate this modulation of ozone by volcanic eruptions using a one-dimensional photochemical model and input the aerosol surface as a time series based on the measurements presented by Hofmann (1990). We have assumed that the aerosols are spherical and can be represented by a log-normal size distribution. The measurements spanned a period from 1974 to April, 1990. Prior to 1974 and from the end of the data set to June 15, 1991, the aerosol surface was kept constant to represent aerosol background conditions. To represent the impact of Pinatubo for the period from June 15, 1991 to October 13, 1994, the aerosol parameters from the El Chichón pulse, taken to span the period from April 4, 1982 to April 1st, 1990, were used and the amount was scaled by 1.5 (Larson et al., 1982). Consequently, we have extended the time series from 1974 to late 1994 (Figure 1). The profiles of aerosol surface adopted were based on measured profiles of aerosol mass mixing ratio taken in mid-1989 (Hofmann, 1990). In our model, the aerosol layer extends from 7 to 27 km with peak mixing ratio at 22 km and the profile is assumed to remain unchanged with time.

They are a number of heterogeneous reactions of possible importance. In this note, we concentrate on one heterogeneous reaction:

$$N_2O_5 \text{ (gas)} + H_2O \text{ (aero)} \rightarrow 2\,HNO_3 \text{ (gas)} \quad (1)$$
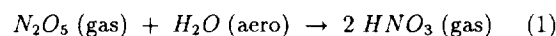
(Evans et al., 1985; Hofmann and Solomon, 1989). This reaction affects the partitioning of nitrogen species. It channels odd nitrogen from a short-lived reservoir species, N_2O_5, to a longer-lived one, HNO_3. Although the destruction of ozone by NO_2 is expected to decrease, it is expected to be offset by an increase in active Cl_x (eg. Rodriguez et al., 1991).

We have used a simple parametrization for the heterogeneous chemistry based on the aerosol surface area and measured reaction probability. Laboratory measurements of reaction probability (γ) of N_2O_5 + H_2O on aerosol surface range from 0.04 at 283°K (Van Doren et al., 1990) to 0.09 and 0.139 at 293°K and 274°K respectively (Mozurkiewich and Calvert, 1988) and to 0.14 at 215°K (Hanson and Ravishankara, 1991). These rates were found to be independent of the relative humidity (Mozurkiewich and Calvert, 1988). To account for possible temperature dependencies in the reaction probability and for uncertainties in total aerosol surface (emerging from assumptions made in its determination from published data), we have
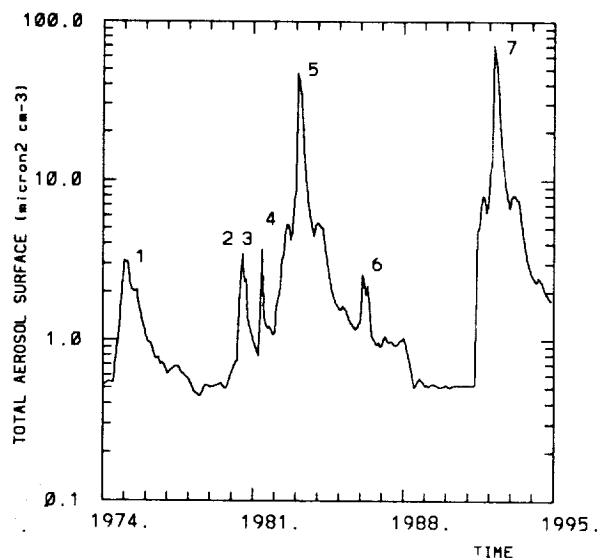
Figure 1: Aerosol surface time series at aerosol peak mixing ratio. See text for details. The peaks represent volcanic eruptions: 1. Fuego, 2. Mount St.Helens, 3. Alaid, 4. Nyamuragira, 5. El Chichón, 6. Nevado del Ruiz, and 7. Pinatubo. The Pinatubo pulse is assumed to be $1.5 \times$ El Chichón's (Larson et al., 1992).

chosen the reaction probability to cover a range of values: 0.02, 0.13 and 0.26. We have compared the results of these runs to a homogeneous chemistry case.

Our analysis spanned a period from January 1974 to October 1994. Scenarios were run with the chlorofluorocarbons and halons fluxes increasing according to OECD estimates to 1980 (OECD, 1981), according to global production rates from 1980 to 1985 and follow both the Montréal Protocol and the London amendments thereafter (eg. McConnell et al., 1990).

Figure 2 shows time series of total column ozone for various values of γ. For the period from early 1974 to late 1994, the loss of ozone due to homogeneous chemistry increases monotonically in response to increasing chlorine loading. Calculations for heterogeneous cases clearly show signatures of major volcanic eruptions especially those of Fuego (1974), El Chichón (1982) and Pinatubo (1991). Ozone loss maximizes for El Chichón (-16 to -19 DU) and Pinatubo (-14 to -19 DU) as compared to the total column ozone in January 1979 and January 1990, respectively. Maximum loss of ozone lags the maximum aerosol surface peak by 2 to 4 months.

The effect of the heterogeneous reaction of N_2O_5 is determined by how close the chemistry is from *saturation* . By saturation it is meant that the rate of reaction N_2O_5 (gas) $+$ H_2O (aero) $\rightarrow$ $2\ HNO_3$ (gas) is limited by the production rate of N_2O_5 which is, in turn, determined by the nightime formation of NO_3 via $NO_2 + O_3 \rightarrow NO_3 + O_2$ (with rate k_2). It is expected that most of the N_2O_5 formed will be converted to HNO_3, generating a significant reduction in NO_2 densities and an

associated increase in ClO concentration. This process increases the ClO concentration above that calculated for unperturbed homogeneous chemistry. The ClO amplification is limited by the amounts of available NO_x which is determined by an equilibrium between the loss of NO_x to N_2O_5 formation and its production from HNO_3 photolysis.

Figure 3 shows time series for the loss time constants for N_2O_5 to form HNO_3 (τ_1) (with $\gamma = 0.13$), to photolyse ($\tau_2 = 1/J_{N_2O_5}$), and for NO_2 loss to O_3 ($\tau_3 = 1/k_2(O_3)$). For $\gamma = 0.13$, the chemistry is saturated with $NO_2 + O_3 \rightarrow NO_3 + O_2$, the slowest reaction, being rate limiting. It can be seen that, during periods of volcanic quiescence (mid-1976 to 1980; 1988-91), photolysis of N_2O_5 is more rapid than the heterogeneous loss of N_2O_5, even for $\gamma = 0.13$. During volcanically active periods (1980-86; 1992-thereafter), the N_2O_5 conversion to HNO_3 is faster than its photolysis. The size of τ_1 versus the length of the night (τ_N) is indicative of the strength of the NO_2 conversion to HNO_3. If $\tau_1 < \tau_N$, most of the N_2O_5 formed during the night will be converted to HNO_3 and the nightime NO_2 loss will be maximized. On the other hand, if $\tau_1 > \tau_N$, a fraction of the N_2O_5 formed during the night will be present at sunrise. The heterogeneous reaction will then be competing with N_2O_5 photolysis. For background aerosol conditions, photolysis dominates the N_2O_5 losses and a large fraction of the N_2O_5 will be converted back to NO_2. This limits the increase in ClO concentration and reduces the ozone loss. The magnitude of the sunrise concentration of N_2O_5 is inversely proportional to the reaction probability making the chemistry more sensitive to γ during periods of volcanic quiescence (Figure 2).

During volcanically active periods, $\tau_1 \ll \tau_2$. We call this situation **absolute saturation** because by sunrise, N_2O_5 will have been mostly converted to HNO_3 with only a small fraction left to regenerate the NO_2 through the relatively slower N_2O_5 photolysis. Under these conditions, lower values of ozone column are found. The balance between $N_2O_5 + H_2O$(aerosol) and N_2O_5 photolysis is determined by the aerosol loading. Periods of enhanced aerosol content tend to favour the heterogeneous reaction leading to a less efficient, but still active, photolysis. For instance, in 1979, our calculations show that 64 % of the daily averaged N_2O_5 was converted back to NO_2 by photolysis and only 34 % was channelled to HNO_3 by the heterogeneous reaction. At the peak of the El Chichón aerosol perturbation (1983), only 4 % of the N_2O_5 was converted back to NO_2 while 96 % was transformed into HNO_3. What emerges from this work is that even for *saturated* chemistry the aerosol loading will modulate the NO_2 and ClO concentrations by controlling the relative balance between heterogeneous conversion of N_2O_5 and its photolysis. This can be seen in the time series of total column of ozone (Figure 2) as the well defined troughs matching the aerosol peaks of Figure 1. It can further be added that for enhanced aerosol levels, the chemistry becomes less sensitive to changes in aerosol loading.
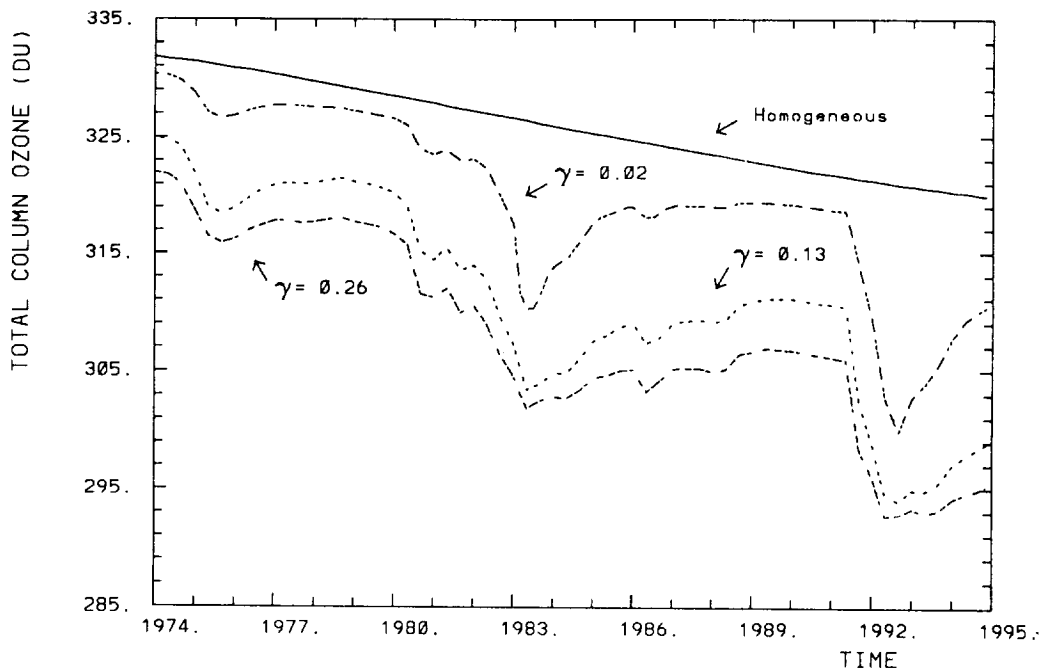
Figure 2: Total column ozone time series from 1974 to 1995. Cases include homogeneous chemistry and the heterogeneous reaction N_2O_5(gas) + H_2O(aero) $\rightarrow$ 2 HNO_3(gas) with γ = 0.02, 0.13, 0.26.

The magnitude of the amplification of ClO densities above the background levels determines how much ozone will be lost with the inclusion of reaction (1): the larger the reaction probability, the lower the possible ClO amplification following volcanic eruptions. For instance, in the lower range of values, for γ = 0.02, the ozone is more sensitive to aerosol loading since there are no, or at least reduced, saturation effects. For this case, total column ozone changes were calculated to be as large as − 5.8% between 1979 (aerosol background conditions) and 1983 (El Chichon's maximum ozone loss). For the same period changes of − 5.3% and − 5.0% were calculated for γ = 0.13 and γ = 0.26 respectively. For the Pinatubo eruption, total ozone changes between June 1990 and March 1992 were calculated to be: −6.0%, −5.2% and −4.6% for γ = 0.02, 0.13, 0.26, respectively. For the larger values of γ, absolute saturation will set in sooner, the time depending on the aerosol surface area, and the apparent ozone loss will not be as great as shown by our calculations.

Following volcanic eruptions, the temporal behaviour of the recovery curve is slower for the higher γ values. For the low γ values, the recovery is more rapid and the effects of the diminished levels of aerosols are seen in ozone recovery with a short time lag. For the large values, the recovery is much slower until the aerosol levels become small enough to lower the efficiency of the heterogeneous reaction beyond the level of absolute saturation. For example, the curves with γ = 0.02 have a 50 % recovery by 1.5 years while it takes about 3 years for the case of γ = 0.26. Our calculations show that for reaction probability

within the range of measured values, the ozone loss between January 1979 and May 1990 is $\leq$ 3.5% (Table 1). These values are consistent the 4 % average loss observed by TOMS in the 20-60° N area (Stolarski et al., 1992;
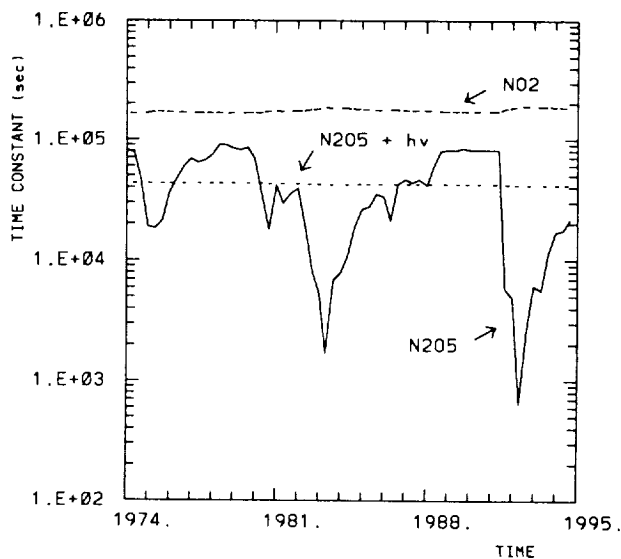

Figure 3: Time series of loss time constants at 20 km from 1974 to Oct. 1994 for NO_2 lost through the reaction $NO_2 + O_3 \rightarrow NO_3 + O_2$; N_2O_5 lost by N_2O_5(gas) + H_2O(aero) $\rightarrow$ 2HNO_3(gas) with γ = 0.13; and N_2O_5 lost by photolysis.

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γ	0.00	0.02	0.13	0.26
O_3 loss (%)	-2.1	-2.4	-3.1	-3.5

Table 1: Total column ozone loss from Jan. 1979 to Jan. 1989.

γ	0.02	0.13	0.26
ClO amplification	1.3	2.1	2.5

Table 2: ClO amplification factor vs γ The amplification factors were calculated at 20 km as the ratio of the ClO concentrations for the heterogeneous to the unperturbed homogeneous cases. For given γ, the ClO amplification factors calculated in Jan. 1979 and Jan. 1990 are identical.

Stolarski et al., 1991). It is also within the limits of the 4 % loss from 1980 to 1990 reported for the North-American stations of the Dobson network (Stolarski et al., 1992).

Anthropogenic emissions of CFC and halon compounds enhance the ozone loss due to reaction (1). For instance, if 1979 and 1990 are assumed to be background years for aerosol loadings and if we use January 1948 as a reference year (334 DU), our calculations show that the ozone loss due to reaction (1) with a $\gamma = 0.13$ was 2.4 % in 1979 and 3.4 % in 1990. The enhanced ozone loss is due mainly to an increase in atmospheric chlorine load. It was found that for lower aerosol levels such as is observed during aerosol background years, the ClO concentration is enhanced above the unperturbed homogeneous chemistry by a fixed factor which depends on the reaction probability of reaction (1) (see Table 2). For instance, for $\gamma = 0.13$, the ClO concentrations in 1979 and in 1990 were 2.1 times the ClO concentrations calculated for the homogeneous chemistry case. Thus, the proportion of the ozone loss will increase as the atmospheric chlorine load increases. Consequently, under aerosol background conditions, a large reaction probability will generate a larger departure from the unperturbed homogeneous chemistry case.

Compared to unperturbed homogeneous chemistry, the heterogeneous reaction $N_2O_5 + H_2O(\text{aero}) \rightarrow 2HNO_3(\text{gas})$ lowers the total column of ozone. Following large volcanic eruptions (eg El Chichón and Pinatubo), maximum losses of 19 DU were calculated with maximum relative losses close to 6 % for the lower reaction probability. Recovery from these eruptions is longer for the larger reaction probability. During background aerosol years, the ozone layer appears more sensitive to the magnitude of the reaction probability with calculated changes in total column of ozone proportional to the reaction probability. These background years correspond to a chemistry which is not absolutely saturated, leaving room for extra NO_x conversion to HNO_3. The 1979-1990 trends in total column of ozone show a small departure from the unperturbed chemistry and remain within the range of observed TOMS

and Dobson data. Finally, the impact on the ozone layer of the reaction studied amplifies with the increasing chlorine loadings.

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