

## Stratospheric denitrification due to polar aerosol formation: Implications for a future atmosphere with increased CO<sub>2</sub>

Giovanni Pitari and Lucrezia Ricciardulli

Dipartimento di Fisica, Università de L'Aquila, Italy

**Abstract.** The amount of stratospheric denitrification produced by NAT aerosol formation is studied with a photochemical two-dimensional model which includes the effects of zonal asymmetries of the temperature field. The model photochemistry is coupled with a microphysical code for aerosol formation and growth, so that the permanent loss of stratospheric nitric acid and water vapor may be taken into account. The model results for nitric acid relative to the atmospheric chemical composition of 1980 are compared with LIMS data. We show that the level of denitrification may rise substantially if the polar vortex cools down, as it could be the case in a future atmosphere richer in carbon dioxide. A three-dimensional model is used to calculate the temperature perturbation due to an increase of CO<sub>2</sub> from 335 ppmv of 1980 (baseline) up to 500 ppmv (predicted for 2050). The photochemical model adopting these new temperatures predicts an average 20% HNO<sub>3</sub> column decrease poleward of 45N with respect to baseline. One consequence is that the relative weight of the NO<sub>x</sub> catalytic cycle for O<sub>3</sub> destruction decreases with respect to the present atmosphere.

### Introduction

Two-dimensional (2D) models are currently used to assess the perturbation of stratospheric chemistry due to natural events and anthropogenic activity. Unfortunately, these models adopt in general a crude representation of heterogeneous processes involving aerosol particles. The most common approach is to introduce a fixed surface area density of sulfate aerosols deduced from satellite measurements (WMO, 1992) and sometime a frequency of appearance of polar stratospheric clouds (PSC). On the other hand, two possible feedback mechanisms are produced by aerosol formation on the stratospheric chemistry, and only one of these may be taken into account with the above parameterization (i.e. the different partition of chemical families due to heterogeneous chemical reactions). The other important effect is that the partition of NO<sub>x</sub> and consequently of the other chemical families is largely upset by the

lower stratospheric denitrification following the formation, growth and sedimentation of nitric acid hydrates.

The only way to model this effect is to couple the photochemistry with an explicit microphysical code for aerosol formation and growth. This has been recently done by Pitari *et al.* (1993) for both sulfate and polar aerosols, which have been assumed to be made of nitric acid trihydrate (NAT) and ice. The size distribution of these classes of aerosols is calculated as a function of time at each model grid-point by taking into account microphysical processes (i.e. heterogeneous nucleation, condensation/evaporation, coagulation), large scale transport, sedimentation and tropospheric washout. The rate of gas removal/production from aerosol condensation/evaporation is included in the continuity equations of sulfuric acid, nitric acid and water vapor, with the mass conservation insured for steady-state calculations.

In the first part of this paper we calculate the amount of denitrification associated to the formation of NAT and ice aerosols over the Arctic region using climatological temperatures. In the second part of the paper we show that the nitric acid loss due to NAT/ice formation may increase greatly if the Arctic polar vortex cools down of few degrees. Such a cooling of the lower stratosphere could be expected in the next century as a consequence of CO<sub>2</sub> increase in the atmosphere (Pitari *et al.*, 1992). This is shown to have important effects on the partitioning of chemical families. It should be kept in mind that we are focusing only on the potential effect of a 'secular trend' of zonal temperatures on NAT formation, while no investigation is made on the effects of year to year fluctuations.

### NAT and ice aerosol formation in the 2D model

The main difficulty of including aerosol formation in 2D models is the description of the temperature field: to take in account the temperature variability due to atmospheric eddy motions, we assume the temperature to be normally distributed at each grid point of the model, with  $T_i$  and  $\sigma_i$  being the monthly-zonally averaged temperature and its standard deviation, respectively. The temperature data above 20 mb are taken from the output of a quasi-geostrophic three-dimensional model (3D) (Pitari *et al.*, 1992), while below 20 mb they are taken from long-term circulation statistics. Temperature standard deviations are tabulated in Oort (1983)

Copyright 1994 by the American Geophysical Union.

Paper number 94GL01136  
0094-8534/94/94GL-01136\$03.00

below 50 mb, while between 20-50 mb we have kept constant the values at 50 mb.

The nucleation and condensation terms in the continuity equation for the size distribution  $n(r, t)$  of polar aerosols are weighted by the normal distribution of temperature below the saturation value  $T^0$ :

$$\left. \frac{\partial n(r, t)}{\partial t} \right)_{nucl.} = \langle J(r, S) \rangle P_c \hat{n}(r, t) \quad (1)$$

$$\left. \frac{\partial n(r, t)}{\partial t} \right)_{cond.} = -\frac{\partial}{\partial r} [\langle g(r) \rangle P_c n(r, t)] \quad (2)$$

$$\langle f \rangle = \frac{1}{P_c} \int_{T_l}^{T^0} f(T) P(T) dT, \quad P_c = \int_{T_l}^{T^0} P(T) dT$$

where  $f$  is any function of temperature,  $P_c$  is the condensation probability and  $T_l$  is the lower limit of  $T$ , typically  $T_l = T_i - 2\sigma_i$ . When  $T^0 < T_l$  no more condensation occurs and aerosol evaporation takes place.

In equations (1-2),  $J(r, S)$  is the heterogeneous nucleation rate,  $g(r)$  is the particle growth rate,  $S$  is the saturation ratio,  $n(r, t)$  is the particle size distribution and  $\hat{n}(r, t)$  is the size distribution of those particles acting as condensation nuclei. More details on the microphysical code and on the photochemical 2D model may be found in Pitari *et al.* (1993). The calculated surface density of sulfate aerosols compares with the SAGE II derived data of 'lower limit' surface density (WMO, 1992) within a 40% uncertainty. A similar agreement is found for the optical thickness above the tropopause in the polar regions when compared to SAM II data.

On the other hand, the results reported in the paper of Pitari *et al.* (1993) for the NAT aerosol size distribution show a too pronounced formation of large particles. As discussed in that paper, this is mostly a consequence of the coarse radial resolution adopted in the 2D model. The effect is an overestimation of particle growth due to gas condensation with respect to nucleation of preexisting sulfate particles whose size distribution is peaked at about  $0.05 \mu m$ . To cure this effect we have included a sticking coefficient  $\alpha = 0.3$  in the calculation of condensation kernels for  $HNO_3$  and  $H_2O$ : although this value is consistent with laboratory measurements, more realistically the sticking coefficient for NAT growth tends rapidly to unity at the stratospheric temperatures where PSC are formed. Our assumption should rather be considered as a numerical cure for the too fast particle growth; the net effect on the size distribution will be discussed later in the paper.

Another source of uncertainty is that in our scheme the formation of NAT starts from depositional nucleation on frozen sulfuric aerosol, while there are evidences that ternary solutions of  $H_2SO_4-H_2O-HNO_3$  may form in the polar vortex as the first stage in the formation of nitric acid hydrates (Molina *et al.*, 1993). In this case the nucleation barrier for the formation of NAT is smaller, so that the loss of gas phase  $HNO_3$  should be enhanced. On the other hand, the statistical approach adopted in our 2D model for including time and longitudinal temperature fluctuations may have the

effect of producing particles somewhat larger with respect to the real atmosphere. This is because fast cooling/warming events are missed, so that the nucleation of the smallest sulfate aerosols is underestimated. For these reasons our calculation should be considered preliminary at this stage of knowledge of the polar aerosol formation mechanisms.

## Numerical experiments

Four different steady-state numerical experiments are conducted with the 2D model, all relative to the atmospheric chemical composition of 1980 (WMO, 1992). They will be referred to as 'G' (gas phase chemistry), 'S' (heterogeneous chemistry on sulfate aerosols), 'P' (heterogeneous chemistry on sulfate, NAT and ice aerosols) and 'P<sub>1</sub>' which correspond to 'P' but with the temperature field modified by a carbon dioxide increase up to 500 ppmv. The latter case corresponds to the  $CO_2$  atmospheric loading predicted for the year 2050: the temperature change with respect to the reference case of 335 ppmv  $CO_2$  has been calculated using the 3D model. The probability for heterogeneous chemical reactions ( $\gamma$ ) is specified as in WMO, 1992, taking into account the deviations of temperature from the monthly-averaged value (Pitari, 1993).

Figure 1 compares the model calculated  $HNO_3$  column for experiments G, S, P with the LIMS data for the winter months in the Northern Hemisphere. As shown by NASA (1993), inclusion of heterogeneous chemistry on the sulfate aerosol layer increases the stratospheric column of  $HNO_3$  by about a factor 2 at the winter high-latitudes. This is mainly a consequence of heterogeneous conversion of  $N_2O_5$ , which represent an important reservoir of odd nitrogen during nighttime. However, the calculated column in case S is significantly overestimated with respect to the LIMS data. In the present study the discrepancy is larger than in NASA (1993): this is partly explained by the additional contribution due to the inclusion of temperature fluctuations in the calculation of  $\gamma$  for chlorine nitrate (Pitari, 1993). Another difference is that here the sulfate aerosol sur-

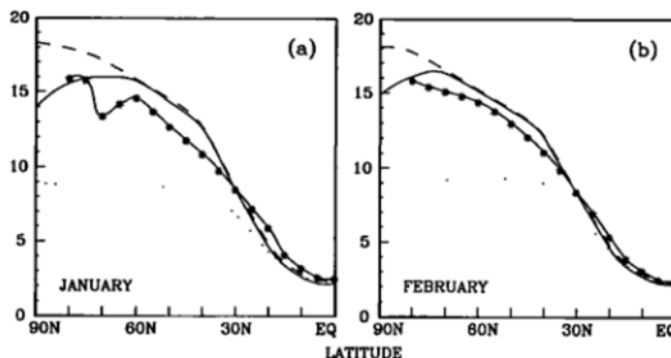


Figure 1.  $HNO_3$  column density ( $10^{15} \text{ mol/cm}^2$ ) above 100 mb (the bottom is set at 70 mb equatorward of 15N). Panels (a,b) refer to January and February, respectively. Dots, dashes and solid line are for model experiments G, S and P, respectively, while the line with stars refers to LIMS measurements (NASA, 1993).

face density is model-calculated and tends to be overestimated by about 20-40% below 100 mb in the Arctic region with respect to the 'lower limit' surface density adopted in NASA (1993). A somewhat too large probability for the  $N_2O_5$  reaction could also account for part of the discrepancy with LIMS.

The formation of NAT aerosols in the Arctic vortex has the effect of subtracting a significant portion of the lower stratospheric nitric acid, so that the calculated column fits better with measurements in the polar region. The nitric acid loss results from two distinct effects: a local temporary loss due to gas condensation in the aerosol particles, and a smaller permanent loss due to aerosol sedimentation. Both may play a role in the lower stratospheric chemistry and from now on we will refer to 'denitrification' as the sum of these two effects. A detailed discussion will be made later in the paper.

The first kind of  $HNO_3$  loss is suggested by the sharp decrease of the LIMS column at about 70N during January: this feature may likely be attributed to a persistent PSC event with associated loss of nitric acid from the gas phase. Nevertheless, the calculated column is still too high at the mid-latitudes. Recently, Rood *et al.* (1993) have studied the  $HNO_3$  distribution using a 3D model with transport parameters calculated from LIMS data. They show that the poleward advection is much stronger than that assumed in 2D models. They find a nitric acid column comparable to the one measured by LIMS in the polar region with only gas phase chemistry. In order to compensate for the large subtraction of  $HNO_3$  from the mid-latitudes, they include there an ad-hoc rate of nitric acid production: heterogeneous chemistry on sulfate particles may act for this purpose. On the other hand the highest concentration of  $N_2O_5$  is found at the winter high-latitudes, so that coupling a stronger poleward advection with this heterogeneous production would produce a much too high nitric acid column in the polar region, unless a removal mechanism would be present there.

The sensitivity of  $HNO_3$  to the probability of NAT formation has been studied by superimposing on the temperature field deduced from long-term circulation statistics the perturbation induced by carbon dioxide increase and calculated with the above mentioned 3D model. The temperature change in the Arctic winter is in the 0-3 K range between 15 and 25 km altitude (Figure 2); in the same figure we show the baseline profile of mean zonal temperature and its standard deviation. The correspondent behavior of nitric acid is shown in Figures 3-4: in particular Figure 3a shows that in the colder Arctic vortex the resulting denitrification is such that the column falls to values comparable to those predicted with pure gas phase chemistry, while at the mid-latitudes the column is closer to the LIMS value. In principle this could mean that the use of a stronger poleward advection along with heterogeneous chemistry on sulfate aerosols and NAT formation in the polar vortex would reconcile the calculated  $HNO_3$  column with the LIMS data. This is also suggested by Figure 3b where a column average is made poleward of 45N. We remind here that year to year temperature fluctuations

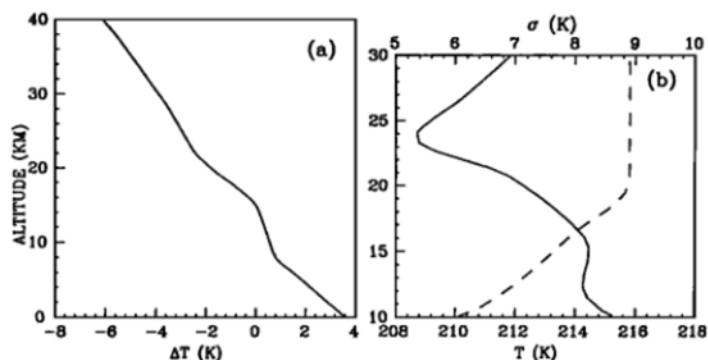


Figure 2. 3D model calculated temperature change due to carbon dioxide increase up to 500 ppmv with respect to baseline (335 ppmv) (panel a). The values refer to 70N and to an average over December-January-February. Panel (b) shows the baseline mean zonal temperature (solid line) and its standard deviation for the same time and latitude (dashed line).

are not considered in our model, so that caution should be taken in comparing the calculation results with the LIMS observations.

Figure 4 shows the behavior of the nitric acid profile and the size distribution of NAT aerosols in experiments  $P$  and  $P_1$ . A log-normal fit of these distributions give a mode radius  $r_0 = 0.63 \mu m$  and  $0.50 \mu m$  in cases  $P$  and  $P_1$ , respectively, and a total number of particles  $N_0 = 0.068$  and  $0.51 cm^{-3}$  (the dispersion is 1.8 in both cases). The decrease of  $r_0$  is consistent with the increased nucleation of small sulfate particles at lower temperatures. Drdla and Turco (1991) have used a 1D model incorporating temperature oscillations and find a size distribution for 'persistent' type 1 PSC with  $r_0 = 0.47 \mu m$ , which is rather close to our value.

When looking at the  $HNO_3$  profile in case  $P_1$  we see that a large fraction of gas is removed by condensation mostly in the 20-24 km altitude layer so that the mixing ratio at 20 km drops to about 3 ppbv from about 7 ppbv in case  $P$  (Figure 4a). It is important to note that the nitric acid sequestered in the NAT particles

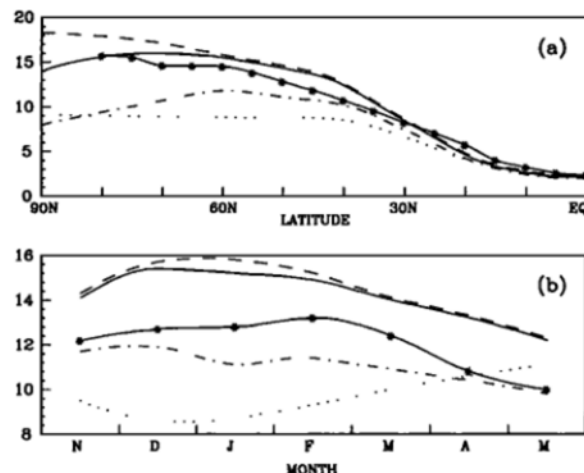
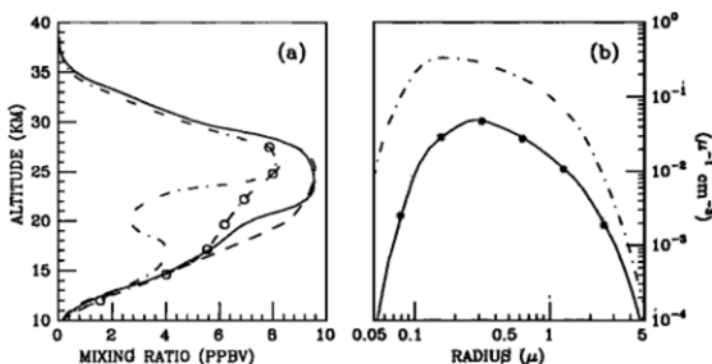


Figure 3. As in Figure 1, but for an average over December-January-February (a), and as a function of time for an average over 45N-85N (b). In this case the results of experiments  $P_1$  are added to those of Figure 1 (dotted-dashed line).



**Figure 4.** January profiles of  $HNO_3$  (ppbv) averaged poleward of 65N (a) and size distributions of NAT aerosols ( $\mu m^{-1} cm^{-3}$ ) averaged poleward of 65N and in the 19-24 km altitude layer (b). Lines in panel (a) are as in Figure 3, while the dotted-dashed line with open circles refers to gas + solid  $HNO_3$  in experiment  $P_1$ .

accounts for a large part of this difference. At the same time, aerosol sedimentation produces a permanent loss localized not only in the aerosol formation region but also in the altitude layer above it and at mid-latitudes, that is where the gas is removed by atmospheric large scale motions to be transported in the aerosol formation region. Dynamical dilution of the wintertime loss prevents a full recovery of  $HNO_3$  at the steady-state with respect to cases  $S$  and  $P$ , as shown in Figure 3b. The yearly averaged decrease of the nitric acid column poleward of 45N and calculated with respect to case  $S$  is about 1.6% and 22% in cases  $P$  and  $P_1$ , respectively.

## Conclusions

The results of our numerical calculation shows that the inclusion of an explicit gas-particle interaction is essential in photochemical models in order to have odd nitrogen sensitive to the formation of nitric acid hydrate particles. A comparison of model results with LIMS data show that the NAT aerosol induced denitrification plays a non-negligible role in the Arctic winter. The probability of NAT aerosol formation is so sensitive to temperature that the balance of active nitrogen in the lower stratosphere could be highly perturbed as a consequence of a polar vortex cooling.

In this paper we have calculated the effects of a stratospheric temperature change due to a carbon dioxide increase up to 500 ppmv, which represents the present estimate for the year 2050. The result of our experiment is that of about 20% decrease of the nitric acid column poleward of 45N and averaged over the entire year. This decrease is caused both by  $HNO_3$  condensation in the aerosol particles during the Arctic winter and by dynamical dilution of the NAT aerosol sedimentation loss: the latter prevents a full restoration of gas phase  $HNO_3$  after particle evaporation.

The photochemical effect of the denitrification is a significant decrease of odd nitrogen at mid-high lati-

tudes, so that the whole chemical composition of the lower stratosphere is perturbed. In particular, we find the contribution of  $Cl_x$  and  $Br_x$  catalytic cycles to increase of more than one order of magnitude with respect to the pure gas phase case. In addition, we find a yearly averaged 30% decrease of the ozone loss frequency due to the  $NO_x$  catalytic cycle when comparing case  $P_1$  to  $P$  (the frequency is averaged poleward of 45N and in the 14-23 km layer). We can say that the presence of polar aerosols decreases the vulnerability of the lower stratosphere to active nitrogen perturbations and this is even more true in a future atmosphere richer in carbon dioxide. It should be considered, however, that the ozone response to a  $NO_x$  perturbation is not obvious, because the  $ClO$  cycle is limited by nitric acid photolysis.

**Acknowledgments.** This work has been partly supported by the CEC and by Agenzia Spaziale Italiana.

## References

- Drdla, K., and R.P. Turco, Denitrification Through PSC Formation: A 1-D Model Incorporating Temperature Oscillations, *J. Atmos. Chem.*, **12**, 319-366, 1991.
- Molina, M.J., R. Zhang, P.J. Wooldridge, J.R. McMahon, J.E. Kim, H.Y. Chang, and K.D. Beyer, Physical Chemistry of the  $H_2SO_4/HNO_3/H_2O$  System: Implications for Polar Stratospheric Clouds, *Science*, **261**, 1418, 1993.
- NASA, The Atmospheric Effects of Stratospheric Aircraft: Report of the 1992 Models and Measurements Workshop. NASA Ref. Publ. 1292, 1993.
- Oort, A.H., Global Atmospheric Circulation Statistics, 1958-1973. NOAA Professional Paper 14, U.S. Department of Commerce, Washington, DC, 1983.
- Pitari, G., S. Palmeri, G. Visconti, and R.G. Prinn, Ozone Response to a  $CO_2$  Doubling: Results From a Stratospheric Circulation Model With Heterogeneous Chemistry, *J. Geophys. Res.*, **97**, 5953-5962, 1992.
- Pitari, G., V. Risi, L. Ricciardulli, and G. Visconti, High-Speed Civil Transport Impact: Role of Sulfate, Nitric Acid Trihydrate and Ice Aerosols Studied With a Two-Dimensional Model Including Aerosol Physics, *J. Geophys. Res.*, **98**, 23141-23164, 1993.
- Pitari, G., Contribution to the Ozone Trend of Heterogeneous Reactions of  $ClONO_2$  on the Sulfate Aerosol Layer, *Geophys. Res. Lett.*, **20**, 2663-2666, 1993.
- Rood, R.B., A.R. Douglass, J.A. Kaye, and D.B. Considine, Characteristics of Wintertime and Autumn Nitric Acid Chemistry as Defined by Limb Infrared Monitor of the Stratosphere (LIMS) Data, *J. Geophys. Res.*, **98**, 18533-18545, 1993.
- WMO, Scientific Assessment of Ozone Depletion - 1991. Global Ozone Res. and Monit. Project - Report 25, 1992.

Giovanni Pitari and Lucrezia Ricciardulli, Dipartimento di Fisica, Università de L'Aquila, via Vetoio, 67010 Coppito, L'Aquila, Italy. (e-mail: pitari@aquila.infn.it)

(received December 3, 1993; revised April 22, 1994; accepted April 29, 1994.)

