

Box model studies of ClO_x deactivation and ozone loss during the 1991/92 northern hemisphere winter

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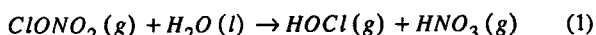
Abstract. Calculations using a photochemical box model from mid-January to early March 1992 show the return from perturbed levels of ClO_x to near background levels, and the associated rise of ClONO₂. The calculated values of ClONO₂ in an in-vortex, background aerosol scenario are in good agreement with those observed by the balloon borne MIPAS-B limb sounder. Implications for ozone loss are discussed.

Introduction

The chemical evolution of the vortex from late November 1991 until January 1992 has previously been discussed (Lutman et al., this issue). In that paper, the activation of chlorine by polar stratospheric clouds (PSCs) on the 475K potential temperature surface was studied using a trajectory model. It was found that by early January large amounts of active chlorine (ClO_x = ClO + 2×Cl₂O₂), over 2ppbv, were produced throughout the vortex by heterogeneous reactions on PSCs. During the second half of January the vortex became more disturbed (Naujokat et al., 1992). When temperatures rose in late January and large scale PSC processing stopped, ClO_x levels began to relax back to background levels through reformation of reservoir species. When chlorine levels were at their peak in mid-January there was not enough sunlight present for appreciable ozone loss to occur. Balloon measurements carried out in early March showed that most ClO_y (HCl+ClONO₂+HOCl+ClO_x) was in the form of ClONO₂ (Oelhaf et al., this issue). By performing photochemical box model runs from mid-January to March a number of problems may be addressed: whether the rapid increase of chlorine nitrate shown by the MIPAS measurements is consistent with known photochemistry, the role the Mt. Pinatubo aerosol played in determining the timescale for ClO_x recovery and the implications of the speed of ClO_x recovery for ozone destruction.

Model Description

The photochemical box model used is described in Lutman et al., (this issue). It includes a full gas phase chemistry scheme and heterogeneous reactions on sulphuric acid aerosol and polar stratospheric clouds (PSCs). For the period from mid-January 1992, the temperature is constrained to be above the critical temperature for PSC formation so only heterogeneous reactions on sulphate aerosols need be considered. The model includes the following two reactions on sulphate aerosol:



A sticking probability, γ , calculated as a function of temperature and reaching a maximum value of 0.1 at around 195K, is used for reaction 1 (Hanson and Ravishankara, 1991). Sulphate aerosol

surface areas available for heterogeneous chemical reactions are calculated in this study for two cases. Firstly ordinary background (surface area $\sim 0.5\text{-}0.75 \mu\text{m}^2\text{cm}^{-3}$) were used which compare well with in-vortex measurements of aerosol on January 18 (Deshler et al., 1993) over Kiruna as described later. Secondly volcanic (i.e. Pinatubo influenced) conditions were used ($\sim 10\text{-}15 \mu\text{m}^2\text{cm}^{-3}$). These are somewhat lower than measurements by Deshler et al., (1992) at Laramie, Wyoming between 26 July and 29 August 1991 of between 9 and $84 \mu\text{m}^2\text{cm}^{-3}$. However as will be seen this does not affect our argument.

The recently determined temperature dependence of the HNO₃ photolysis cross section (Rattigan et al., 1992) is included in the model. The effect of the temperature dependence of the HNO₃ photolysis rate on the chlorine relaxation in the model is discussed below.

Method

We follow a different approach to the companion study (Lutman et al., this issue) where chlorine activation was investigated. Here, in order to study the chemical behaviour of the polar vortex after PSC activation has ceased, integrations covering 55 days were performed from 20 January to 5 March 1992 at 50mb. The model was initialised assuming a pre-processed, i.e. high ClO_x atmosphere (see Table 1). Other species take values suitable for winter/spring high latitudes with a background aerosol. The air parcel follows an idealised temperature history which rises linearly from 198K to 213K at the end of the run. This approach does not reproduce periods when temperatures may again have dropped below the critical temperature for PSC formation in late January or early February (Naujokat et al., 1992) or when oscillations in temperature caused by transport around the vortex may have lowered the temperature. These temperature changes will make little difference to the gas phase chemistry. However if the temperature dropped below 195K levels of ClONO₂ would have been lowered due to heterogeneous reactions. Again this strengthens our conclusions as shall be discussed later. However for the purposes of this study the idealised model temperatures were in broad agreement with the general temperature trend of this period. Thus the temperature dependent reaction 1 is only effective for approximately the first 10 days of the runs in which sulphate aerosol reactions are included, while reaction 2 is effective throughout these runs.

By performing box model runs at 65°N a picture can be developed of chlorine relaxation inside, and on the edge of the polar vortex from late January to mid March 1992. Since the effects of excursions to lower latitudes, namely greater insolation, will be omitted by taking this approach, the results from 55°N and 75°N are also discussed.

TABLE 1. Chemical Initialisations / ppbv for 55°N-75°N.

Latitude	ClO _x	ClONO ₂	HCl
75/65°N	2.0	0.3	0.4
55°N	1.0	1.1	0.2

(At all latitudes HOCl = 0.2, HNO₃ = 10.5, NO_x = 0.24, N₂O₅ = 0.4, O_x = 3.5E+3, Br_x = 8.0E-3 ppbv.)

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Results

In figure 1 are shown nitric acid concentrations as a function of day of run, where day 1 is January 20 1992 for 65°N. Three cases are shown, perturbed aerosol similar to a Mt. Pinatubo scenario (case A), background aerosol, (case B), and only gas phase chemistry, (case C) for both temperature dependent and room temperature nitric acid photolysis rates. Using the older room temperature cross-sections compared to cross-sections calculated at 200K resulted in a doubling of the nitric acid photolysis rate at 20km, 0° solar zenith angle. The relative effect increases with solar zenith angle and is therefore of great importance at high latitudes.

In the cases including heterogeneous chemistry there is clearly some immediate adjustment to the initialisation during the first 3 days, greatest in the case of the large aerosol loading. In all three cases there is then a rather slow photolytic loss of HNO₃ (and an associated increase in NO_x, see figure 3). The difference in day 55 values arises from the increased rate of formation of HNO₃ in heterogeneous cases A and B and in the slower nitric acid photolysis rate when using temperature dependent cross-sections (Toumi et al. 1993a).

Figure 2 shows midnight values of chlorine nitrate for the same 3 cases. In case A (volcanic aerosol) ClONO₂ decays initially following reaction 1. Levels of ClONO₂ then rise as the recombination reaction of ClO and NO₂, arising from nitric acid photolysis, is faster than the loss of ClONO₂ due to its photolysis. In case A around 1ppbv is formed by the end of the run. The reformation is controlled by the levels of NO₂, which as can be seen from figure 3 are lowest in case A.

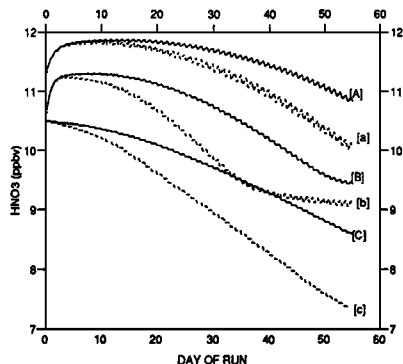


Fig. 1 HNO₃ (ppbv) as a function of day of run, at 50mb. Volcanic aerosol (A), background aerosol (B), pure gas phase chemistry (C). Effect of temperature dependent [capitals] and room temperature [lower case] absorption cross-sections for nitric acid photolysis shown.

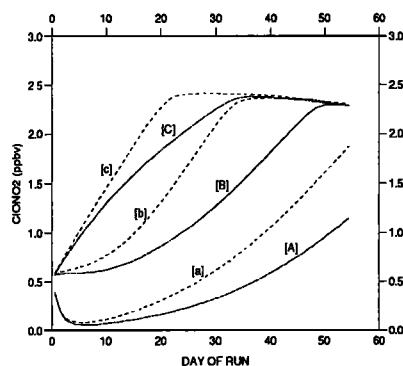


Fig. 2 As in Fig. 1 but for midnight values of ClONO₂ (ppbv).

In case B, with background levels of sulphate aerosol, the levels of NO_x are somewhat higher than in case A. Even at the beginning of the run, formation of ClONO₂ is faster than its destruction on aerosol and it rises slowly, peaking at 2.3 ppbv at day 50. It is then destroyed slowly by photolysis.

In case C (pure gas phase chemistry) the ClONO₂ rises most steeply at first since there is more NO_x available and there is no heterogeneous destruction. ClONO₂ peaks on day 37 at 2.35 ppbv before declining gently throughout the rest of the run.

A key test of our understanding of the chemical processes controlling chlorine deactivation is how well chlorine nitrate concentrations are calculated. Observations by Oelhaf et al., (this issue) showed high ClONO₂ at 50mb in March 1992 in the centre of the vortex. We have run three cases, volcanic aerosol (run A), background aerosol (run B) and gas phase (run C). The results show that the background aerosol and gas phase cases are consistent with the ClONO₂ measurements of Oelhaf et al. In contrast by running with volcanic aerosol we cannot produce sufficient ClONO₂ by mid March. Thus our background aerosol runs are consistent with the low aerosol measured by Deshler et al. (1993) on January 18 1992 inside the vortex at Kiruna which indicated that at 50mb (approximately 19 km) background values of 0.7 μm²cm⁻³ were present, and also with the high ClONO₂ values observed in March by Oelhaf et al. (this issue).

Temperature dependent nitric acid photolysis rates.

The background aerosol case agrees best with the data whether using room temperature or temperature dependent nitric acid absorption cross-sections. Clearly with the larger (room temperature) photolysis rates there is more NO_x available to reform ClONO₂. However no difference is made to the day 55 values of ClONO₂ using room temperature cross-sections for cases B and C even though the peak in ClONO₂ occurs approximately 12 days earlier in case B when using room temperature cross-sections. However in the volcanic aerosol case run, A, ClONO₂ is produced more rapidly with the faster photolysis rates but still only reaches 1.8ppbv by the end of the run, i.e. much less than the background aerosol case.

The latest evaluation of the temperature dependence of nitric acid absorption cross-sections (R.A. Cox, pers. comm.) results in a small increase in the 200K photolysis rates. This does not alter our conclusions since this increase in photolysis rates would speed up the formation of ClONO₂ in our background run. However on day 55 of the volcanic run, values of ClONO₂ would still be much lower than measurements.

The evolution of HCl is considered using the temperature dependent nitric acid photolysis rates in figure 3. HCl is produced mainly via the reactions

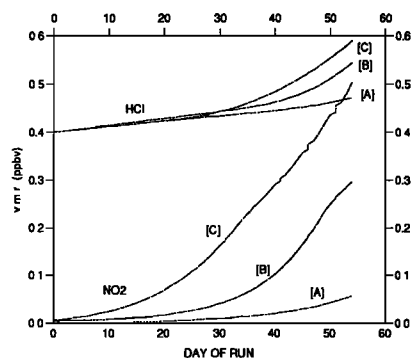
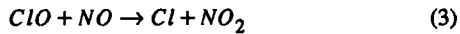


Fig. 3 HCl and noon values of NO₂ (ppbv) as a function of day of run. Temperature dependent JHNO₃ are used.



In case A, where ClONO_2 values are lowest, HCl values increase very slightly during the run. In case C, where NO values are higher, HCl concentrations rise to a value of 0.6 ppbv by the end of the run. Case B lies between the other cases.

End point values of ClONO_2 and HCl may be compared to those at 55°N and 75°N in Table 2.

TABLE 2. Volume mixing ratios in ppbv of ClONO_2 and HCl after 55 day integrations for various scenarios.

Lat.	Species	Volc. (A)	Backgr. (B)	Gas ph. (C)
75°N	ClONO_2	0.64	1.3	2.1
	HCl	0.46	0.47	0.47
65°N	ClONO_2	1.1	2.2	2.2
	HCl	0.47	0.55	0.60
65°N^\dagger	ClONO_2	1.9	2.2	2.2
	HCl	0.53	0.57	0.61
55°N	ClONO_2	1.4	1.8	1.8
	HCl	0.34	0.46	0.65

65°N^\dagger -using room temperature photolysis rates.

The dependence of the removal of ClO_x on the sulphate aerosol concentration and the nitric acid photolysis rate is shown in figure 4. In the gas phase chemistry case (C), ClO_x returns to steady state levels of around 0.2ppbv in 35 days. In case B the decay takes 50 days before ClO_x comes to steady state. In the volcanic case, (A), there are still high concentrations of ClO_x of 0.7ppbv remaining by day 55.

High values of HOCl (not shown) are calculated in case A, peaking at 0.95ppbv, produced by reaction 1. These values are higher than those indicated by column measurements inside and outside the vortex during EASOE (Toon et al., 1992a). A possible problem is thus indicated in our understanding of reaction 1 as discussed in Lutman et al., (this issue), this reaction may either be slower than currently thought or may not even occur on aerosol at all. In the background aerosol case (B), HOCl values peak at 0.45ppbv which compares well with 1989 values of HOCl inferred by Toon et al., (1992b) which peaked around 0.4ppbv at 70°N .

Although by day 55 in the background aerosol run, values of ClO_x have dropped to less than 500pptv, the vortex still contains high amounts of ClONO_2 as previously discussed. The implications for ozone loss in the springtime due to a cycle involving ClONO_2 photolysis are discussed by Toumi et al., (1993b).

In summary, recovery depends on available NO_x , and hence aerosol amount, and also latitude (i.e. zenith angle); at 75°N , 55 days is not long enough for recovery in cases A and B, this is

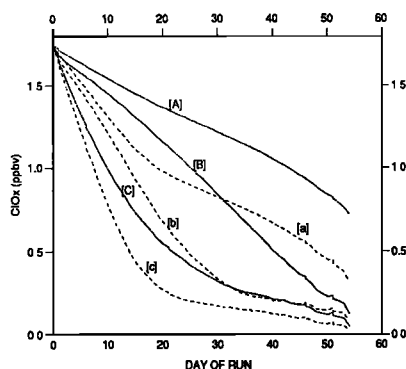


Fig. 4 As in Fig. 1 but for noon values of ClO_x (ppbv).

especially true in the runs performed using the new temperature dependent nitric acid photolysis rate. At 65°N our run B (background aerosol) results compare best with ClONO_2 observations. This is supported by in-vortex measurements of aerosol on January 18 over Kiruna. However at lower altitudes aerosol surface areas rose from background values of 0.7 to $10 \mu\text{m}^2\text{cm}^{-3}$ at 16.5km (Deshler et al., 1993). Our calculations show that March chlorine nitrate measurements are inconsistent with volcanic aerosol.

Absolute values of ClONO_2 in March will depend in part on our total chlorine content. MLS measured a maximum of 2ppbv of ClO at 46mb in January (Waters et al., 1993) suggesting that our total chlorine values are on the low side. However in-vortex measurements of ClO_y in January 1992 by Schmidt et al. (this issue) gave values of under 3.0ppbv at 475K.

Note that over a period of 2 months an air parcel would be likely to experience many latitudinal excursions, producing increased solar radiation - particularly, in the case of in-vortex air, when the vortex is distorted by tropospheric weather systems and warmings. This may have the effect of accelerating the formation of chlorine nitrate as is indicated by our 55°N runs. However this may be counterbalanced by the reactivation of ClO_x caused if temperatures dropped again below the threshold temperature for type 1 PSC which would delay the reformation of ClONO_2 , again suggesting that only our background aerosol runs could be comparable to measurements of ClONO_2 .

Ozone Loss.

The various catalytic cycles which deplete ozone are described, for example in Wayne (1991). In figure 5 the noon rates of ozone loss due to the well known cycles and also the direct ozone loss from the cycle involving ClONO_2 photolysis (see Toumi et al., (1993b) for derivation) are presented. Since ClONO_2 calculations in run B (background aerosol case) compare best with ClONO_2 observations, the respective cycles are presented only for the background aerosol case (run B).

The chlorine and bromine cycles dominate ozone destruction over the classic $\text{O}+\text{NO}_2$ and $\text{O}+\text{HO}_2$ cycles (not shown) during late winter and early spring in the background aerosol case. The largest contributors to ozone loss in the model are the cycles $\text{ClO}+\text{O}$, $\text{ClO}+\text{BrO}$ and $\text{ClO}+\text{HO}_2$. The noon loss rates due to cycles $\text{ClO}+\text{O}$ and $\text{ClO}+\text{BrO}$ peak near the beginning of the run at 0.8 and 0.7ppbvhr^{-1} respectively. At this time the highest ClO levels are present. These two cycles then decay throughout the run as ClO

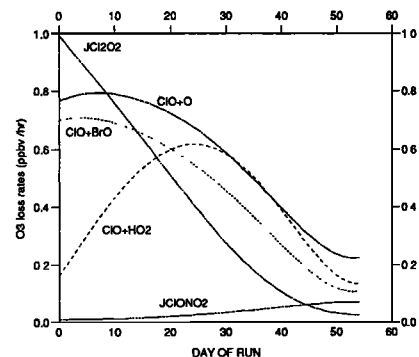


Fig. 5 Noon O_3 destruction rates / v.m.r. per hour as a function of day of run, at 50mb, for background aerosol case only. E.g. rate of ozone loss due to reaction $\text{ClO} + \text{BrO} \rightarrow \text{Cl} + \text{Br} + \text{O}_2$ is calculated as $2k[\text{BrO}]\times[\text{ClO}]\times[\text{M}]\times 3600.0$. The cycle involving JClONO_2 is included. Temperature dependent JHNO_3 are used.

concentrations are depleted. The effectiveness of the ClO+BrO cycle is limited by our relatively low initialisation of Br_x.

The loss rate due to ClO+HO₂ peaks on day 27 at 0.6ppbv hr⁻¹. In the model, levels of NO₂ are rising with the increasing photolysis of nitric acid as solar zenith angles decrease during the spring. This loss rate then drops off slowly towards the end of the run.

The rate of the dimer cycle, initially larger at 1 ppbv hr⁻¹, decays rapidly and is the least important of the chlorine loss rates by day 55. This cycle is evidently not so important with the higher temperatures used in the model. This model uses the most recent evaluation of the ClO dimer photolysis rate (Burkholder et al., 1990).

The cycle involving ClONO₂ photolysis which was shown to be important later in the year by Toumi et al., (1993b) is unimportant during the period of this run due to the low levels of ClONO₂ present at this time of year. However, this loss rate can be seen to be rising steadily throughout the run as levels of ClONO₂ and solar radiation increase.

The chlorine and bromine cycles are more effective in the volcanic runs (case A) due to more available ClO_x and Br_x. The cycle ClO+HO₂ is more effective in the volcanic run due to larger levels of ClO caused by the production and subsequent photolysis of large amounts of HOCl. In the gas phase chemistry run (case C), the chlorine and bromine cycles are less effective, e.g. the cycle involving Cl₂O₂ photolysis rates drops off by day 10. The effects of the NO₂+O cycle is however larger in the gas phase run.

A local net percentage ozone destruction (not shown) is implied of between 14% and 20% in 1991-92 and 27% to 35% in a winter with volcanic sulphate aerosol, such as 1992-93. However the observed ozone loss will be expected to be smaller since the effects of mixing will dilute concentrations of ClO_x and latitudinal excursions will increase NO_x concentrations through photolysis of HNO₃ thus speeding its relaxation to reservoir species.

Conclusions

The relaxation of highly perturbed levels of chlorine in the polar vortex from mid-January to early March has been modelled using a photochemical box model. Using a background aerosol scenario, ClO_x is observed to have fallen to near background levels by early March. Chlorine nitrate levels are found to have risen to over 2ppbv, consistent with levels measured balloon borne MIPAS-B limb sounder, and levels of HOCl of around 0.4ppbv were calculated, consistent with the inferred levels in March. In contrast, when using a volcanic aerosol scenario, lower values of chlorine nitrate and high levels of HOCl were calculated, inconsistent with measurements. It is noted that O₃ loss is expected to continue well after the time when high ClO ceases, and that in 1992/3, when more volcanic aerosol was present, larger O₃ losses might be expected.

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