

Trajectory model studies of ClO_x activation during the 1991/92 northern hemispheric winter

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Abstract. Calculations with a chemical box model along air parcel trajectories between November 1991 to January 1992 show a build up of reactive chlorine in late December and early January, culminating in values of ClO_x greater than 2.0 ppbv widespread in the vortex on 9 January 1992. These values are quantitatively comparable to the MLS satellite measurements of ClO . We discuss the chemistry occurring within the vortex, around the vortex edge and outside the vortex.

Introduction.

Substantial declines in ozone have been observed in the northern hemisphere in the last decade (Stolarski et al., 1991). The prerequisite for O_3 destruction is the production of levels of ClO which are enhanced significantly above the usual lower stratospheric values. This release of ppb-levels of reactive chlorine compounds is referred to as 'chlorine activation'.

Daily meteorological analyses of wind and temperature obtained from the European Centre for Medium Range Weather Forecasts (ECMWF) were used to calculate air parcel trajectories which have been used in this study with a photochemical box model. The use of trajectories allows the recent photochemical history of air masses, including the exposure to polar stratospheric clouds (PSCs), to be evaluated. By coupling trajectories with a photochemical model, estimates may be made of the photochemical evolution and, in particular, the chlorine activation in and around the polar vortex. In this study the chlorine activation is calculated. Two sorts of trajectories are used, ten-day isentropic trajectories and long duration three-dimensional trajectories, running from 26 November 1991 to 9 January 1992.

Method

The box model used includes a detailed photochemical and microphysical scheme. The photochemical and radiation scheme is an extension of that used by Lary and Pyle (1992). The usual four heterogeneous reactions which occur on PSC surfaces were included in the model using sticking coefficients taken from WMO (1990).

The reaction $\text{HCl} + \text{HOCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$ ($\gamma=0.07$) is included (Hanson and Ravishankara 1991) and given the sticking coefficient suggested by Abbatt and Molina (1992) for "H₂O-rich NAT". Two reactions also occur on sulphate aerosol in the model, with a sticking probability of 0.1 for the reaction $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3$. The sticking probability is calculated as a function of temperature for the reaction $\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3$ and reaches a maximum value of 0.1 at around 195K (Hanson and Ravishankara 1991).

A microphysical scheme is included for PSCs (Larsen, 1991). Sulphate aerosol surface areas available for heterogeneous chemical reactions are also calculated. Firstly, inside the vortex an

"ordinary" background surface area ($\sim 0.5\text{-}0.75 \mu\text{m}^2\text{cm}^{-3}$) was used which compares well with in-vortex measurements of aerosol over Kiruna on January 18 (Deshler et al. 1993), when $\sim 0.7 \mu\text{m}^2\text{cm}^{-3}$ was measured at 50mb. Secondly, outside the vortex "volcanic" (i.e. Pinatubo influenced) conditions are calculated ($\sim 10\text{-}15 \mu\text{m}^2\text{cm}^{-3}$). These surface areas are somewhat lower than measurements by Deshler et al. (1992) at Laramie, Wyoming between 26 July and 29 August 1991 of between 9 and $84 \mu\text{m}^2\text{cm}^{-3}$.

The recently re-evaluated temperature dependence of the HNO_3 photolysis cross section (Rattigan et al., 1992) is included.

Two sets of trajectories were used. First we used the ensembles of 10 day, backward isentropic trajectories (Knudsen and Carver, this issue) which were run over the 475K potential temperature surface. End points include all the EASOE measurement stations as well as points along the 40°W longitude line between 84°N and 42°N and along 40°E from 84°N to 30°N (see figure 1, Knudsen and Carver, this issue). Given some initialisation, the chemical evolution along the trajectories can be calculated. By running a whole series of trajectories on, say, the 475K surface, a time series of the evolution of the two dimensional (latitude, longitude) chemical behaviour is built up. To allow crudely for transport chemical data sets, as shown in Table 1, are used to initialize the in- and out-of-vortex cases (judged by the steepest gradients in potential vorticity, (Braathen et al. 1992)).

The initialisation gives a total inorganic chlorine (ClO_x) of 3.5ppbv in the vortex and 2.9 outside. These values could be a little high. For example, Schmidt et al. (this issue) calculate, using measurements of the CFCs, only a little over 3ppbv within the lower stratospheric polar vortex during EASOE, while Oelhaf et al. (this issue) measured 3.3 ppbv of ClONO_2 deep inside the vortex in mid March 1992. This approach, in which only in- or out-of- vortex cases are considered, will also oversimplify the structure on any particular surface. Nonetheless, it should allow us to identify the impact of processing by PSCs and aerosol, the main objective of this study.

This approach does not take into account the effect of downward motion inside and around the polar vortex further changing the latitudinal gradients of Cl_y and other species as the winter proceeds. Nor do the 10 day trajectories have any "memory" of previously calculated ClO_x from one run to the next; the chlorine calculated is that which is activated during each 10 day run. To overcome these problems we have also run three-dimensional forward trajectories covering 48 days from 26 November 1991 to 9 January 1992, again based on the ECMWF analyses. Initialisation is still a problem; for simplicity we have again used the in / out-vortex values in Table 1, except for ClONO_2 and HCl as described later. Trajectories were studied which ended between 45 and 60mb on 09.1.92. In the following we present results at the trajectory end points showing the build up of ClO_x ($\text{Cl} + \text{ClO} + 2 \times \text{Cl}_2\text{O}_2$).

Results from 10 day Trajectories.

By late December the vortex had spun up considerably. Temperatures from 15 December to 25 December were around 198K in polar regions. However from 19.12.91 to 21.12.91 small pools of air around 193K were formed near the pole. This was reflected in the ClO_x field calculated for 25.12.91. Several air

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TABLE 1. Initialisations /ppbv for position relative to vortex.

	HCl	NO _x	N ₂ O ₅	HNO ₃	CH ₄	N ₂ O
In	2.7	2.4E-1	0.3	10.7	5.0E+2	9.0E+1
Out	2.1	5.0E-1	1.1	3.7	1.0E+3	1.9E+2

(and at all latitudes HOCl = 0.2, ClO_x = 0.2, ClONO₂ = 0.4, O_x = 3.5E3, HNO₄ = 0.2, Br_x = 8.0E-3, CO = 1.8E+1, H₂O₂ = 1.0E-3, H₂O = 5.0E+3 ppbv).

parcels experienced low enough temperatures for PSC formation and patches of ClO_x were observed with values of around 0.4ppbv, for example, over northern Scandinavia and Greenland. However the cold temperatures were not widely prevalent throughout the vortex. Many air parcels had not been chemically activated, having missed the patches of cold air during the previous ten days. Nonetheless, the picture is clear with local activation having occurred, but with a rather patchy geographical distribution; the areas of high ClO_x were larger than, and not necessarily collocated with, the cold patches.

During late December and early January the vortex moved across to the European sector. Low temperatures were widespread inside the vortex. Figure 1 shows considerable ClO_x activation on 09.1.92 of over 1ppbv, which appears to be contained within the vortex (the 30PV unit contour, a rough indication of the vortex edge, is shown in the figure). The highest ClO_x values of over 1.5ppbv are located over Iceland and Scandinavia.

The ClO_x values calculated on 09.01.1992 are in qualitative agreement with the satellite MLS ClO observations (Waters et al., 1993). In addition, the modelled chlorine activation agrees well with the large reduction in HCl within the vortex reported by Bell et al. (this issue). However absolute values of ClO (with a maximum of between 1-1.6ppbv) are somewhat lower than those measured by MLS, where a maximum of more than 2ppbv is widely observed at 45mb. The difference reflects in part the problem of chemical initialisation of our calculations. The high ClO_x values had been activated within the previous 10 days only and ClO_x produced earlier in December, for example, is not carried forwards. Also the low ClONO₂ initialisation limits the activation. Another problem is the non-uniform nature of the trajectory grid, chosen to coincide mainly with the EASOE measurement stations, which limits the geographical extent of our chlorine map, e.g. very few trajectories were produced which ended between 40E and 40W where some high ClO was seen by MLS.

Results from 48 day trajectories.

Because of the difficulties with trajectory initialisation and the non-uniform distribution of trajectory endpoints, complementary three-dimensional trajectories were run starting in late November

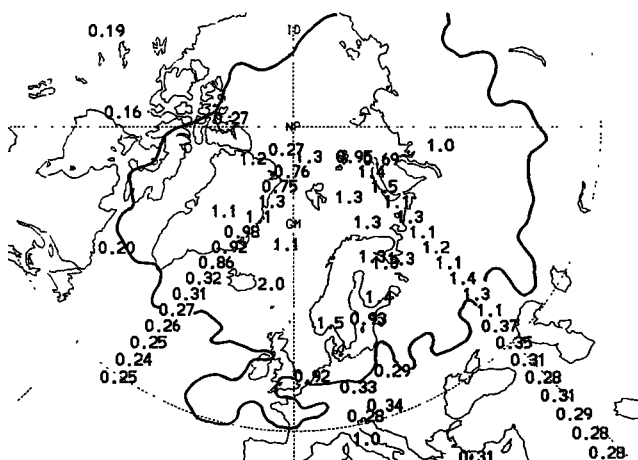


Fig. 1 ClO_x (ppbv) for 09.01.92 at 475K. Calculated using 10 day trajectories. The 30PV contour is shown.

and ending on 09.1.92. We note that photochemical trajectory calculations in the stratosphere have not traditionally been run for longer than about 10 days. However O'Neill (personal communication) has shown that the features revealed by long-duration, "domain filling" trajectories, calculated after data assimilation of meteorological analyses, exhibit a coherent structure which agrees well with other, independently derived quantities, e.g. potential vorticity.

As our levels of ClO in figure 1 are lower than those seen by MLS a new trajectory initialisation was used with ClONO₂ = HCl = 1.55ppbv. We discuss the implications of this later. Figure 2 shows ClO calculated using these long 3-D trajectories.

The chlorine activation presented in figure 2 may be divided into several sections.

High in-vortex ClO_x. The entire vortex region is now full of highly processed air. Calculated values of ClO_x (figure 3) are mainly between 2 and 3ppbv, higher than in figure 1. Both the spatial extent of the chlorine activation and the magnitude of the ClO mixing ratios shown in figure 2 agree well with MLS observations for 09 January 1992. The highest ClO values (1.5 - 2.0 ppbv) are found at around 60°N, stretching eastwards across Europe. There is a strong gradient of ClO across the terminator. Our ClO pattern is displaced slightly eastwards compared to MLS, but generally the agreement is very good.

The levels of ClO_x produced inside the vortex in our calculations depend on several factors: total Cl_y, initial chlorine partitioning and choice of heterogeneous reaction probability. As expected our new initialisation (ClONO₂ = HCl = 1.55ppbv) produces higher levels of ClO, between 1.5 and 2.3 ppbv, comparable to those measured by MLS. Whether this higher level of ClONO₂ is realistic depends on either high levels of chlorine nitrate being present initially, or on levels of NO₂ being sufficient to recycle some ClO_x back into ClONO₂. Such levels of NO₂ are not produced in our model with the fast reaction N₂O₅ + H₂O occurring on aerosol and with slow nitric acid photolysis rates. If this level of chlorine nitrate is unrealistic then we must conclude that we do not yet fully understand the processes controlling the magnitude of the ClO_x activation.

When a lower value was chosen for total ClO_y, lower ClO values were calculated. Our quantitative agreement with the MLS data requires the high ClO_y initialisation.

If ClONO₂ was depleted, for example due to reacting with water on aerosol, and thus unable to react with HCl, the reaction HCl + HOCl becomes potentially very important for activating chlorine.

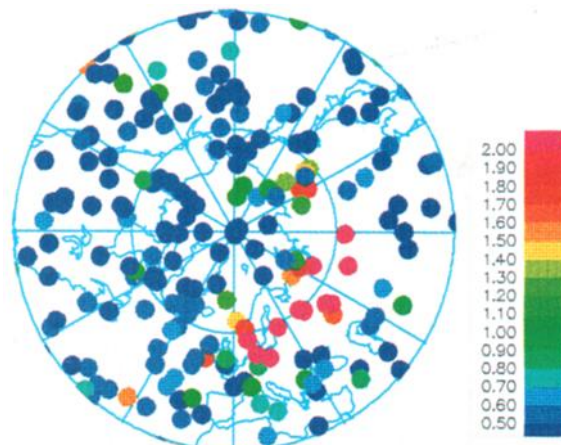


Fig. 2 09.01.92 ClO(ppbv) between 45 and 60 mbar at local noon, calculated using 48 day trajectories. The terminator determines the sharp ClO edge inside the vortex. High activation, in the form of Cl₂O₂, is found polewards of the terminator. Note that the out-of-vortex activation is generally produced through reactions on sulphate aerosol although there are also some incidents of high ClO produced through activation in the tropics. These occur mainly at the lower latitudes which are not shown in the figure.

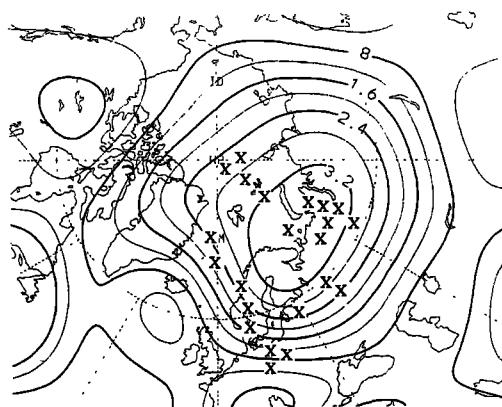


Fig. 3 ClO_x (ppbv) for 09.01.92 between 45 and 60 mbar at local noon. Calculated using 48 day trajectories. Locations on the trajectories below the PSC threshold are also shown (X) for 07.01.92, the day with the largest area of PSC temperature.

The sticking probability for this reaction is still uncertain (Abbatt and Molina, 1992). If it is set to the lower value of 0.002 as indicated for "HNO₃-rich NAT" by Abbatt and Molina (1992), ClO_x levels are again reduced. In-vortex levels of ClO are then calculated to be below 1.5ppbv, and indeed only a few points have values of ClO greater than 1ppbv. Thus quantitative agreement with MLS data also requires use of a high sticking coefficient for the reaction $\text{HCl} + \text{HOCl}$.

The spatial area of perturbed ClO_x is significantly larger than the area of cold temperatures which is seen by the model. Figure 3 also shows a snapshot in time of the area of PSC activation seen by the trajectories (marked by X). The figure shows day 45.89 (07.01 1992), chosen as the model day with the largest area with temperatures below the NAT point calculated in our model. Figure 3 again confirms the idea put forward by Jones et al. (1990), and others, describing the northern hemispheric vortex as being characterised by air flowing through relatively small patches of cold temperatures, and processing the entire vortex.

Edge of vortex activation on PSCs. High values of ClO_x (over 2ppbv) are calculated for several trajectories ending over the Mediterranean (figure 2). In order to study the chlorine activation in detail, in figure 4 we consider the chemical evolution along a typical trajectory ending at 45.03°N, 6.41°E on 09.01.1992. The latitudinal movement of the air parcel (not shown) falls into two distinct periods. The trajectory is confined to the vortex edge for most of the run, undergoing considerable latitudinal excursions between 45°N and 75°N. Zenith angles are always greater than 70° but there is sufficient ultraviolet radiation to initiate photochemistry.

The temperature of the air parcel (not shown) remains mostly between 200K and 230K, too warm for heterogeneous reactions on sulphate aerosol or PSC formation, apart from 3 short periods. On days 24 and 45 (20.12.91 and 09.01.92) temperatures drop below 200K, cold enough for heterogeneous reactions on sulphate aerosol. On day 36 (02.12.91) a PSC is encountered as the temperature drops to 193K.

The temperature history is reflected in the behaviour of the chlorine reservoirs. Throughout the first (warm) half of the run ClONO_2 values remain high, until day 24 (20.12.91) when the temperature drops below 200K and ClONO_2 is converted into HOCl. HCl values drop slowly through gas phase chemistry until day 36 (02.12.91) when the PSC is encountered. 1.1ppbv of ClO is activated, mostly through ClONO_2 reacting with HCl. The final value of ClO_x is 0.79ppbv, lower than levels inside the vortex but still representing significant activation. More ClO_x would be produced if the trajectory was run on, due to photolysis of the HOCl which was formed during the run. Appreciable ozone loss (7% in 48 days) occurs in this calculation, mainly when the air parcel moves away from the vortex edge to somewhat lower latitudes, during the last few days of the run.

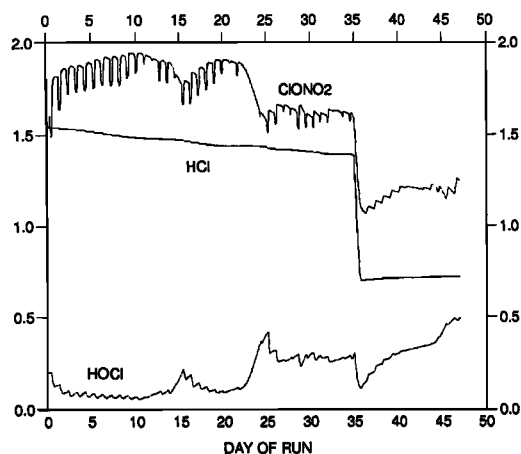


Fig. 4 An "edge of vortex" trajectory ending at 45.03°N, 6.41°E. ClONO_2 , HCl and HOCl / ppbv versus day of run are shown. Day 0 = 26 November 1991.

Out-Vortex activation on aerosol. Waters et al. (1993) report patches of elevated ClO outside the vortex. Modest chlorine activation compared to that observed inside the vortex is seen in our calculations for some air parcels between the vortex edge and approximately 40°N, with ClO values between around 400 and 800 pptv. Some activation is evident in figure 2 while some occurs at lower latitudes (not shown). There is some structure in the amount of activation. Some trajectory endpoints in this region show very small values of ClO_x interspersed with other points of higher ClO_x ; there are some isolated cases of high ClO_x at even lower latitudes. Apart from the cases specifically mentioned in the above section, these trajectories have not seen any PSC activation. Instead, chlorine activation has occurred in the model on volcanic sulphate aerosol. The levels of chlorine activation predicted by our model are thus heavily dependent on the rates of these aerosol reactions. As yet there is little field evidence, as opposed to laboratory measurements, that ClONO_2 reacts with water in the atmosphere on sulphate aerosol. Should this reaction occur more slowly than is currently thought, or even not occur at all, the gradients of ClO_x would become much sharper across the vortex boundary than is shown in figure 2. Rerunning these trajectories with the background aerosol, instead of the volcanic aerosol, produces much smaller values of ClO_x , around 10-100pptv.

These out-of-vortex air parcels have moved widely in mid latitudes, remaining in general between 40°N and 70°N. Due to the large latitudinal excursions experienced, these moderate levels (400-600pptv) of ClO_x produce substantial amounts of ozone destruction, in general around 10% during the 48 days.

Tropical Activation. As mentioned above, over the 48 day run, many trajectories appear to move in the surf zone, repeatedly experiencing large latitudinal excursions, the majority moving between 40°N and 70°N. Some small number of the trajectories seen in middle latitudes had spent time at considerably lower (tropical) latitudes including some which started and finished in middle latitudes. If this air had initially a chemical composition characteristic of middle latitudes (e.g. some chlorine in the inorganic forms, HCl and ClONO_2), then some tropical PSC activation could have taken place. Certainly, in a few of the trajectory runs, PSCs were activated and due to our chlorine initialisation high amounts of ClO_x (over 1ppbv) were produced and transported to mid-latitudes. One such trajectory moved between 5°N and 60°N and the chlorine produced (over 1ppbv) led to over 25% ozone depletion during the run. Even though such air parcels did not produce as much ClO_x as air inside the polar vortex, large amounts of ozone destruction ensued due to the greater insolation. Tropical activation may or may not be an explanation for the small areas of high ClO observed by MLS in mid to low latitudes. However it does seem to be a mechanism which should be explored further, particularly at higher pressures than 50mb where extra tropical air temperatures are, on average, colder.

No other evidence was found of the patches of high ClO observed in mid latitudes by MLS on 09.1.92. This could be because our 350 trajectories missed air parcels which were activated inside the vortex, before peeling away from it (as described above). The trajectories may also have missed local small scale temperature fluctuations which were cold enough to activate chlorine. It is also possible that if we had included the reaction between HOCl and HCl on sulphate aerosol as proposed by Cox et al., (this issue) higher amounts of ClO_x could have been produced at the lower latitudes where some aerosol activation was calculated (see above). We note also that the patches of ClO may not have been real, but could arise from spurious instrument noise (Waters et al., 1993).

Conclusions.

The activation of chlorine during EASOE in early January 1992 has been modelled using a trajectory model. The period appears to have been well reproduced using three-dimensional trajectories. The spatial extent of the largest chlorine activation is in good agreement with satellite measurements. The small scale detail in ClO depends critically on assumptions of chemical initialisation and details of heterogeneous chemistry. We can only reproduce the magnitude of the ClO values seen by MLS using a high total chlorine concentration of 3.5ppbv, and by using a high initialisation of ClONO₂. A high sticking coefficient for the heterogeneous reaction HCl + HOCl is also necessary to reproduce the measurements of ClO.

Some PSC activation occurred in the model around the vortex edge, activating high values of ClO. Moderate chlorine activation was also seen outside the vortex edge; this was produced in the model on sulphate aerosol and is very dependent on assumptions made regarding the rates of heterogeneous reactions on sulphate aerosol.

No other evidence was seen of the patches of ClO seen at mid latitudes by MLS. If this high ClO was real, it has been missed by our trajectories.

In a companion paper, the deactivation of chlorine and ozone loss during the 1991/92 northern hemisphere winter is discussed. (Lutman et al., this issue.)

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