

SPATIAL AND TEMPORAL VARIABILITY OF THE EXTENT OF CHEMICALLY PROCESSED STRATOSPHERIC AIR

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Abstract. Simulations of the spatial and temporal variability of the extent of chemically processed air in the Arctic stratosphere have been carried out using a three-dimensional chemistry-transport model for the winters of 1979 and 1989. Chemically processed air is identified in the model as that in which the amounts of hydrogen chloride (HCl) calculated with parameterized loss for conditions appropriate to polar stratospheric cloud (PSC) formation are substantially smaller than those calculated in a model with gas phase chemistry only. It is seen that chemically processed air may be identified over much of the Arctic lower stratosphere from early January to late February, with HCl depletions being larger in 1989 than in 1979. Near the latitude of the Arctic circle, there is important spatial and temporal variability in the extent of chemically processed air. There is some evidence for transport to mid-latitudes of processed air during these winters, but the HCl reductions are much smaller and more sporadic than those near the pole. At 62 and 42N, processed air is calculated to occur preferentially over the longitude regions from 60-120E and 270-330E.

Introduction

It is now clear that chemical reactions occurring on the surface of polar stratospheric cloud (PSC) particles constitute a crucial component in the sequence of chemical reactions responsible for the high latitude springtime ozone depletion observed in the Antarctic lower stratosphere [WMO, 1990]. The most important of these reactions convert normally chemically inactive reservoir forms of chlorine, such as hydrogen chloride (HCl), into other forms of chlorine which may be more easily converted into catalytically active forms [WMO, 1990]. There is also evidence for mid-wintertime ozone depletion in the Arctic lower stratosphere [Browell et al., 1990; Schoeberl et al., 1990]. Although the magnitude of this depletion is much smaller than in the Antarctic, the basic mechanism is believed to be the same. Evidence from the aircraft missions to both the Antarctic (AAOE, Airborne Antarctic Ozone Experiment) and Arctic (AASE, Airborne Arctic Stratospheric Expedition) has shown important reductions in the total column of HCl inside the polar vortex, consistent with this conversion [Coffey et al., 1989; Toon et al.,

1989; Mankin et al., 1990; Toon et al., 1990, private communication]. Air which has been depleted in HCl in this way is typically referred to as "chemically processed air."

A question of critical importance is whether chemically processed air can be transported to mid-latitudes in late winter or early spring. If so, this air, which has larger amounts of available chlorine (which after exposure to sunlight will include the catalytically active molecule ClO), could cause more rapid ozone destruction than usually expected. This enhanced destruction could perhaps be responsible for some of the large ozone depletion found for northern mid-latitude winter [WMO, 1990].

Since the chemical processing occurs in regions whose locations and sizes vary with time, its contribution to the overall stratospheric chlorine budget (and the total extent of the chemically processed air) is difficult to assess. Further, since the location of processed air is governed both by its production and its redistribution by stratospheric wind systems, accurate understanding of its extent requires the simultaneous consideration of both chemical and dynamical processes in the stratosphere.

Such calculations have been carried out previously for the Arctic in the winter of 1989 [Kaye et al., 1990] using a three-dimensional chemistry/transport model (CTM) in which the heterogeneous conversion of HCl to other forms of chlorine is parameterized. This model, which uses winds from a data assimilation procedure [Rood et al., 1990a], has been shown to represent accurately several of the features in the stratospheric distributions of HCl and also hydrogen fluoride (HF) measured in the AASE mission. In particular, it successfully simulated the reduction of hydrogen chloride in regions of air which have undergone chemical processing but left HCl distributions in regions of unprocessed air unchanged. It also successfully simulated the differing relationships between HCl and HF with potential vorticity observed in the aircraft data [Mankin et al., 1990].

Since HCl amounts can vary enormously over a specific location in the winter [Kaye et al., 1989a], it is not sufficient simply to associate low calculated HCl amounts with chemically processed air. Instead, a good measure of processed air is the ratio of HCl calculated with the model in which heterogeneous loss has been included to that calculated with gas phase chemistry only. This ratio effectively normalizes the HCl amounts, removing the dynamical variability associated with changing stratospheric meteorology.

We have run our HCl calculations with standard gas phase chemistry and with parameterized heterogeneous loss for the winters of 1979 and 1989. We report here the results of these calculations.

Model Calculations

The way in which the CTM solves the continuity equation, including the effects of both chemical and advective

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processes, has been described by Rood and Kaye [1989]. Its application to HCl during the AASE mission has been presented by Kaye et al. [1990]. The 1989 calculations have been repeated because of a change in the horizontal transport scheme from spectral to a modified Van Leer scheme [Allen et al., 1990]. The new scheme has improved conservation properties, especially at high latitudes. The period of calculation has been extended to cover the time 12/28/88 to 3/21/89. The horizontal resolution of the model has been changed to 2.5 degrees in longitude by 2 degrees in latitude. We assume no chemical processing occurred prior to the start of integration on 12/28/88. The 1979 calculations, carried out similarly to the 1989 ones, covered the period from 12/1/78 to 3/31/79. The quality of transport calculations in this time period has been demonstrated in simulations of ozone [Rood et al., 1990b].

In addition to the standard (gas phase reactions only) and parameterized heterogeneous depletion calculation (abbreviated DHCl) described previously [Kaye et al., 1990], we have also carried out an "enhanced recovery" run for the depleted-HCl case (abbreviated EHCl). In this latter calculation, the gas phase production rate of HCl is increased over its normal value to account for the presence of larger amounts of atomic chlorine (Cl) when there has been conversion of HCl to other inorganic forms of chlorine. The partitioning of these other forms of inorganic chlorine (Cl, ClO, HOCl, ClONO₂) is assumed to be given by that in the GSFC two-dimensional model [Douglass et al., 1989]. This change is implemented in a way such that where the HCl amounts in the enhanced recovery run are the same as those in the standard run, the rate of chemical production is unchanged from its value in the normal run. The loss coefficients for HCl are assumed to be unchanged in the enhanced recovery run.

The two runs (DHCl, EHCl) should represent lower and upper limits to the rate of the photochemical recovery, with the EHCl run probably providing a better representation of the HCl production in the atmosphere. It is possible, however, that loss of NO and NO₂ from the stratosphere due to heterogeneous conversion of NO₂ into nitric acid could reduce the Cl/ClO ratio, thus reducing the HCl production rate. For this reason we consider the EHCl run to be an upper limit to the rate of recovery.

Results and Discussion

The calculations show that the effect of the parameterized heterogeneous loss is to reduce markedly the amount of HCl in the northern hemisphere, corresponding to the production of large amounts of chemically processed air. The ratio of the total amount of HCl calculated in the runs with parameterized depletion to that calculated with gas phase chemistry north of 42 degrees latitude for both years studied is shown in figure 1. The loss of HCl in 1989 maximizes near the end of January at about 18 percent of the total amount calculated in the normal gas phase chemistry run, while the maximum loss in 1979 is approximately 8 percent. The effect of the enhanced recovery (EHCl run) is to dramatically reduce the calculated HCl deficit from early February to late March. A large difference between the late March HCl depletions calculated for 1979 and 1989 was found for the standard recovery (DHCl) case, while

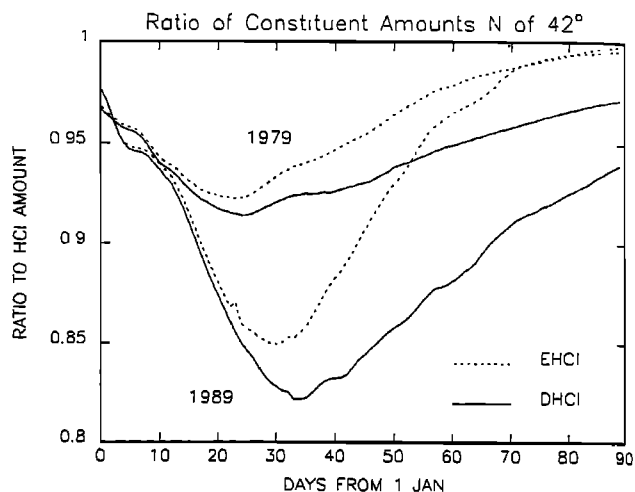


Fig. 1. Plot showing ratio of total amount of HCl north of 42N calculated with parameterized heterogeneous depletion (DHCl, solid line) and heterogeneous depletion with enhanced recovery (EHCl, dotted line) to that calculated with standard gas phase chemistry. The top pair of curves is for 1979 while the bottom pair is for 1989.

very small and nearly identical depletions were found in the enhanced recovery (EHCl) case.

The spatial and temporal extent of processed air in the Arctic lower stratosphere in 1989 may be seen in figure 2, in which the ratio of the HCl mixing ratios at 53.1 mb calculated in the enhanced recovery (EHCl) run to those calculated in the standard gas-phase chemistry run (HCl) are plotted vs. time in the month of January and February. These ratios are plotted at the model grid points closest to four high latitude locations which have been suggested as possible sites for Network for Detection of Stratospheric Change (NDSC) [Kurylo and Solomon, 1990].

Above Alert, the northernmost of these stations, the oc-

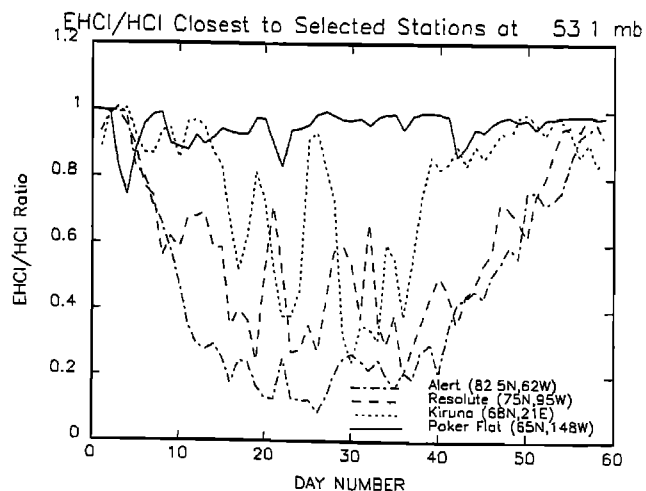


Fig. 2. Plot showing the EHCl/HCl ratio calculated for 1989 as a function of time at 53.1 mb over six high latitude stations for the month of January and February. Line types, station names, and station locations are given in the figure.

currence of chemically processed air sets in rapidly. There is little short-term variation in the magnitude of the processing there. It takes somewhat longer for strongly chemically processed air to be found over Resolute. There is much greater short-term variability in the magnitude of the processing there than over Alert. In mid-to-late January, the air over Resolute is always less extensively processed than that over Alert. Occurrence of processed air sets in even more slowly over Kiruna, and the short-term variability in the magnitude of processing is very large late in the month. Poker Flat, Alaska, only 2.5 degrees south of Kiruna but nearly halfway around the world, rarely sees appreciably processed air. The isolation of Poker Flat from processed air is driven by the Aleutian anticyclone, which keeps the polar vortex away from northwestern North America.

In February, the magnitude of the short-term variability in the extent of processing of the overlying air is much smaller than it was in January. The extent of processing over the two higher latitude stations is similar throughout the month, becoming quite small (approximately 5 per-

cent) by the end of February. The extent of processed air over Kiruna decreases much earlier in the month, however; reductions on the order of 5 percent are observed at the end of the first week of February. Poker Flat again rarely sees any evidence for overlying processed air.

The differences between the January and February plots may be understood by noting that most of the chemical processing was terminated in early February, when temperatures low enough for PSC formation became far less frequent. When no new processing was occurring, the composition of air in the vortex became quite homogeneous. Thus, the high latitude stations in the vortex had equivalent amounts of processing. This continued throughout the month as the HCl amounts increased due to photochemical recovery, which is assumed to be zonally symmetric.

The three-dimensional model shows to what extent processed air is expected to be found above lower latitudes. This may be seen in figure 3, in which the 53.1 mb values of the EHCl/HCl ratio during January and February 1989 are shown as a function of longitude at 62N (top) and 42N (bottom). At both latitudes, there are important longitudinal asymmetries in the extent of processing. Processed air is calculated to be found preferentially in the 60E-120E and 270-330E regions; almost no processed air is expected in the 160-240E region. The maximum extent of processing observed at 62N can be quite large, reaching values in excess of 80 percent. At 42N, however, the level of processing became large only once (this was associated with an ozone mini-hole in the very early part of February).

The corresponding figures for 1979 are very similar in character to those for 1989 but show less HCl depletion. In 1979 at 62N there was no appreciable HCl depletion in the 270-330E longitude bin after approximately January 20 as opposed to 1989 when these occurred till the end of February. At 42N, the only depletion greater than 10 percent started near 270E on about January 25 and moved eastward to approximately 60E at the very beginning of February.

Summary and Conclusions

We have used a three-dimensional chemistry/transport model to simulate the distribution of chemically processed air in the winter of 1989. There are important differences in the magnitude and day-to-day variability in the extent of chemically processed air in 1989 at the highest latitude (75N) regions considered. At slightly lower latitudes (65-70N), very different amounts of processing were calculated for different positions.

At slightly lower latitudes (62N), chemically processed air was found to occur preferentially over the 60E-120E and 270-330E longitude regions, with more strongly processed air occurring over the former region (HCl reductions as much as 80 percent were calculated). This preferential structure was found for both 1979 and 1989, although larger HCl depletions were found for 1989.

Over mid-latitudes (42N), however, there was almost no evidence for chemically processed air during January 1989 and only occasional evidence for the existence of weakly processed air in February 1989; some HCl-depleted air was calculated for a few days at the end of January 1979, however.

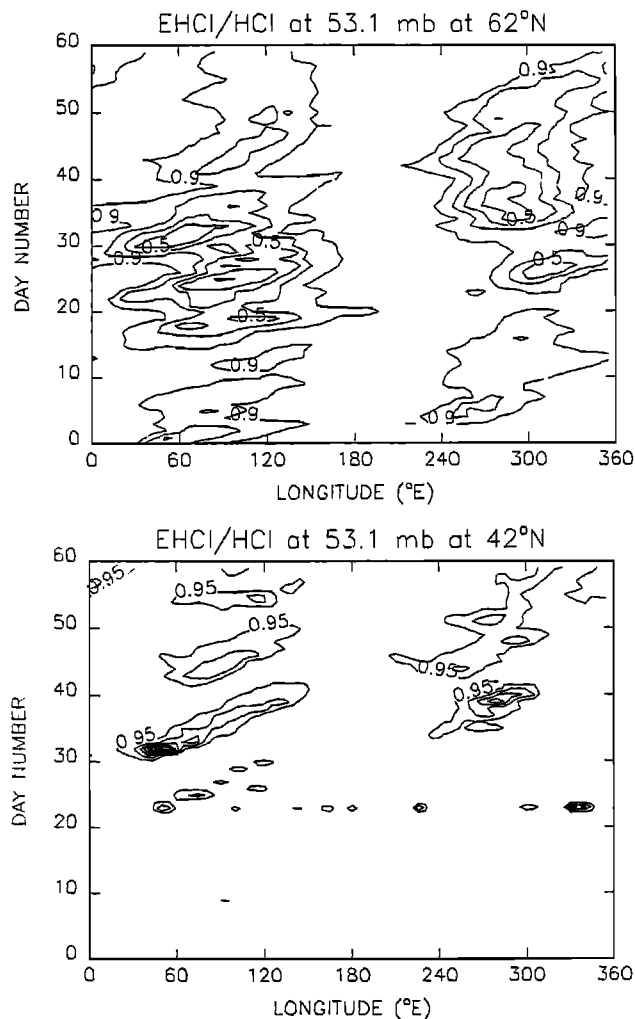


Fig. 3. Plot showing the EHCl/HCl ratio calculated for 1989 as a function of time and longitude at 53.1 mb for 60N (top) and 44N (bottom). Contour interval is 0.2 (with contour values ranging from 0.1 to 0.9) and 0.05, respectively.

These results show that in the winters of 1979 and 1989 there was little transport of clearly chemically processed air to mid-latitudes. What mid-latitude transport did occur was preferentially localized to two isolated longitude regions, which were located where the polar vortex was most likely to become distorted. One of these regions corresponds to the area in which enhanced ClO was observed by the AASE's ER-2 aircraft on its return ferry flight from Stavanger, Norway to the NASA Ames Research Center in California [Douglass et al., 1990].

It is therefore unlikely that a sizable enhancement of the rate of mid-latitude ozone destruction occurred in the late winter of these years in regions not reached by the polar vortex. In fact, the longitude of largest mid-latitude ozone losses as seen in total column data for 1989 from the Total Ozone Mapping Spectrometer (TOMS) instrument with the Nimbus 7 satellite is over the mid-Pacific [Newman et al., 1990], where the model simulations suggest little transport to mid-latitudes of HCl-depleted air. Further analysis of this point requires the detailed treatment of interacting chemical constituents so that all the catalytic processes responsible for ozone destruction and the meridional dependence of ultraviolet photolysis rates in the lower stratosphere are explicitly included. Such calculations have been carried out for brief periods of time [Kaye and Rood, 1989] and will be extended to the time period here with appropriate modification of treatment of odd nitrogen chemistry to account for repartitioning and possible sedimentation of nitrogen-containing compounds [Fahey et al., 1990].

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