THREE DIMENSIONAL SIMULATION OF HYDROGEN CHLORIDE AND HYDROGEN FLUORIDE DURING THE AIRBORNE ARCTIC STRATOSPHERIC EXPEDITION

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Abstract. Simulations of the evolution of stratospheric distributions of hydrogen chloride (HCl) and hydrogen fluoride (HF) have been carried out for the period of the Airborne Arctic Stratospheric Expedition (AASE) with a three-dimensional chemistry-transport model. Simulations were performed assuming only homogeneous gas phase chemistry for HF and both homogeneous gas phase and heterogeneous chemistry for HCl. Results show heterogeneous loss of HCl is needed to provide agreement with infrared column measurements. Estimates of the impact of heterogeneous loss on the global HCl distribution are obtained from the model. Reductions of HCl due to heterogeneous loss are calculated to be localized to regions of high vorticity, even after more than a month of integration.

Introduction

Hydrogen halides are the most abundant reservoir molecules for halogens in the stratosphere and are unreactive towards ozone. Evidence exists, however, that the heterogeneous conversion of hydrogen chloride (HCl) into more easily destroyed reservoirs of chlorine occurs on polar stratospheric cloud (PSC) particles in the winter and spring Antarctic stratosphere.

Infrared absorption measurements made during the Airborne Antarctic Ozone Experiment (AAOE) confirm this change. Coffey et al. [1989] and Toon et al. [1989] showed that the column of HCl above the DC-8 aircraft in the Antarctic polar vortex was greatly depleted during the early part of the mission, with column amounts as small as one fifth the amounts typically measured at high northern latitudes having been observed.

Hydrogen fluoride (HF) behaves very differently, however. It is the most stable fluorine-containing reservoir and has no known chemical loss processes. It is therefore believed to act as a chemically inert tracer in the stratosphere (although there has recently been some suggestion of heterogeneous production of HF from CF2O, however [Wofsy et al., 1990]). Its column abundance is thus believed to reflect dynamical processes, particularly vertical motion.

Decreases in the HCl/HF ratio observed during the AAOE [Coffey et al., 1989] lend strong support to the hypothesis of chemical destruction of HCl, because vertical motion could not produce such signals.

Measurements of the HCl column made from the DC-8 during the Airborne Arctic Stratospheric Expedition (AASE) showed that decreases in HCl and in the HCl/HF ratio also occurred in the Arctic, and there were sizable differences between in-vortex and out-of-vortex amounts and ratios. These measurements were very limited in space and time and cannot be simply extrapolated to cover the entire Arctic or assess global questions such as the degree of isolation of HCl decreases to the polar vortex.

To help answer these questions we have simulated the distributions of HCl and HF during the AASE period with a three-dimensional chemistry-transport model (CTM) using parameterized chemistry and winds from a data assimilation procedure. This CTM has previously been applied to HCl for the January 1979 time period [Kaye et al., 1989] as well as to nitric acid (HNO3) [Rood et al., 1989]. We extend its application here to HF and also to HCl with a parameterized loss designed to simulate the heterogeneous conversion of HCl to less stable chlorine reservoir species. We analyze these results to assess the importance of heterogeneous loss and to compare the calculated HCl and HF columns to infrared measurements made during the AASE.

Model Calculations

The basic CTM solves the continuity equation for a single species including both chemical and advective processes. The winds and temperatures are from the STRATAN assimilation system [Rood et al., 1990]. The model is operated in the same manner as in Rood et al. [1988]. Computational and numerical aspects associated with this model have been described in more detail elsewhere [Rood and Kaye, 1989]. The model integration covered 45 days (Dec. 28, 1988 to Feb. 12, 1989).

Initial conditions for the CTM were determined from the HCl and HF distributions calculated from the two dimensional model mapped to three dimensions using an initialization procedure based on vorticity [Douglass et al., 1990]. The production rate and loss coefficient for HCl (homogeneous gas phase run) and HF were taken from a two-dimensional model [Douglass et al., 1988]. Gas phase HCl chemistry is as in our previous calculations [Kaye et al., 1989]. For HF, production was assumed to follow immediately on photolysis of CFCIO and CF2O, the latter of which is an important fluorine reservoir species in the lower stratosphere [Raper et al., 1987]. CF2O is assumed to form on the destruction of all chlorofluorocarbons containing two or more fluorine atoms; CFCIO is formed when CF3O is destroyed. Photolysis is the only loss process in the stratosphere for both CFCIO and CF2O; the cross sec-
tions used are those given by DeMore et al. [1987]. HF is lost only by rainout in the troposphere.

The 2D model neglected tropospheric rainout of both CFC10 and CF2O, which has led to an overestimate of both CF2O amounts and HF production in the stratosphere. Consequently, the distribution of HF calculated in the 2D model produces stratospheric HF columns greater than those observed from previous column measurements as well as those made early in the mission and to correspondingly smaller HCl/HF ratios.

In the run with parameterized heterogeneous loss of HCl, an additional loss process for HCl with a three day time constant [Douglass and Stolarski, 1989] was assumed whenever the temperature fell below a threshold value which is appropriate for PSC formation at a given pressure. The threshold temperatures are 199, 197, 195, and 192 K for the top tropospheric level (a sigma surface centered approximately at 175 mbar) and the lowest stratospheric levels of 91, 53, and 31 mbar, respectively. They were chosen on the basis of the vapor pressure data of Hanson and Mauersberger [1988] and assumptions of typical stratospheric H2O (5 ppmv) and HNO3 (5-10 ppbv) levels.

Results and Discussion

The calculations show that no major changes in the stratospheric HCl and HF columns are expected over the course of the simulation in the absence of heterogeneous chemistry. In figure 1, for example, we compare the zonal mean stratospheric columns (defined as that above 200 mb for similarity with the aircraft measurements) of HCl (bottom panel), HF (center panel), and their ratio (HCl/HF, top panel) for the initial day (Dec. 28, 1988, dashed lines) and after 33 days of model integration (Jan. 30, 1989) for runs with gas phase chemistry only (solid lines) and, for HCl, heterogeneous loss as well (dotted lines). With only gas phase chemistry, there is a slight shift in the meridional distribution of both HCl and HF; column amounts are slightly reduced at low latitudes and increased at high latitudes. Outside of very high northern latitudes (80-90N), the overall change in HCl and HF distributions is fairly small over the 45 days of simulation. The HCl/HF ratios changed only very slightly, with values remaining between 2 and 2.5 everywhere between 15 and 85N. Transient numerical problems north of 80N lead to sporadic growth of HCl and HF columns near the pole, and the increases in these quantities closest to the pole are not significant.

When heterogeneous chemistry for HCl is introduced, the results change substantially. HCl amounts at high latitudes decrease, leading to a reversal in the meridional gradient of the HCl column (see bottom panel of figure 1). As a result, a marked decrease in the HCl/HF ratio from 50N to 80N is also obtained.

The HCl columns calculated with heterogeneous chemistry usually compare better to observations than those calculated with gas phase chemistry only. In figure 2 we compare the observed values for the HCl and HF columns above the DC-8 on Jan. 26, 1989 (+ for NCAR data, * for preliminary JPL data) with those calculated from the model using the geometrical position of the DC-8 assuming a flight level of 200 mb and the model results at noon Greenwich time for that day. On this day, the DC-8 flight track passed through air both outside and inside the polar vortex during the leg of its flight in which the infrared observations were made. This leg was at 70N latitude and covered the longitudinal region from approximately 14E (11:20 GMT) to 43W (14:10 GMT), crossing into the vortex at approximately 15W (12:50 GMT).

The results calculated with only gas phase chemistry provide a clearly incorrect representation of the longitudinal dependence of the HCl column (figure 2a), as the model results show increasing HCl as one penetrates the vortex, while both data sets show a marked decrease in the HCl column amounts. The run with heterogeneous loss does show

![Fig. 1. Plot showing zonally averaged columns above 200 mbar as a function of latitude for HCl (bottom panel), HF (center panel), and their ratio (HCl/HF, top panel) on beginning of model integration at Dec. 28, 1988 (dashed lines) and after 33 days of model integration (Jan. 30, 1989) for runs with gas phase chemistry (solid lines) and heterogeneous loss (dotted lines). Units for columns are $10^{15}$ molecules cm$^{-2}$.](image1)

![Fig. 2. Plot comparing calculated HCl (left) and HF (right) columns along the DC-8 flight track on Jan. 26, 1989 with those measured by the JPL (*) preliminary data and NCAR (+) instruments. For HCl the solid line indicates values calculated with gas phase chemistry only, while the dashed line assumes added heterogeneous loss. Column densities are in units of $10^{15}$ molecules cm$^{-2}$.](image2)
A decrease of HCl as one enters the vortex, in qualitative agreement with the observed data. Neither model especially well represents the range of values observed, however. In particular, the heterogeneous loss model greatly underestimates the reduction of HCl values inside the vortex.

The quantitative consideration of the HCl column amounts is complicated by the systematic difference between the JPL and NCAR measurements, the source of which is currently under investigation. This difference also occurred in the data from the AAOE; see the papers by Coffey et al. [1989] and Toon et al. [1989]. Since the emphasis here is on the spatial variation of the data, which is very similar for the two data sets (see figure 2), the difference between the two data sets is unimportant for our purposes.

For HF, the model represents the longitudinal variation of the column amount above the aircraft accurately. In figure 2b we compare the calculated HF distribution on Jan. 26 with that observed by the two instruments. Both instruments showed HF amounts to increase as one enters the polar vortex, and this feature was well reproduced by the model.

The changes in the HCl distributions due to heterogeneous loss are extremely non-zonal. This may be seen by comparing in figure 3 the stratospheric HCl columns at 67.6N on Jan. 26, 1989 (a day with a highly asymmetric polar vortex [Newman et al., 1989] and one in which the DC-8 flew both inside and outside the polar vortex) with and without heterogeneous loss. The regions of difference between the two calculated HCl distributions are highly correlated with vorticity in the lower stratosphere. At longitudes of high vorticity (50-170E, 240-350E) the HCl column for the case with heterogeneous chemistry is dramatically below that with gas phase chemistry only; at longitudes of low vorticity (0-50E, 170E-240E) the differences are very small. Even after long periods of integration, the HCl reductions occurring in the low temperature regions do not appear to be spreading significantly outside the vortex. For comparison, we also show the HF distribution, which like HCl with gas phase chemistry, is well correlated with vorticity. We note that essentially all the air within the vortex has been depleted in HCl by the heterogeneous loss.

This longitudinal dependence leads to an interesting dependence of the HCl vertical profile on vortex position. In figure 4 we compare the HCl profiles calculated for Jan. 26, 1989 at 67.6N at positions both outside (left, 15E) and inside (right, 319E) the vortex (see figure 3). The main difference between the profiles with gas phase chemistry (solid lines) is that in the vortex the profile is shifted downward in the lower and middle stratosphere. There is always more HCl inside the vortex than there is outside it. In the presence of heterogeneous loss (dashed lines), however, there is no such simple relationship between the in- and out-of-vortex profiles. In the lower stratosphere, the out-of-vortex profile calculated with heterogeneous loss is only slightly reduced from the gas phase chemistry value from approximately 20-35 km. Thus, at this location, heterogeneous chemistry has had little effect on the HCl profile. Inside the vortex between 20 and 25 km, lower values of HCl are calculated than at the same latitude outside it. Higher in the stratosphere (at and above 30 km) the heterogeneous chemistry does not appreciably affect the HCl distribution. As a result, the vertical gradient of the HCl mixing ratio inside the vortex is much sharper than would be expected in the absence of heterogeneous loss.

**Summary and Conclusions**

By using a three-dimensional coupled chemistry and transport model we have examined the temporal and spatial variability of HCl and HF in the northern hemisphere during the AASE and assessed the global impact of localized regions of heterogeneous loss on the HCl distribution. The model appears to adequately simulate the spatial variability of HF, although there is a bias in the initial conditions used so that calculated HF columns are higher than typically observed early in the mission. For HCl the observed decreases in HCl over the course of the mission and the spatial dependence of the measured data are better modeled with a heterogeneous loss process occurring at
low temperatures in the lower stratosphere. With parameterized HCl loss in our model, depletions of the total HCl column extend as far south as 45N. The depletions at high latitude are localized in the lower stratosphere and confined to regions of high vorticity. All the air in the vortex is HCl deficient. The HCl depletions can be large enough to produce a reversal of the meridional gradient of the HCl mixing ratio.

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