

THE INFLUENCE OF POLAR HETEROGENEOUS PROCESSES ON REACTIVE
CHLORINE AT MIDDLE LATITUDES: THREE DIMENSIONAL MODEL IMPLICATIONS

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Abstract. Three dimensional model calculations with the NASA/GSFC chemistry and transport model have been designed to consider the impact of heterogeneous processes occurring on polar stratospheric clouds (PSC's) in the Arctic vortex on the HCl distribution. By examining the HCl concentration for a calculation with PSC's relative to a calculation with gas phase chemistry only, we infer the impact of polar processing on reactive chlorine species at middle latitudes. Results from the chemistry and transport model reproduce basic features of the ClO measurements [Toohey et al., 1991], which were made on the ferry flights of the ER-2 from Stavanger, Norway to Moffett Field, California via Wallops Island, Virginia on February 20 and 21, 1989. The model indicates that perturbed air which is contained within the polar vortex during winter is not homogeneously mixed, and that the ferry flights were made through air with the largest conversion of HCl to reactive chlorine that is seen at middle latitudes.

Introduction

Measurements of HCl, ClONO₂ and ClO in both the Antarctic and Arctic support the view that heterogeneous chemical reactions on the surfaces of polar stratospheric clouds (PSC's) release reactive chlorine species from the reservoir species HCl and ClONO₂, leading to large ClO enhancements [e.g., Anderson et al., 1989; Coffey et al., 1989; Mankin et al., 1990; Brune et al., 1990a]. The measurements indicate that the regions of perturbed chemistry are largely confined to the polar vortex. The impact of such processes on the stratosphere outside the polar vortex is in question. For the Antarctic case, following the break-up of the polar vortex, air that is depleted in ozone, water (dehydrated), and nitrogen oxides (denitrified) and high in active chlorine species is transported to middle latitudes. The impact on middle latitudes is caused by both mixing of the ozone poor air [Sze et al., 1989; Prather et al., 1990] and further chemical ozone losses due to high levels of active chlorine [Prather and Jaffe, 1990].

The dramatic ozone loss observed in Antarctic spring is not observed in the Arctic. Furthermore, although there is evidence for dehydration and denitrification in the Arctic, both the magnitude and extent of these effects are reduced

relative to the Antarctic [Kelly et al., 1990; Mankin et al., 1990]. However, the northern hemisphere wintertime long term trends in total ozone, as derived from Total Ozone Mapping Spectrometer (TOMS) measurements, are larger than expected from calculations with increasing fluorocarbons and normal gas phase photochemistry [WMO, 1990]. It has been suggested that transport to middle latitudes of air which has experienced PSC processing and contains elevated levels of active chlorine could influence middle latitude ozone levels [e.g., Newman et al., 1990]

We have examined the impact of polar processing on middle latitudes using a three-dimensional chemistry and transport model. A description of the ClO measurements [Toohey et al., 1991] considered here is followed by a brief discussion of the model and the model experiments designed to simulate the effects of PSC's. The HCl difference for calculations with and without PSC processing is computed for aircraft flight tracks through the model fields, and is compared with the aircraft measurements of ClO. The ferry flights of the ER-2 from Stavanger Norway to Moffett Field California via Wallops Island Virginia on February 20 and 21, 1989 are shown to have encountered processed air. It is also shown that polar processed air is confined in longitude at middle latitudes.

The Data

Here we consider ClO measurements on three ferry flights of the NASA ER-2. These include the December 30 1988 flight from Moffett Field, California (37.3N, 122 W) to Wallops Island, Virginia (37.8N, 75.5W), and flights from Stavanger, Norway (59N, 6E) to Moffett Field, California via Wallops Island, Virginia on February 20 and 21, 1989. A fourth transit flight from Wallops Island to Stavanger took place at night and is not considered. These measurements were made as part of the Airborne Arctic Stratospheric Expedition (AASE) using the Harvard University ClO-BrO instrument aboard the NASA ER-2 aircraft. A description of the experiment and measurements during the mission are given by Brune et al. [1990a].

On the February 20 flight, ClO mixing ratios higher than 200 part per trillion by volume (pptv) were measured (Figure 1a); these measurements took place between 10 am and 2 pm local time. The following day, also during late morning to early afternoon, values as high as 160 pptv were observed (Figure 1b). These values may be contrasted with measurements from the December 29 flight from Moffett Field to Wallops (Figure 1c). The maximum ClO mixing ratios observed near local noon on the

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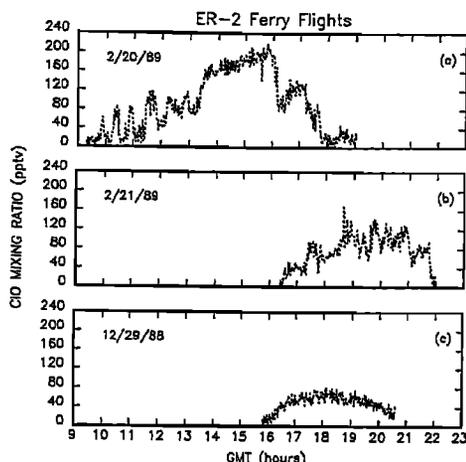


Fig. 1 (a) ClO measured on February 20, 1989 (Stavanger to Wallops Island) (b) ClO measured on February 21, 1989 (Wallops Island to Moffett Field) (c) ClO measured on December 29, 1988 (Moffett Field to Wallops Island)

December flight are approximately 60 pptv; the measurements on February 20 and 21 are significantly larger. This large fractional difference is not explained by seasonal effects. This is supported by comparison with previous measurements [Brune et al., 1990b], and by two-dimensional model calculations which indicate a relatively small fractional difference between the December and February daytime average ClO values at 50 mb at middle latitudes.

The Model

The chemistry and transport model (CTM) uses winds and temperatures from the STRATAN assimilation system [Rood et al., 1989]; the STRATAN representation of the AASE period is discussed by Rood et al. [1990a]. In previous applications [Kaye and Rood, 1989; Kaye et al., 1990], constituent transport was calculated using a spectral scheme. Difficulties with the spectral scheme near the pole led to adoption of a grid point scheme described by Van Leer [1979]. Horizontal resolution for the transport is 2 degrees latitude by 2.5 degrees longitude; details concerning the adaptation of this scheme to the CTM are given by Allen et al. [submitted manuscript 1990]. Recent calculations for ozone with the grid point transport scheme show that the model total ozone fields evolve in a similar manner to TOMS measurements for periods of at least 90 days [Rood et al., 1990b].

Model studies of HCl, one with normal gas phase chemistry and two with parameterized heterogeneous loss, are considered here. Heterogeneous effects are simulated simply by including an additional loss for HCl, with a time constant of three days, whenever the temperature falls below a threshold value for PSC formation at a given pressure. The threshold temperatures are 199, 197, 195 and 192 K for the top tropospheric model level and the first three stratospheric levels (approximately 175, 91, 53 and 31 mb). The decrease in HCl produced by heterogeneous reactions is as large as 80% of the HCl value calculated with gas phase chemistry at the end of January. A shorter time constant for HCl loss would produce somewhat larger

decreases in HCl, but the amount of air which is processed would be unchanged. The sensitivity to the temperature criterion was tested by repeating the calculation with the threshold temperatures increased by 2 degrees. This increases both the amount of air which is processed and the time during which processing occurs. A previous work [Kaye et al., 1990] considers the same HCl calculations, however the spectral transport scheme was used and problems with the polar region limited the calculation to 45 days (Dec. 28 to Feb. 11).

The calculation of photochemical production and loss terms for HCl following an encounter with a PSC is not trivial. If a parcel has been denitrified, the balance between Cl and ClO may be controlled by reactions with odd oxygen species rather than the usual case of control by reactions with odd nitrogen species. Even if a parcel is not denitrified, NO and NO₂ will have been converted to the reservoir HNO₃, and the balances within both the odd nitrogen family and the chlorine family are altered. These possibilities are considered in a detailed photochemical model by Prather and Jaffe [1990].

Here we consider a single constituent model and calculate production and loss by two methods. In the first method, diurnally averaged values of the photochemical production and the loss frequency are taken from the Goddard two-dimensional model, and updated every 15 days. This is a lower limit for HCl production because it is assumed that inorganic chlorine species are partitioned normally, i.e., HCl and ClONO₂ are the most important species. In the second case, production of HCl is enhanced in proportion to the change in HCl due to processing. This accounts for the possibility that production of HCl in processed air is larger than the normal case due to increased Cl. This method assumes that the ratio of Cl to ClO is not changed by the perturbed chemistry. A more detailed study by Prather and Jaffe [1990] considers the rates of decrease of ClO for processed air and for denitrified and dehydrated processed air. The rate of production of HCl inferred for processed air is intermediate to that for the cases considered here. For air which has been denitrified, a slower rate of production of HCl is expected because of the importance of NO to the Cl/ClO ratio.

Discussion

The difference ΔHCl (i.e., HCl calculated with normal gas phase chemistry minus HCl calculated with parameterized heterogeneous loss) is most clearly interpreted as a measure of a parcel's encounters with temperatures at or below the formation threshold for PSC's. It is not realistic to expect quantitative agreement between measured ClO and the difference ΔHCl for the following reasons: first, this calculation assumes that ClO is present initially, and that free chlorine produces ClONO₂ so that the change in HCl is limited only by the duration of encounters with cold temperatures; second, this calculation does not consider processes important to chlorine partitioning, such as ClO dimer formation, conversion of odd nitrogen species to HNO₃, recovery of odd nitrogen species in the absence of PSC's, and mechanisms for denitrification; third, even if ΔHCl could be correctly partitioned, this would relate to the enhancement of ClO compared to normal background

values rather than the total ClO which is measured; fourth, the total difference in reactive chlorine also includes the difference in ClONO₂. Despite these problems, it is not unreasonable to expect the change ΔHCl to be proportional to the change in daytime ClO.

The differences ΔHCl for both normal and enhanced recovery calculations are given for the transit flight from Stavanger to Wallops in Figure 2a and from Wallops to Moffett Field in Figure 2b. The ClO measurements are superposed for comparison. Both ΔHCl and the maximum value of ClO are smaller on the second flight than the first. The qualitative behavior of the observed ClO closely tracks the behavior of calculated ΔHCl, suggesting that the ER-2 observed high values of ClO because it had encountered processed air.

A polar plot of ΔHCl (normal recovery) is given in Figure 3 for February 20 for the northern hemisphere; Stavanger, Wallops and Moffett Field are indicated on the figure by stars. The flight track between Stavanger and Wallops is also given. The large differences as seen along the flight track are confined to a relatively narrow range of longitudes; at 50 N differences greater than 50 pptv are confined to two longitude intervals (105-155 E and 245-335 E). Outside these intervals the average value of ΔHCl is about 30 pptv; inside these intervals the ΔHCl averages 130 pptv. For the latitude band between 46 and 62 N, values of ΔHCl as high as 100 pptv, which are seen on the aircraft track, appear for less than 20% of the band. This suggests that elevated values of ClO would not be observed generally at middle latitudes.

The area of enhanced ClO values decreases with time due to photochemical production of HCl and mixing. ΔHCl (normal recovery) is given for March 1 in Figure 4. The area with the largest values has moved south, and has shifted eastward. The values of ΔHCl greater than 50 pptv are again confined to two longitude intervals, 305-35 E and 85-135 E (Figure 4). Although the maximum value of ΔHCl has decreased substantially, from about 500 pptv to about 300 pptv, the mean value at 50 N is unchanged.

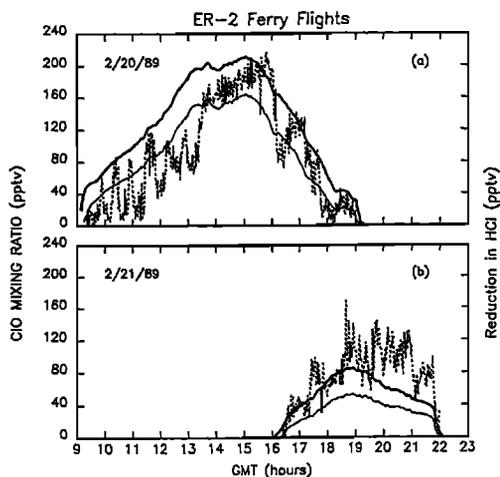


Fig. 2 (a) ΔHCl for normal gas phase chemistry (bold line) and ΔHCl for enhanced HCl recovery (solid line) compared with ClO measurements for February 20, 1989 (Stavanger to Wallops Island) (b) same as (a) for February 21, 1989 (Wallops Island to Moffett Field)

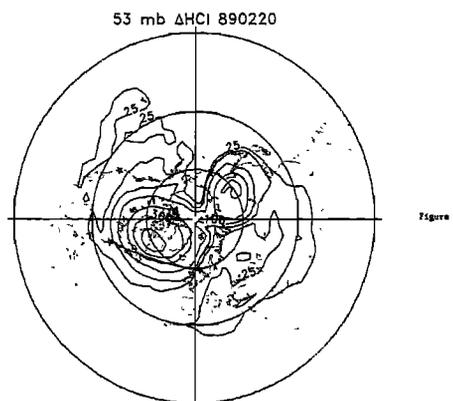


Fig. 3. ΔHCl for normal gas phase chemistry for the northern hemisphere on February 20, 1989. Stavanger, Wallops Island and Moffett Field are indicated by stars. Contour intervals are 25, 50, 100, 200, 300, 400 pptv.

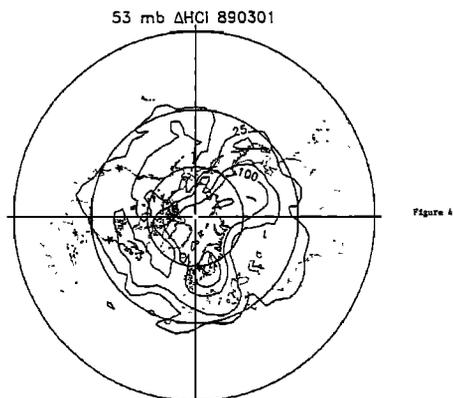


Fig 4. Same as Fig. 3 for March 1, 1989.

Model values of ΔHCl are much smaller on March 1 compared to February 20-21 along the flight tracks.

As a sensitivity study, the calculations were repeated with the threshold temperature for PSC formation increased by 2 degrees. Results are qualitatively similar to results shown here, although the values of ΔHCl at middle latitudes are generally larger. On February 20, for the longitude 105-155 E and 245-355 E the average value of ΔHCl is about 180 pptv; the average outside these intervals is about 40 pptv. The horizontal gradient in ΔHCl is larger for the sensitivity study than for the baseline case.

Conclusions

The ClO mixing ratios measured on February 20 and 21 are significantly enhanced relative to measurements on December 29. This enhancement is not explained by diurnal or seasonal effects; the model indicates that the high ClO values are a result of heterogeneous processes during the polar night and the transport of polar air masses towards lower latitudes. However, these calculations show that the impact on middle latitude ozone is limited by both the geographical extent and duration of perturbed air. The model calculations indicate that ClO values which are

enhanced as a result of polar processed would not be observed generally at middle latitudes. The perturbed air which is contained within the polar vortex during winter has not been homogeneously spread to middle latitudes, and enhanced reactive chlorine is primarily confined to two longitude bands. By the time more complete mixing has occurred, the perturbation to reactive chlorine has decreased through production of reservoir species HCl and ClONO₂ through normal gas phase reactions.

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