Measurements of chlorine partitioning in the winter Arctic stratosphere

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Abstract. Measurements of the concentration profiles of key stratospheric reactive, reservoir and source gases, ClO, O_3, HCl, N_2O and CCl_2F_2, were made during two balloon flights in the Arctic on 27 January and 08 March 1995 that were part of the Second European Stratospheric Arctic and Mid-latitude Experiment (SESAME). On 27 January, low abundances of HCl ($\sim$250 ppt at 50 hPa) were measured in air parcels that had been at temperatures below the type I PSC existence threshold accompanied by high concentrations of ClO (1.6 ppb at 50 hPa). Calculations using the currently recommended photochemical data yield a ratio of [ClO]+2[Cl_2O_2]+[HCl] to [Cl_y] near unity in these air parcels. The 08 March flight sampled warm stratospheric conditions outside the vortex with normal mid-latitude ClO ($<$100 ppt at 50 hPa) and HCl abundances comprising about half of the available chlorine at 50 hPa.

1. Introduction

Under the extremely cold conditions in the polar winter stratosphere, heterogeneous reactions involving HCl and $ClONO_2$ on the surfaces of polar stratospheric cloud (PSC) particles can release large amounts of reactive chlorine (i.e., Cl, ClO) from these reservoirs leading to rapid chemical loss of ozone in the Arctic lower stratosphere during late winter and early spring [e.g., *WMO*, 1995]. Under these cold conditions, ClO exists in equilibrium with the ClO dimer, Cl_2O_2. Photolysis of Cl_2O_2 produces Cl that propagates the chlorine catalyzed O_3 loss cycle. Although this view of polar processes is widely accepted, observations and models of the partitioning of Cl_y between the HCl and $ClONO_2$ reservoir gases prior to heterogeneous processing have not been fully reconciled [*Webster et al.*, 1998; *Chang et al.*, 1996; *Engel et al.*, 1997]. Large uncertainties also remain in the model estimates of [Cl_2O_2], which has yet to be measured. *Jaeglé et al.* [1997] adopted the Cl_2O_2 absorption cross section measurements of *Huder*

and *DeMore*[1995] to analyze the stoichiometry of heterogeneous chlorine activation in the Antarctic. These cross sections lead to photolysis rates of Cl_2O_2 that are 40% slower than those derived from cross sections in the JPL97-4 compendium[*DeMore et al.*, 1997]. *Pierson et al.* [1999], using photolysis rates of Cl_2O_2 faster than those derived from the *Huder and DeMore* [1995] cross sections but slower than those derived from the JPL97-4 cross sections, infer that the Cl_2O_2/ClO equilibrium constant at 200 K is significantly smaller than the value given in JPL97-4.

In this paper, we use measurements obtained using balloon-borne instruments to examine, for the Arctic winter of 1995, the budget of inorganic and organic chlorine, the altitude variation of the degree of chlorine activation, and the speciation of activated chlorine between its various compounds. These observations constitute a comprehensive examination of key reactive, reservoir, and source chlorinated species over a wide range of altitudes in the Arctic vortex and should provide important constraints for future three-dimensional model studies of Arctic ozone.

2. Instrumentation and Observations

The observations reported here were made during balloon flights on 27 January and 08 March 1995 that were launched from the ESRANGE facility near Kiruna, Sweden (68°N, 21°E). Instrumentation included whole air samplers from the Forschungzentrum Jülich (FZJ) and the submillimeterwave limb sounder instrument (SLS) from the Jet Propulsion Laboratory (JPL).

The FZJ whole air sampler [*Bauer et al.*, 1994] collected ambient pressure samples during descent of the gondola that were subsequently analyzed using gas chromatography with electron capture detection for CCl_2F_2, CCl_3F, $C_2F_3Cl_3$ and N_2O.

The SLS is a high resolution heterodyne radiometer-spectrometer that measures atmospheric limb thermal emission spectra of ClO, HCl, N_2O, O_3 and HNO_3 at frequencies near 600 GHz. Constituent profiles were retrieved by fitting a parameterized atmospheric radiance model to the flight averaged spectra [*Stachnik et al.*, 1992].

3. Meteorology

The lower stratosphere during the Arctic winter of 1994/1995 was characterized by persistent low temperatures. At 50 hPa, temperatures below the existence threshold of type I (nitrate-containing) PSCs were observed in the polar vortex from mid-December 1994 until late-February when a warming occurred. Vortex cooling accompanied by chlorine activation was again observed in early through mid-March 1995 [e.g., *Manney et al.* 1996].

During and several days prior to the 27 January flight the cold center of the vortex at the 475K Θ level was located to the east of Kiruna over northern Russia.

During this flight, the SLS viewing direction was set to place the 20 km height tangent point 300 km closer to the vortex cold center. The FZJ grab samples were collected ~250 km southeast of Kiruna. An ECMWF (European Centre for Medium Range Weather Forecast) 10 day back-trajectory analysis shows that air parcels above Kiruna from 380 K to 550 K Θ on 27 January had been exposed to temperatures below the type I PSC existence threshold.

In contrast, the flight on 08 March 1995 took place during warm conditions in the local lower stratosphere. Although the polar vortex was intact, low temperatures were now located over northern Canada and the 10 day trajectory analysis indicates that these air parcels were extra-vortex and had not recently been exposed to temperatures low enough for NAT PSC existence.

4. Results

Figure 1 shows the vertical profiles for $[CCl_2F_2]$, [ClO] and [HCl] measured during the flights on 27 January 1995 (panel A) and 08 March 1995 (panel B). Concentration profiles of the long-lived tracer N_2O, measured by both instruments on both balloon flights, are shown in Figure 2. A mid-latitude profile of $[N_2O]$ measured by SLS over Aire sur l'Adour, France (44°N, 0°W) on 07 October 1994 is included.

Observations of $[N_2O]$ on 27 January indicate that significant diabatic descent had occurred, as expected for air within the polar vortex. In contrast, the 08 March profile of $[N_2O]$ exhibits little descent in comparison to the mid-latitude reference profile and is consistent with the trajectory analysis indicating that this flight sampled extra-vortex air. The close agreement between the SLS and FZJ observations of $[N_2O]$ for both flights indicates that the instruments were sampling dynamically similar air parcels.

The first step in examining the budget and activation of chlorine is to establish the expected profile for $[Cl_y]$, the sum of the chlorine contained in inorganic species including ClO, Cl_2O_2, $ClONO_2$, HCl, HOCl, Cl, etc. Two estimates of $[Cl_y]$ are shown in Figure 1.

The first is based on the profile of $[N_2O]$ measured by SLS using a relation between $[Cl_y]$ and $[N_2O]$ derived from ER-2 observations of organic source molecules dur-
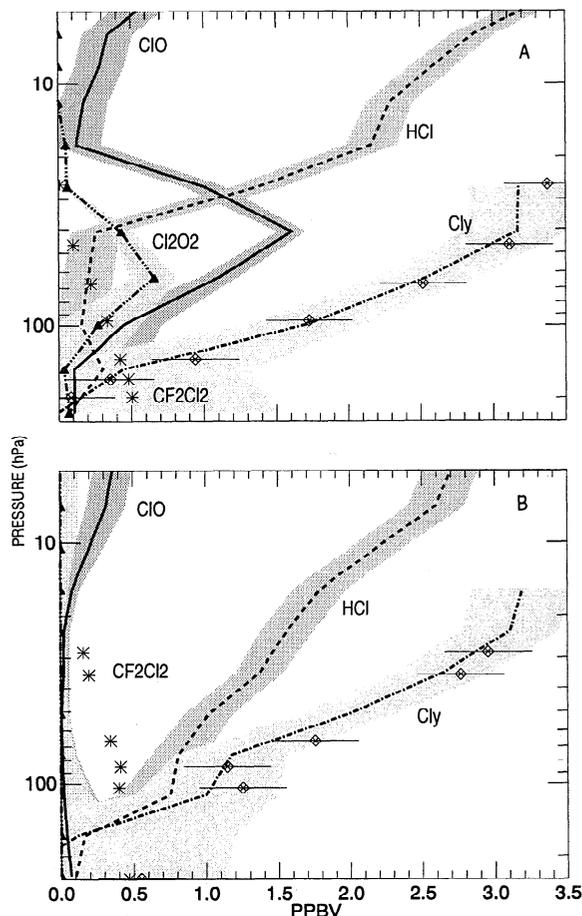
Figure 1. Measured and derived profiles for [HCl](dashed), [ClO](solid), $[CCl_2F_2]$(asterisks), $[Cl_y]$(dash-dot), and $[Cl_2O_2]$ (triangles) from balloon data for (A) 27 January 1995 and (B) 08 March 1995. $[Cl_y]$ estimates are shown derived from both SLS $[N_2O]$ (dash-dot) and from FZJ $[CCl_2F_2]$(diamonds with extents). The shaded regions indicate the SLS measurement 90% confidence limit.

ing 1992 [*Woodbridge et al.*, 1995]. These values of $[Cl_y]$ have been increased by 3%/year to adjust for the rise in the stratospheric burden since the time of the ER-2 observations. The second estimate of Cl_y is based on the profile of $[CCl_2F_2]$ measured by the FZJ sampler using the relation $[Cl_y] = [Cl_{total}] - [CCl_y]$. The value of $[Cl_{total}]$ (total stratospheric chlorine) is assumed to be constant with altitude at a value of 3520 ppt, the abundance of HCl near the stratopause measured by ATMOS/ATLAS-3 in November 1994 [*Zander et al.*, 1996]. Due to the recent leveling of the temporal evolution of tropospheric chlorine and the relative uniformity of the age of stratospheric air, only a small gradient in $[Cl_{total}]$ with altitude is expected. The value of $[CCl_y]$ (the total chlorine content of the organic source gases) is given by a relation established from recent balloon flights of the FZJ cryosampler [*Schmidt et al.*, 1994; *Engel et al.*, 1997] $[CCl_y] = 125.8 + 1.84 \times [CF_2Cl_2] + 0.0094 \times [CF_2Cl_2]^2$, where the mixing ratio units are
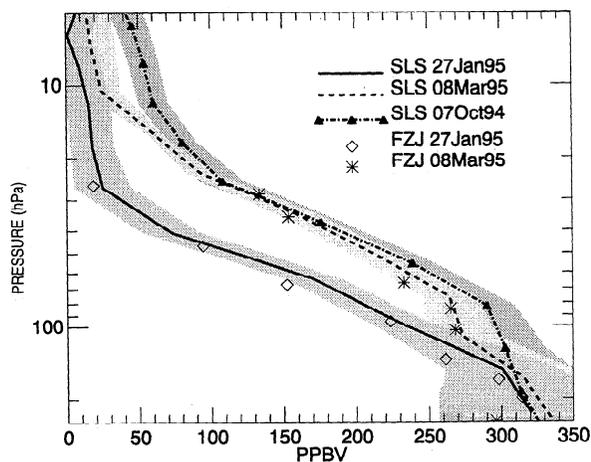
Figure 2. [N$_2$O] profiles measured by the FZJ grab sampler and SLS for 27 January 1995 and 08 March 1995. Included is a mid-latitude (44°N) [N$_2$O] profile measured by SLS on 07 October 1994. Shaded regions indicate the SLS measurement 90% confidence limit.

ppt. The good agreement of the SLS-based and FZJ-based [Cl$_y$] estimates for both flights shown in Figure 1 provides confidence that both estimates are accurate and suggests that the expected profile of total inorganic chlorine has been well established for both flights.

An estimate of the mixing ratio of ClO dimer, Cl$_2$O$_2$, is required to examine the budget and activation of chlorine inside the polar vortex because this species can comprise a significant fraction of Cl$_y$.

We have calculated the mixing ratio profile of [Cl$_2$O$_2$] based on its diurnal steady state relation with observed [ClO] [*Salawitch et al.*, 1993] using photochemical parameters from the JPL97-4 compilation. For the 27 January 1995 vortex flight, the calculated [Cl$_2$O$_2$] (Figure 1A) peaks at a value of 0.6 ppb near 70 hPa. The chlorine content of the ClO dimer exceeds [ClO] near the peak. For the 08 March 1995 extra-vortex flight, the calculated [Cl$_2$O$_2$] is negligible due to small [ClO].

The calculated profile of [Cl$_2$O$_2$] for the vortex flight is sensitive to its rate of formation and photolysis and insensitive to the rate of thermal decomposition. To illustrate this sensitivity, results based on calculated [Cl$_2$O$_2$] using the absorption cross sections of *Huder and DeMore* [1995] are also shown. There is considerable uncertainty in the value of these cross sections due to, among other complications, possible impurities of Cl$_2$O in the various laboratory experiments [*DeMore et al.*, 1997]. As shown below, uncertainty in the photolysis rate of [Cl$_2$O$_2$] limits our ability to quantitatively evaluate our observations.

We have not attempted to directly calculate [ClONO$_2$] for the present analysis. During periods of chlorine activation inside the vortex, the concentration of [ClONO$_2$] is expected to be small. The partitioning of [ClONO$_2$] and [HCl] outside the vortex is, as mentioned above, the subject of considerable uncertainty. We investigate [ClONO$_2$] for both conditions by examining the residual between [Cl$_y$] and the sum [ClO]+2[Cl$_2$O$_2$]+[HCl].

Chlorine activation and the budget of chlorine are examined for both flights in Figure 3. The ratio of [Cl*] $\equiv$ ([ClO] + 2[Cl$_2$O$_2$]) to [Cl$_y$] represents the fraction of inorganic chlorine that is activated and available to remove ozone. The ratio ([HCl]+[Cl*])/[Cl$_y$] tests our understanding of the chlorine budget for the vortex flight and our understanding of [ClONO$_2$] vs [HCl] partitioning for the extra-vortex flight. The estimate of [Cl$_y$] used in Figure 3 is based on the SLS measurement of [N$_2$O]; however, results are insensitive to which estimate of [Cl$_y$] is used.

The ratio of [Cl*]/[Cl$_y$] for 27 January 1995 shows that, to within the accuracy of the measurements, nearly
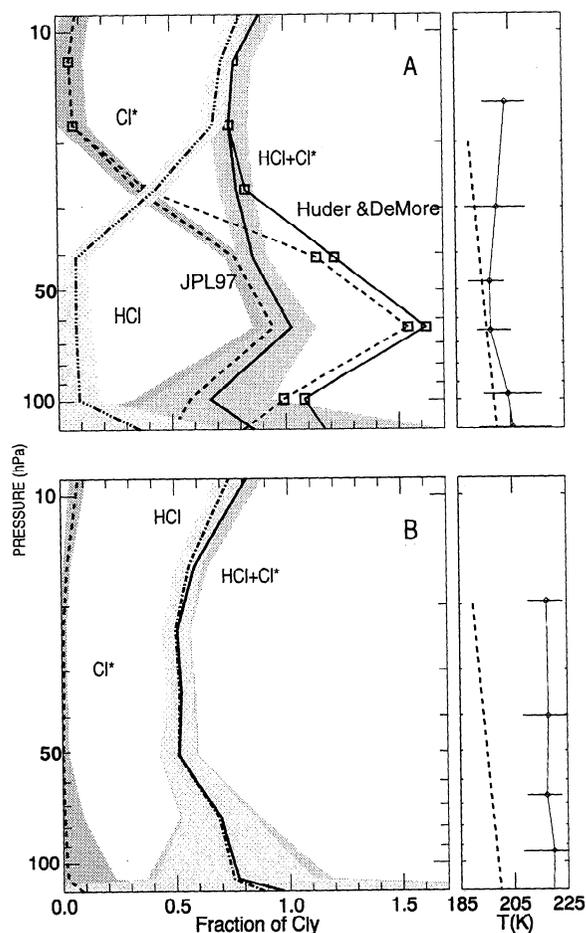
Figure 3. Ratios of [HCl](dash-dot line), [Cl*](dashed line), where [Cl*]$\equiv$([ClO] + 2[Cl$_2$O$_2$]) (solid line), and [HCl]+[Cl*] to available chlorine, [Cl$_y$] for measurements on 27 January 1995 (A) and on 08 March 1995 (B). [Cl*]/[Cl$_y$] (squares and dashed line) and ([HCl]+[Cl*])/[Cl$_y$] (squares and solid line) calculated using Cl$_2$O$_2$ absorption cross sections from *Huder and DeMore*[1995] are included in panel A. [Cl$_y$] was calculated from SLS measurements of [N$_2$O]. Shaded regions represent the measurement 90% confidence limit. Panels on the right show the 10 day back-trajectory mean temperature (solid line). The extents show the temperature extremes along each trajectory. The dashed line shows the type I PSC existence temperature for [H$_2$O]=5 ppm, [HNO$_3$]=5 ppb using the HNO$_3$ vapor pressure data from *Hanson and Mauersberger*[1988].

all the available chlorine was converted to ClO and Cl_2O_2 from the 70 hPa to the 45 hPa level. The 10 day temperature history for these air parcels (Figure 3, right panel) indicates that air in this region had recently experienced temperatures below the NAT existence threshold. Consequently, the levels of activated chlorine within the vortex are broadly consistent with expectation based on heterogeneous processing on PSCs. In this "activated" region [HCl] comprises ~10% of $[Cl_y]$ and we infer that $[ClONO_2]$ was nearly depleted since $([HCl]+[Cl^*])/[Cl_y]$ is near unity.

The estimates of $[Cl^*]$ based on the *Huder and De-More* [1995] cross sections for Cl_2O_2 are substantially larger than the estimated level of $[Cl_y]$ throughout the range of enhanced [ClO]. This uncertainty complicates identification of the upper altitude of the region of chlorine perturbation and precise determination of the fraction of available chlorine that is activated. Our observations suggest that the photolysis rate of Cl_2O_2 must be larger than that derived from the cross sections of *Huder and DeMore* [1995], a result consistent with the conclusions of *Pierson et al.* [1999]. Clearly, better laboratory definition of kinetics related to Cl_2O_2 would enhance the quantitative analysis of observations of [ClO] obtained under cold conditions in the wintertime vortices.

The data obtained for extra vortex conditions on 8 March 1995 exhibit a distribution qualitatively similar to that observed at mid-latitudes [e.g., *Zander et al.*,1996], with a broad minimum in $[HCl]/[Cl_y]$ near 40 hPa. Both [ClO] and $[Cl_2O_2]$ comprise a negligible fraction of $[Cl_y]$ (0 ± 0.1) for altitudes below 15 hPa. The data show that $[HCl]/[Cl_y]$ is equal to 0.52 ± 0.15 at 50 hPa, in good agreement with the ratio measured by ER-2 instruments in 1994 at similar pressures but lower latitudes [*Webster et al.*, 1998]. A similar $[HCl]/[Cl_y]$ ratio (0.6 ± 0.1) was observed by SLS and FZJ instruments within the polar vortex in February 1994, when only moderate chlorine activation ([ClO] ~230 ppt at 22.5 km) had occurred [*Engel et al.*, 1997]. However, the [HCl] measured by SLS on 8 March is less (by 0.3 to 0.4 ppb for 150 ppb $<$ $[N_2O]$ $<$ 250 ppb) than mid-latitude measurements of [HCl] obtained by SLS in October 1994 (44°N) and by ATMOS during the ATLAS-3 Shuttle mission (4 to 9 November 1994, 30° to 51°N) [*Chang et al.*, 1996]. Our extra-vortex observations may have been influenced by mixing of PSC-processed vortex air or even moderate exposure to PSCs. Consequently, it is unclear whether it is meaningful to compare these observations to mid-latitude measurements.

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