Evolution of HCl concentrations in the lower stratosphere from 1991 to 1996 following the eruption of Mt. Pinatubo


Abstract. In situ measurements of hydrochloric acid in the lower stratosphere reveal that its mean abundance relative to that of total inorganic chlorine (Cl) has evolved upwards from HCl/Cl=40% in late 1991 to 70% in 1996. This fraction is generally anticorrelated with aerosol surface area concentration, which has been diminishing since the 1991 volcanic eruption of Mt. Pinatubo. Calculations incorporating new laboratory results of faster heterogeneous chemistry show that air parcels with high aerosol loading exposed to temperatures below 205 K can experience enough chlorine activation to drive the HCl/Cl below 50%, but overestimate observed ClO/Cl.

Introduction

The massive enhancement in aerosol loading of the lower stratosphere following the June 1991 eruption of Mt. Pinatubo [McCormick et al., 1995; Jonsson et al., 1996] provided an opportunity to expand our understanding of the role of heterogeneous chemistry on sulfate aerosol particles. As the dense volcanic aerosol of Pinatubo spread into a relatively clean atmosphere, aircraft, balloon, ground-based, and space measurements reported large reductions in concentrations of stratospheric NO (Fahey et al., 1993; Koike et al., 1994; Webster et al., 1994a), and in response, a doubling of concentrations of chlorine monoxide (ClO) [Avalon et al., 1993]. Solomon et al. [1993] attributed high ClO observed over Antarctica to sulfate aerosol processing at temperatures ~203 K, well above PSC threshold. Despite the large impact on NO and ClO, amounts [Salawitch et al., 1994; Hanson et al., 1994], photochemical model calculations incorporating the heterogeneous hydrolysis of N2O5 and ClONO2 predicted only small changes (~15%) in HCl amounts. Column HCl abundance showed no volcanic injection into the stratosphere [Mankin et al., 1992]. Space-based measurements of either HCl or ClONO2 were limited to altitudes above the dense volcanic cloud.

Although HCl is recognized as the principal reservoir of chlorine in the middle and upper stratosphere, discrepancies exist between models and measurements of HCl both above 24 km where models tend to under-predict HCl abundances [Michelsen et al., 1996], and below 24 km where models over-predict HCl abundances [Webster et al., 1994b]. Since 1991, JPL's Aircraft Laser Infrared Absorption Spectrometer (ALIAS) instrument [Webster et al., 1994c] has flown more than 150 times on NASA's ER-2 aircraft. HCl mixing ratios first measured by this instrument [Webster et al., 1993] from 15-20 km were about a factor of two lower than model predictions [Salawitch et al., 1994]. Results from 1993 illustrated the difficulties in balancing the inorganic chlorine budget using the low HCl measurements. In the absence of in situ measurements of ClONO2, simultaneous measurements of ClO, NO, and O3 were used to infer ClONO2 abundances [Stimpfle et al., 1994]. With an inferred fraction of ClONO2/Cl = 14% (ranging from 6 to 28%), the measured ClO amounts implied that if ClO comprised mainly HCl and ClONO2, HCl/Cl should be ~86%, compared to the observed value of 40%. The aircraft measurements of 1993 therefore left ~30% of inorganic chlorine apparently unaccounted for. An analysis of MarkIV FTIR balloon data from a September 1993 flight yielded the proposal that 20-30% of Cl may be sequestered as perchloric acid (HClO4) produced from the heterogeneous reaction of ClO and H2SO4 on sulfate aerosols [Jaegle et al., 1995]. Two other studies reported HCl/Cl ratios of 60±20%, consistent with either the aircraft ALIAS measurements of 50% in 1993, or with the model predictions of 80%: balloon measurements of ClO at 20 km [Avallone et al., 1993] and a recent analysis of HALOE HCl and CLAES ClONO2 measurements from the UARS satellite [Dessler et al., 1995]. In an intercomparison with overflights of ATMOS in Nov. 1994, and with an earlier flight of MarkIV in May 1994, the ALIAS data lay midway between the two FTIR data sets for NO values ≤210 ppbv, where HCl mixing ratios were ≥1 ppbv. ALIAS measurements were ~10% lower than that of ATMOS [Chang et al., 1996], and ~10% higher than those of the MarkIV [G. Toon, private communication] for similar NO amounts.

This paper brings together six years of HCl measurements made during the years of gradual decay of the Mt. Pinatubo aerosol loading of the stratosphere. Model results incorporating new laboratory results of faster heterogeneous chemistry are presented, which show that air masses with high aerosol loading exposed to temperatures typical of the midlatitude lower stratosphere (200-210 K) can experience enough chlorine activation to drive HCl/Cl below 60%, as observed, although a discrepancy remains between model and observed partitioning between HCl and ClO.

A recent analysis of HALOE satellite data [Dessler et al., 1997], has also identified a significant increase (16±9%) in HCl/Cl over a 3-year period from late 1992 at somewhat higher altitudes than the ER-2 data. While these authors conclude that there is no evidence to support the larger increase observed by ALIAS, they recognize that their observed increase is 4 times larger than their model prediction, and that they cannot attribute the observed change to any cause.

The aircraft measurements

The ALIAS instrument is a 4-channel scanning tunable diode laser spectrometer that uses high-resolution laser absorption in the 3-8 μm

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midlatitudes than of polar origin [Michelsen et al., 1997b], which is 70%, a trend that is maintained within the latitude range 40-60°N, as (STRAT) show HCI/CI fractions of typically 40%, 50%, 55-60%, and included in the least-squares correlation fit. From tracer correlations, except for the flights of 11 May and 1 May 1993, which are not populations of low and high HCI values. The 1993 SPADE HCI shown in Fig. 2B.

The aerosol number, SA, and volume concentrations reported here were determined from three particle size spectrometers flown simultaneously as part of the ER-2 aircraft payload, with overall uncertainties of 35%: the condensation nucleus counter (CNC) measured particle concentrations > 0.008 μm dia. [Wilson et al., 1983]; the focused cavity aerosol spectrometer (FCAS) instrument measured size distributions from 0.6 to 2 μm dia. [Jonsson et al. [1992]]; the forward scattering spectrometer probe (FSSP-300) detected particles between 0.4 and 20 μm dia. [Bauwignard et al., 1992] and flew on the ER-2 during 1991/2 and 1993. We used measurements from FSSP for AASE (Airborne Arctic Stratospheric Expedition)-II, from FCAS for ASHOE/MAESA (Airborne Southern Hemisphere Ozone Expedition/Measurements of the Atmospheric Effects of Stratospheric Aircraft) and STRAT (Stratospheric Tracers of Atmospheric Transport), and from all three spectrometers for SPADE (Stratospheric Photochemistry and Dynamics Experiment). N₂O was measured directly by the ALIAS instrument, except for a few flights in which N₂O measurements from the ATLAS instrument [Podolske and Loewenstein, 1993] were used. CIO was measured using resonance fluorescence detection of CI atoms at 118.9 nm, generated by chemical conversion of ambient CIO to CI by addition of NO [Stimpfle et al., 1994], with a measurement uncertainty of ±30%. O₃ was measured using UV absorption [Proffitt et al., 1983].

Figure 1 shows plots of HCI vs. N₂O recorded by ALIAS during four missions: in 1991/2 (AASE-II), 1993 (SPADE), 1994 (ASHOE/MAESA), and in 1996 (STRAT). These data are principally from latitudes 20-70°N and are restricted to pressures < 67 mbar and CIO < 150 pptv to remove data from air masses that have undergone very low temperature processing. The AASE-II data collected from a series of flights from 4 Oct. 1991 through 22 March 1992 fall mainly within a single correlation group except for the striking anomalies from the two earliest flights of 4 Oct. and 6 Oct. 1991. These flights covered the latitude range 37.85°N and were sufficiently close in time to the June Pinatubo eruption to sample regions of rapidly-changing aerosol loading [Jonsson et al., 1996]. The data appear divided into two populations of low and high HCI values. The 1993 SPADE HCI values are generally more tightly correlated with measured N₂O, except for the flights of 11 May and 1 May 1993, which are not included in the least-squares correlation fit. From tracer correlations, these flights have been identified as sampling air more typical of midlatitudes than of polar origin [Michelsen et al., 1997b], which is more typical of most of the HCI data from the SPADE mission. Least-squares fits of data from Fig. 1 are plotted in Fig. 2A, where an evolution with time of the HCI/C is ratio is apparent. Data from 1991/2 (AASE-II), 1993 (SPADE), 1994 (ASHOE/MAESA), and 1996 (STRAT) show HCI/C fractions of typically 40%, 50%, 55-60%, and 70%, a trend that is maintained within the latitude range 40-60°N, as shown in Fig. 2B.

Chlorine activation on sulfate aerosols

The chemistry responsible for the formation of the ozone hole is initiated by the heterogeneous conversion of reservoir species such as HCl and ClO₂ to reactive radicals (such as Cl and ClO), a process known to occur on the surfaces of polar stratospheric cloud (PSC) particles and supercooled liquid sulfate aerosols (see the review by Fahey et al. [1995]). Heterogeneous loss of HCl [Webster et al., 1993] is associated with temperatures < 195 K. Building on the earlier work of Hofmann and Solomon [1989], the reactions

\[
(1) \text{N}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \\
(2) \text{BrO} + \text{H}_2\text{O} \rightarrow \text{HOBr} + \text{HNO}_3 \\
(3) \text{ClO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3 \\
(4) \text{ClO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3 \\
(5) \text{HOCI} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O} \\
(6) \text{HOBr} + \text{HCl} \rightarrow \text{BrCl} + \text{H}_2\text{O}
\]

on sulfate aerosols are significant under volcanic conditions (see Jones et al., 1995). From 200 to 210 K, 1996/97 measurements of reaction rates now available are as much as a factor of three higher than 1994 rates used in previous studies for reactions (3)-(5). Using these higher rates in a recent study of ATMOS, SAGE II, and UARS data from the northern hemisphere polar vortex, Michelsten et al. [1997b] concluded that reactions mediated by liquid sulfate aerosols (60% wt%) could have a greater effect than previously believed on the midlatitude partitioning of Cl and NO, species. These authors also studied correlations of CH₄, N₂O, NO, H₂O, and aerosol abundances from ATMOS, SAGE, and ER-2 data sets to discriminate between vortex, midlatitude, and tropical air masses. From this framework, it was identified [Michelsen et al., 1997b] that much of the air sampled during SPADE had tracer signatures of polar air, i.e., low CH₄, low NO, low O₃, low aerosol SA, low HCl, and low H₂O amounts.

We have tailored the heterogeneous model results of Michelsten et al. [1997a,b] to estimate the sensitivity of HCl/ClO to aerosol SA concentration and temperature, for comparison with the aircraft data. We have compared the flight-average HCl/ClO, ClO/CI ratios vs. aerosol surface concentration with those calculated assuming photochemical steady state and incorporating the full set of heterogeneous reactions (1)-(6). At temperatures < 206 K, these reactions proceed rapidly enough on liquid sulfuric acid (60 wt%) aerosol particles to provide a significant channel for Cl production at the expense of HCl. Within 16-19 km, our model calculations show that reactions (4) and (5) account for 40-50% of each of the partitioning, with reactions (1), (2), (3), and (6) making little (<15%) contribution. Under these conditions, the 1996/97 rates of reactions (4), and (5), are higher than those from 1994 by about 20%, and 220%, respectively. Since HCl/ClO has a significant dependence on O₃ abundance, we restrict data to points lying in the range 1500 < O₃ < 2500 ppbv (with the additional restrictions of NO₂ < 260 ppbv, pressure < 67 mbar, ClO < 150 pptv, and < 82°C). A plot of HCl/ClO against aerosol SA concentration shows that with important exceptions (4 and 6 Oct. 1991; 1 and 11 May 1993; and 13 Dec. 1996), flights from 1991-96 appear to demonstrate a mass decay in HCl/ClO with increasing SA, as shown in Fig. 3. In Fig. 4, the flight averages of Fig. 3 are included with those of 4 and 6 Oct. 1991, of 1 and 11 May 1993, and of 13 Dec. 1996, for comparison with model calculations run at several temperatures initialized with values of NO₂, CH₄, O₃, H₂O, and NO measured during the flight of 2 Nov.1994. For high SA concentrations, the observed decay in HCl/ClO is best represented by model calculations with temperatures < 203 K. There is a tendency, however, for the observed decay to be steeper at lower SA, and flatter at larger surface areas. Analysis based on flight conditions is more consistent with the measurements than results of previous modeling studies, but still shows disagreement with measured values when photochemical steady-state is assumed for the instantaneous temperatures measured during the flight. For the high SA flight of 17 Feb 1992, for example, in which temperatures of 210-225 K were encountered with a mean HCl/ClO value close to 0.4, flight-tailored model calculations produce HCl/ClO values of 0.36, 0.51, and 0.62 for temperatures of 205 K, 207 K, and 221 K, respectively, with corresponding values of 0.006, 0.05, and 0.046 for ClO/Cl₂.
The time scales for both the development of low HCl through sulfate processing and its recovery vary with season. In summer near 20 km, this timescale is a few days, while in winter it is as long as several weeks. Model results are therefore sensitive to the duration of low temperatures recently encountered, and back-trajectory calculations of the temperatures experienced by the sampled air masses are not reliable over timescales of greater than about 10 days. During the AASE-II, ASHOE/MAESA, and STRAT missions, flight temperatures were rarely lower than 210-215 K, but during the SPADE mission flight temperatures in the range 203-208 K were often recorded; this range therefore represents an upper value for the minimum temperatures experienced over the last few days. The flights of 1 and 11 May 1993 were recorded at the higher temperatures of 215-220 K, and 220 K, respectively, and the flight average HCl/Cly ratios are seen in Fig. 4 to be higher than the 1992-96 fit. Tracer correlations indicate that these flights should be in photochemical steady-state for midlatitude conditions, consistent with the model results.

The data from each of the October 1991 flights appear to be separated into two distinct distributions, characterized by different SA concentrations and HCl/Cly fractions (and are therefore assigned two points in Fig. 4). The fractions observed at the higher SA values fall within the range of the 200 K and 203 K model calculations, whereas those observed at the lower SA values are significantly lower than both model calculations and other data. This discrepancy is currently not understood unless this air experienced temperatures ≤ 201 K, which is unlikely for this time of year at these latitudes; temperatures this low are not generated from back trajectory calculations. The striking fractionation of the HCl vs. N2O correlation plot seen for October

Figure 1. HCl vs. N2O from 1991 through 1996, compared with expected total inorganic chlorine (Cly) [Woodbridge et al., 1995]. Dashed lines are polynomial fits to the data, where the flights of 4 and 6 Oct. 1991, and those of 1 and 11 May 1993 are not included.

Figure 2. A. Superposition of the polynomial fits to the ALIAS HCl vs. N2O mixing ratios, showing the apparent time evolution. B. Measured HCl/Cly vs. latitude over the range 40-60 °N for data constrained by: pressures < 67 mbar, N2O < 260 ppbv, ClO < 150 pptv, and 1500 < O3 < 2500 ppbv. Solid lines are average values over the given latitude range.

Figure 3. Measured HCl/Cly vs. aerosol SA concentration. All data are constrained as in Fig. 2. The lower panel shows the flight-average values and an exponential least-squares fit to these points. Error bars represent the root-square-sum of the 1σ deviation from the mean and the measurement accuracy (±35% for SA>2 μm²/cm³, ±50% for SAs 2 μm²/cm³; and 7% for HCl).

Figure 4. Comparison between theory and measurements. Flight-average values of HCl/Cly and ClO/Cly vs. aerosol SA are constrained as in Fig. 3. In addition to the flights of Fig. 3, flights of 4 and 6 Oct. 1991, 1 and 11 May 1993, and 13 Dec. 1996, are included. Calculated values at 18 km are plotted for temperatures of 200, 201, 203, 205, and 210 K.
1991 (Fig. 1A) appears to represent a case intermediate between the SPADE (high aerosol) and STRAT (low aerosol) correlation data.

The dependence of measured ClOCl on aerosol surface concentration is also compared with model predictions in Fig. 4. These data were selected to cover a narrow range of solar zenith angles (62-82°) and have been normalized to 0 amount by a small correction term generated from the observed dependence of ClOCl on measured ozone. The SPADE CIO data of May 1993 [Stimpfle et al., 1994] are significantly lower than the 1991/2 CIO data [Toohey et al., 1993] for similar particle SA concentrations of -2-6 μm²/cm² due to higher NOx values. When dependence on NOx is taken into account, the consistency in the ClO/Cl measurements is very good. The model results do show that low ClO/Cl values can be expected in a high aerosol environment at only moderately low (<203 K) temperatures. Lower ClO/Cl ratios are usually associated with increased reactive chlorine, which may contribute to the underestimation by atmospheric models [Solomon et al., 1996] of observed ozone loss in volcanic aerosol conditions. However, a discrepancy between ClO/Cl and HCl/ClCl, still remains, in that the temperatures needed to match the HCl/ClCl observations are somewhat lower than those needed for ClO/Cl. Simultaneous in situ measurements of HCl and ClONO2 in volcanic aerosol conditions are needed to resolve these differences and to determine the extent to which other processes such as the production of HClO3 [Jaegle et al., 1995] may be contributing.

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