Evolution of HCl Concentrations in the Lower Stratosphere from 1991 to 1996 Following the Eruption of Mt. Pinatubo

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In situ measurements of hydrochloric acid (HCl) concentrations in the lower stratosphere from 1991 to 1996 reveal that its abundance relative to that of total inorganic chlorine (Cl⁻) has evolved upwards from HCl/Cl⁻ = 40% in late 1991 to 70% in 1996. The observed fraction is anticorrelated with aerosol surface area concentration, which has been diminishing since June 1991 following the volcanic eruption of Mt. Pinatubo. For several years, calculations from photochemical models including heterogeneous chemistry predicted little change in HCl/Cl⁻, and were unable to reproduce these observations. However, calculations incorporating new laboratory results of faster heterogeneous chemistry show that air parcels with high aerosol loading exposed to temperatures of 200-210 K experience enough chlorine activation to drive the HCl/Cl⁻ fraction below 60%, as observed. This repartitioning of Cl⁻ increases ozone loss at all latitudes.

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 test and develop our understanding of the role of heterogeneous chemistry on sulfate aerosol particles [Jones et al., 1994]. As the dense aerosol volcanic cloud spread into a relatively clean atmosphere, aircraft, balloon, ground-based, and space measurements reported large reductions in concentrations of stratospheric NO₃(NO+NO₂) relative to those of total reactive nitrogen (NOₓ)[Fahey et al., 1993; Koike et al., 1994; Webster et al., 1994a], and in response, a doubling of concentrations of chlorine monoxide (ClO) [Avallone et al., 1993] and chlorine dioxide (ClO₂) [Solomon et al., 1993]. Heterogeneous hydrolysis of dinitrogen pentoxide (N₂O₅) and chlorine nitrate (ClONO₂) to nitric acid (HNO₃) were identified as the reactions responsible for the observed changes in atmospheric composition. Column measurements of HCl before and after the eruption showed no
significant injection of volcanic HCl into the stratosphere [Mankin et al., 1992], and photochemical model calculations incorporating the heterogeneous hydrolysis of N₂O₅ predicted little change (≤ 15 %) in stratospheric HCl amounts despite the large impact on NOₓ and ClOₓ amounts [Salawitch et al., 1994]. Space-based measurements of either chlorine reservoir HCl or ClONO₂ were limited by the dense volcanic cloud to altitudes above the high aerosol loading where heterogeneous chemistry was occurring. In situ measurements of ClONO₂ have never been made, and in situ measurements of HCl below 25 km have only been available (this work) since late 1991, significantly after the volcanic material had spread.

Since 1992, the stratospheric aerosol loading has decayed considerably; the surface area layer available in 1996 for heterogeneous chemistry has diminished by over an order of magnitude to the low background levels existing before the Pinatubo eruption [McCormick et al., 1995]. Mapping the recovery over the last four years of radical and reservoir abundances to pre-eruption levels offers a rigorous test of models incorporating heterogeneous chemistry, since this period was one of slow reduction in a more homogeneously-distributed aerosol concentration, with more frequent sampling opportunities. During this time, in situ aircraft measurements of HICl have been made, and the remote-sensing instruments have been better able to penetrate the volcanic aerosol and sample lower in the stratosphere.

In the lower stratosphere where heterogeneous chemistry has a profound effect on the contribution of the ClOₓ, NOₓ, and HOₓ catalytic cycles to ozone loss (see the review of Jones et al., [1994]), the relative amount of HCl and ClONO₂ takes a special importance through chlorine nitrate’s role as a temporary reservoir for reactive forms of both chlorine and nitrogen oxides. Unlike HCl, ClONO₂ is readily photolyzed to produce Cl or ClO. The relative abundances of HCl and ClONO₂ can therefore determine the extent of ozone loss. 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., 1994 b].

Since 1991, JPL’s Aircraft Laser Infrared Absorption Spectrometer (ALIAS) instrument [Webster et al., 1994c] (IS) has flown more than 150 times on the NASA’s I.R-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 the 1993 Stratospheric Photochemistry and Aerosols and Dynamics (SPAD) campaign out of Moffett Field, California, 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, NO₂, and O₃ were used to infer ClONO₂ abundances [Stimpflie et al., 1994]. With an inferred fraction of ClONO₂/Cl₂ of 14% (ranging from 6 to 28%), the measured ClO amounts implied that if Cl₂
comprised only HCl and ClONO₂, I( Cl/Cl₃ should be -86%, compared to the observed value of 40%. The aircraft measurements of 1993 therefore left >=30% of inorganic chlorine apparently unaccounted for, indicating that the photochemistry involving HCl and ClONO₂ was not well understood. An analysis of data recorded in September 1993 during a balloon flight of the MarkIV FTIR spectrometer yielded the proposal that 20-30% of Cl³ may be sequestered as perchloric acid (HClO₄) produced from the heterogeneous reaction of ClO and H₂SO₄ on sulfate aerosols [Jaeglé et al., 1995]. Two other studies report HCl/Cl₃ ratios consistent with both the model predictions of 80% and with the aircraft AIIAS measurements of 1993. These studies include: balloon measurements of ClO at 20 km [Avallone et al., 1993], and a recent analysis of HALO:HCl and Cl.AIÉS ClONO₂ measurements from the UARS satellite [Dessler et al., 1995] observed between August 1992 and March 1993, both of which reported HCl/Cl₃ =60 ± 20 %. In an intercomparison of 1994 aircraft data with overflights of ATMOS in Nov. 1994, and with an earlier flight of MarkIV in May 1994, the AIIAS data lie midway between the two FTIR data sets for N₂O values ≤210 ppbv, where HCl mixing ratios are ≥ 1 ppbv. AIIAS measurements are about 10% lower than that of ATMOS [Chang et al., 1996], and about 10% higher than those of the MarkIV [G. Toon, private communication], for similar ozone abundances.

This paper brings together six years of HCl measurements to show a remarkable consistency in the aircraft database and its evolution with time from 1991-96. It places earlier HCl measurements in context with those made more recently (1992-96) during the years of gradual decay of the Mt. Pinatubo aerosol loading of the stratosphere. Particularly intriguing about the time history of the aircraft measurements is the observation of an HCl fraction of total inorganic chlorine (Cl₃), which has increased with time as the Mt. Pinatubo aerosol loading has diminished; values of HCl/Cl₃ range from 40% in 1991/1992 to 70% in 1996, now evolved upward into good agreement with earlier model predictions. We present here model results incorporating new laboratory results of faster heterogeneous chemistry, which show that air masses with high aerosol loading exposed to temperatures typical of the midlatitude lower stratosphere (200-210 K) experience enough chlorine activation to drive the HCl/Cl₃ fraction below 60%, as observed. Significant repartitioning of chlorine reservoir species from low-temperature sulfate aerosol chemistry and enhancement in ozone depletion is therefore predicted at all latitudes from even moderate future volcanic activity.

The aircraft instruments

The Aircraft Laser Infrared Absorption Spectrometer (AI,AS) instrument is a 4-channel scanning tunable diode laser spectrometer that uses high-resolution laser absorption in the 3-8 μm wavelength region [Webster et al., 1994c] to directly and simultaneously measure any four of the gases HCl, NO₂, CH₄, CO, and N₂O. Both direct absorption and second harmonic detection techniques are used to measure the fractional absorption from individual or groups of rovibrational lines for each gas, with line-center absorption typically a few percent for the tracers N₂O, CH₄, and CO, and less than 0.05% for HCl and NO₂. The instrument samples the atmosphere using a fast flow system with a flow rate of 16 liters/see
at 65 mbar driven by inlet ram pressure and by aerodynamic vacuum at the exhaust. The flow system is in two parts, a heated inlet with wall temperatures of 60-70°C, and a multipass optical (Herriott) cell. All interior surfaces are coated with a halocarbon wax from a chloroform solution to minimize wall loss. Extensive calibration and testing of the inlet and sampling system, including post-flight ion-analysis of the inlet residue, has revealed no systematic instrument or sampling error that could result in HCl loss of greater than 10%. The fidelity of the measurement of I [CI] in the multi-pass cell is checked by simultaneous recording of strong CHCl lines close to the HCl absorption line. The precision of the data can vary from flight to flight, but is typically a constant value of about 0.05 ppbv. The accuracy of the measurement is about 5-7%, producing total measurement uncertainties of about 10-15% for HCl.

The aerosol number, surface area, 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% estimated from intercomparison. The condensation nucleus counter (CNC) measured particle concentrations larger than 0.008 μm in diameter [Wilson et al., 1983], with an accuracy of a few percent. The focused cavity aerosol spectrometer (FCAS) instrument measured size distributions from 0.06 to 2 μm diameter range [Wilson et al., 1992], producing a particle size spectrum every 10 seconds. The forward scattering spectrometer probe (FSSP) detected particles between (1.4 and 20 μm diameter [Baumgardner et al., 1992], and flew on the ER-2 during 1991/2 and 1993. We used measurements from FSSP for AASI-II, from FCAS for ASHOE/MAESA and STRAT, and from all three spectrometers for SPADE.

For most of the flight data presented here, the tracer N2O was measured directly by the ALIAS instrument. However, for a few flights in which ALIAS data were unavailable or of poor quality, N,O measurements from the Airborne Tunable Laser Absorption Spectrometer (ATLAS) instrument [Podolske and Loewenstein, 1993] were used. Cl() was measured using resonance fluorescence detection of Cl atoms at 118.9 nm, generated by chemical conversion of ambient ClO to Cl by addition of NO [Stimpfle et al., 1994]. O3 was measured using UV absorption [Proffitt et al., 1983].

The aircraft measurements of HCl

Figure 1 shows plots of HCl vs. N2O recorded by the ALIAS instrument as part of the payload of the ER-2 aircraft during four major missions: the 1991/2 Airborne Arctic Stratospheric Expedition (AASI-II), the 1993 SPADE experiment, the 1994 Airborne Southern Hemisphere Ozone Expedition/Measurements of the Atmospheric Effects of Stratospheric Aircraft (ASI IOE/MAESA), and the 1996 Stratospheric Tracers of Atmospheric Transport (STRAT) mission. These data are principally from latitudes between 20° and 70° N and have been restricted to pressures less than 67 mbar and ClO amounts less than 150 pptv to remove data from air masses that have undergone severe heterogeneous low-temperature processing. Also plotted are the calculated values of Cl,
expected from the observed \( N_2O \) values and a polynomial least-squares fit to the data.

The 1991/2 AASE-II data collected from a series of flights from 4 Oct. 1991 through 22 March 1992 fail mainly within a single correlation group except for the striking anomalies from the two earliest flights of 4 Oct. (blue triangles) and 6 Oct. (black diamonds) 1991. These latter two flights covered the latitude range 37-85°N and were sufficiently close in time to the June 1991 eruption of Mt. Pinatubo to sample regions of rapidly-changing aerosol loading [Jonsson et al., 1992]. The data from these two early flights appear divided into two populations of low and high \( HCl \) values, whose variation with aerosol surface area is described later. The 1993 SPADE\( HCl \) values are generally more tightly correlated with measured \( N_2O \), except the flights of 11 May (orange triangles) and 1 May (green circles) 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., 1997a] (see next section).

The least-squares fits of Fig. 1 from each mission are plotted in Fig. '2A, where an evolution with time of the \( ICl/Cl \) ratio is apparent. The data from 1991/2 (AAS-III), 1993 (SPADE), 1994 (ASHOE/MAI;SA), and 1996 (STRAT) show \( ICl/Cl \) fractions of typically 40%, 50%, 55-60%, and 75%, a trend that is maintained with latitude within the range 40-60°N, as shown in Fig. 211, where data from all missions are included.

**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 \( ClONO_2 \), 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, as described in the review by Fahey et al. [1995]. This heterogeneous loss of \( HCl \) is associated with low temperatures, i.e., less than 195 K, and is not expected to be significant at higher temperatures.

In a recent study of ATMOS, SAGE II, and UARS data from the northern hemisphere polar vortex, however, Michelsen 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 \( NO_3 \) species, and on global ozone loss throughout the lower stratosphere. These reactions were found to repartition \( Cl \) and \( NO_3 \) at temperatures warmer than 197 K, which are more typical of those existing outside the polar vortex. In a second study, these authors studied correlations of \( CH_4, N_2O, NO_3, H_2O \), and aerosol abundances from ATMOS, SAGE II, and ER-2 data sets to discriminate between vortex, midlatitude, and tropical air masses. From this framework, it was identified [Michelsen et al., 1997a] that much of the air sampled during SPADE had the tracer signatures of polar air, characterized by low \( CH_4 \), low \( NO_3 \), low \( O_3 \), high aerosol surface area, low \( HCl \), and low \( H_2O \) amounts. Aircraft data from other years were not considered.
We have tailored the heterogeneous model results of *Michelsen et al.* [1997a,b] to estimate the sensitivity of the ratio $\text{HCl/Cl}_y$ to aerosol surface area concentration and temperature for comparison with the aircraft data, to assess whether heterogeneous sulfate chemistry can quantitatively reproduce the observations of a five-year data base. In Fig. 4A the flight-average $\text{HCl/Cl}_y$ ratios vs. aerosol surface concentration for all flights studied are compared with those calculated by a model assuming photochemical steady state and incorporating the full set of heterogeneous reactions:

\begin{align*}
(1) \quad & \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \\
(2) \quad & \text{BrONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOBr} + \text{HNO}_3 \\
(3) \quad & \text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOC}1 + \text{HNO}_3 \\
(4) \quad & \text{ClONO}_2 + \text{HCl} - \text{Cl}_2 + \text{HNO}_3 \\
(5) \quad & \text{HOC}1 + \text{HCl} - \text{Cl}_2 + \text{H}_2\text{O} \\
(6) \quad & \text{HOBr} + \text{HCl} \rightarrow \text{BrCl} + \text{H}_2\text{O}.
\end{align*}

At temperatures below about 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, leading to enhanced ClONO$_2$ production from the gas-phase reaction of NO$_3$ and CIO. In this way the partitioning of Cl$_y$ between HCl and ClONO$_2$ is shifted from HCl dominance to that of ClONO$_2$. The importance of including heterogeneous bromine chemistry has been emphasized by the recent studies of Lary et al. [1996] and Tie and Brasseur [1996], whose studies suggested that significant reduction in HCl/Cl$_y$ could be achieved from low temperature heterogeneous bromine chemistry alone. Within the 16-19 km region from which the A1JAS data predominantly originates, our model calculations show that reactions (4) and (5) account for 40-50% each of the repartitioning, with reactions (1), (2), (3), and (6) making little (~15%) contribution.

Since HCl/Cl$_y$ has a significant dependence on O$_3$ abundance, we first restrict data to points lying in the range 1500 $\leq$ O$_3$ $\leq$ 2500 ppbv (with the additional restrictions of N$_2$O $\leq$ 260 ppbv, pressure $\leq$ 67 mbar, C1OS 150 pptv, and sza $\leq$ 82°). A plot of HCl/Cl$_y$ against aerosol surface area concentration shows that with few exceptions (4 and 6 Oct. 1991; 1 and 11 May 1993; included in Fig. 4 and discussed later), flights from 1991-6 appear to demonstrate a smooth decay in HCl/Cl$_y$ with increasing surface area, as shown in Fig. 3. The lower panel is a fit to the flight-average points using an exponential decay function.

The flight averages of Fig. 3 are included with those of 4 and 6 Oct. 1991, and of 1 and 11 May, 1993, for comparison with model calculations run at several temperatures initialized with values of NO$_x$, CH$_4$, O$_3$, H$_2$O, and N,0 measured during the flight of 2 Nov. 1994. For high surface area concentrations, the observed decay in HCl/Cl$_y$ is generally well-represented in Fig. 4 by the model calculations for a temperature of about 207 K. There is a tendency, however, for the observed decay to be steeper at lower surface areas, and flatter at larger surface areas. A more thorough analysis based on conditions measured for each flight is again more consistent with the measurements than the 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 surface area flight of 17 February 1992, for example, in which temperatures of 210-225 K were encountered with a mean ICl/Cl\textsubscript{2} value close to 0.4, flight-tailored model calculations produce ICl/Cl\textsubscript{2} values of 0.2, 0.49, and 0.67 for temperatures of 205, 207, and 221 K, respectively. The model results are sensitive to the duration of low temperatures recently encountered, and back-trajectory calculations of the temperatures experienced by the sampled air masses are needed for all of the flights for better comparison with the model results. During the AASL-11, ASI-10)VMASA, 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 ICl/Cl\textsubscript{2} 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.

Because the combination of high surface area and moderately cold temperature is necessary to repartition ICl, an altitude dependence to I Cl/Cl\textsubscript{2} is expected. Above ER-2 altitudes, temperatures are generally warmer. The pressure-dependent ICl vs. N\textsubscript{2}O relationship shown by several data sets [Webster et al., 1994b] may reflect the ineffectiveness of aerosol chemistry at the altitudes above ER-2 where higher temperatures are found, despite the enhanced aerosol loading.

Also plotted in Fig. 4 are the flight-average data for the early flights of 4 and 6 Oct. 1991, which have particularly low ICl/Cl\textsubscript{2} ratios for surface area concentrations only 2-5 times background levels. Although the model calculations suggest that these data may be from air masses that had earlier experienced temperatures of 203 K or less, temperatures this low are not generated from back trajectory calculations five days before the flights. Looking back at Fig. 1A, the striking fractionation of the I Cl vs. N\textsubscript{2}O correlation plot seen for October 1991 appears to represent a case intermediate between the SPADE (high aerosol) and STRAT (low aerosol) data. The initial volcanic material spreading out from the lower latitudes is known to have different chemical composition than the aerosol characteristic of the later decaying period, and it may be that the heterogeneous rates are even faster on the smaller, younger sulfate aerosol matter.

The observed dependence of ClO/Cl\textsubscript{2} on aerosol surface concentration is also compared with model predictions in Fig. 4. These data have been selected to cover a narrow range of solar zenith angles (62-82°), and have been normalized to O\textsubscript{3} amount with a small correction term generated from the observed dependence of ClO/Cl\textsubscript{2} on measured ozone. The SPADE ClO data of May 1993 [Stimpfle et al., 1994] are significantly lower than the 1991/2 ClO data [Toohey et al., 1993] for similar particle surface area concentrations of around 2-6 \(\mu\text{m}^2/\text{cm}^3\), due to higher NO\textsubscript{3} values. These lower ClO data of SPADE were used [Stimpfle et al., 1994] to infer (low) ClONO\textsubscript{2}/Cl\textsubscript{2} ratios, which were discrepant with
the direct HCl/Cl\textsubscript{2} measurements of ALIAS. When dependence on NO\textsubscript{x} is taken into account, the consistency between the model calculations and the measured ClO/Cl\textsubscript{2} is very good. However, the plots of Fig. 4 illustrate that a discrepancy between ClO/Cl\textsubscript{2} and HCl/Cl\textsubscript{2} still remains, in that the temperatures needed to match the HCl/Cl\textsubscript{2} observations are somewhat lower than those needed for ClO/Cl\textsubscript{2}. Nevertheless, the model results do show that low HCl/Cl\textsubscript{2} values of 40% can be expected in a high aerosol environment at only moderately low (< 207 K) temperatures. Furthermore, these results are consistent with the results of a companion paper [Dessler et al., 1997], which report satellite observations of a 26% increase in HCl/Cl\textsubscript{2} from 1992 to 1996.

The observed dependence of lower stratospheric HCl concentration on surface area concentration over the five-year period following the volcanic eruption of Mt. Pinatubo demonstrates that aerosol chemistry at temperatures > 200 K has a more pronounced effect on Cl\textsubscript{2} partitioning than previously believed. Lower HCl/Cl\textsubscript{2} ratios are associated with increased reactive chlorine, products of enhanced heterogeneous chemistry on sulfate aerosol which is responsible [Michelsen et al., 1997] for the underestimation by atmospheric models [Solomon et al., 1996] of observed ozone loss in volcanic aerosol conditions.

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**FIGURE CAPTIONS**

Figure 1. HCl vs. N2O from 1991 through 1996, compared with expected total inorganic chlorine (ClY) mixing ratios calculated from the N2O values [Woodbridge et al., 1995]. The dashed lines are polynomial fits to the data, where the flights of Ott. 4 and 61991, and those of May 1 and 11 1993 are not included.

Figure 2. A. Superposition of the polynomial fits of Fig. 1 to the AlIAS HCl vs. N2O mixing ratios divided by ClY, 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. The solid lines are the average values over the given latitude range to illustrate the apparent evolution with time of HCl/ClY over this latitude range.

Figure 3. Measured HCl/ClY vs aerosol surface area concentration for several flights from December 81992 through July 2.21996. All data are constrained by: pressures 67 mbar, N2O≤ 260 ppbv, and ClO≤ 150 pptv, and 1500≤ O3≤ 2500 ppbv. The lower panel shows the flight-average values with one-sigma standard deviations from the mean, and an exponential least-squares fit to the flight-average points.

Figure 4. Comparison between theory and measurements. Flight-average values of HCl/ClY and ClO/ClY vs aerosol surface area are constrained by pressure< 67 mbar, N2O≤ 260 ppbv, ClO≤ 150 pptv, and 1500≤ O3≤ 2500 ppbv. In addition to the flights of Fig. 3, flights of Oct. 4 and 6, 1991, and May 1 and 11, 1993 are included. Calculated values at 18 km are plotted for temperatures of 2.01, 204, and 230 K.
Figure 2

(A) HCl (ppbv) vs. N₂O (ppbv) plot showing the data for different years:
- Cly* 1996
- Cly* 1991
- 1994
- 1993
- 1991/2

(B) HCl/Clᵥ vs. Latitude (°N) plot with data points for:
- 1992
- 1993
- 1994
- 1996
Figure 4