



Calhoun: The NPS Institutional Archive

Faculty and Researcher Publications

Faculty and Researcher Publications

1998-04

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

Jaeglé, L.



Calhoun is a project of the Dudley Knox Library at NPS, furthering the precepts and goals of open government and government transparency. All information contained herein has been approved for release by the NPS Public Affairs Officer.

Dudley Knox Library / Naval Postgraduate School
411 Dyer Road / 1 University Circle
Monterey, California USA 93943

<http://www.nps.edu/library>

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

C.R. Webster¹, R.D. May¹, H.A. Michelsen², D.C. Scott¹, J.C. Wilson³, H.H. Jonsson³, C.A. Brock³, J.E. Dye⁴, D. Baumgardner⁴, R.M. Stimpfle⁵, J.P. Koplów⁵, J.J. Margitan¹, M.H. Proffitt⁶, L. Jaeglé², R.L. Herman¹, H. Hu¹, G.J. Flesch¹, M. Loewenstein⁷

Abstract. *In situ* measurements of hydrochloric acid in the lower stratosphere reveal that its mean abundance relative to that of total inorganic chlorine (Cl_x) has evolved upwards from $\text{HCl}/\text{Cl}_x=40\%$ 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_x below 50%, but overestimate observed ClO/Cl_x .

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_x [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]. Solomon *et al.* [1993] attributed high OClO observed over Antarctica to sulfate aerosol processing at temperatures ~ 203 K, well above PSC threshold. Despite the large impact on NO_x and ClO_x amounts [Salawitch *et al.*, 1994; Hanson *et al.*, 1994], photochemical model calculations incorporating the heterogeneous hydrolysis of N_2O_5 and ClONO_2 predicted only small changes ($\leq 15\%$) in HCl amounts. Column HCl abundance showed no volcanic injection into the stratosphere [Mankin *et al.*, 1992]. Space-based measurements of either HCl or ClONO_2 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 ClONO_2 , simultaneous measurements of ClO, NO_2 , and O_3 were used to infer ClONO_2 abundances [Stimpfle *et al.*, 1994]. With an inferred fraction of $\text{ClONO}_2/\text{Cl}_x = 14\%$ (ranging from 6 to 28%), the measured ClO amounts implied that if Cl_x comprised mainly HCl and ClONO_2 , HCl/Cl_x should be $\sim 86\%$, compared to the observed value of 40%. The aircraft measurements of 1993 therefore left $\geq 30\%$ 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_x may be sequestered as perchloric acid (HClO_4) produced from the heterogeneous reaction of ClO and H_2SO_4 on sulfate aerosols [Jaeglé *et al.*, 1995]. Two other studies reported HCl/Cl_x ratios of $60 \pm 20\%$, 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 ClONO_2 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 N_2O values ≤ 210 ppbv, where HCl mixing ratios were ≥ 1 ppbv. ALIAS measurements were $\sim 10\%$ lower than that of ATMOS [Chang *et al.*, 1996], and $\sim 10\%$ higher than those of the MarkIV [G.Toon, private communication] for similar O_3 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_x 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 ($16 \pm 9\%$) in HCl/Cl_x 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

¹Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109.

²Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138.

³Department of Engineering, Univ. of Denver, Denver, CO 80208.

⁴National Center for Atmospheric Research, Box 3000, Boulder, CO 80307.

⁵Department of Chemistry, Harvard University, Cambridge, MA 02138.

⁶Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80303.

⁷NASA Ames Research Center, Moffett Field, CA 94035.

Copyright 1998 by the American Geophysical Union.

Paper number 98GL00548.
0094-8534/98/98GL-00548\$05.00

wavelength region [Webster *et al.*, 1994c] to directly and simultaneously measure any four of the gases HCl, NO₂, CH₄, CO, and N₂O. The instrument samples the atmosphere using a fast flow system with all interior surfaces coated with halocarbon wax. Extensive calibration and testing, including post-flight ion-analysis of the inlet residue, has revealed no systematic instrument or sampling error that could result in HCl loss of > 10%. The fidelity of the measurement of HCl in the multipass cell is checked by simultaneous recording of strong CH₄ lines close to the HCl absorption line. The precision of the data varies from flight to flight, with a 1σ precision of typically ±50 to ±100 pptv. The accuracy of the measurement is about 5-7%, producing total root-squared measurement uncertainties of ~10-15% for 1 ppbv.

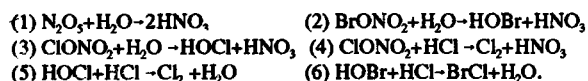
The aerosol number, SA, and volume concentrations reported here were determined from three particle size spectrometers flown simultaneously as part of the ER-2 aircraft payload, with overall uncertainties of 35%: the condensation nucleus counter (CNC) measured particle concentrations ≥ 0.008 μm dia. [Wilson *et al.*, 1983]; the focused cavity aerosol spectrometer (FCAS) instrument measured size distributions from .06 to 2 μm dia. [Jonsson *et al.* [1992]]; the forward scattering spectrometer probe (FSSP-300) detected particles between 0.4 and 20 μm dia. [Baumgardner *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. ClO 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], with a measurement uncertainty of ±30%. O₃ was measured using UV absorption [Proffitt *et al.*, 1983].

Figure 1 shows plots of HCl 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 ClO < 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 HCl values. The 1993 SPADE HCl 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 HCl 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 HCl/Cl₂ ratio is apparent. Data from 1991/2 (AASE-II), 1993 (SPADE), 1994 (ASHOE/MAESA), and 1996 (STRAT) show HCl/Cl₂ 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 ClONO₂ 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



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, 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 Cl₂ and NO₂ species. These authors also studied correlations of CH₄, N₂O, NO_y, 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_y, low O₃, high aerosol SA, low HCl, and low H₂O amounts.

We have tailored the heterogeneous model results of Michelsen *et al.* [1997a,b] to estimate the sensitivity of HCl/Cl₂ to aerosol SA concentration and temperature, for comparison with the aircraft data. We here compare the flight-average HCl/Cl₂ and ClO/Cl₂ 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% each of the repartitioning, 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/Cl₂ 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 N₂O ≤ 260 ppbv, pressure ≤ 67 mbar, ClO ≤ 150 pptv, and sza < 82°). A plot of HCl/Cl₂ 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 smooth decay in HCl/Cl₂ 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 NO_y, CH₄, O₃, H₂O, and N₂O measured during the flight of 2 Nov. 1994. For high SA concentrations, the observed decay in HCl/Cl₂ is best represented by model calculations with temperatures of ~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/Cl₂ value close to 0.4, flight-tailored model calculations produce HCl/Cl₂ 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.

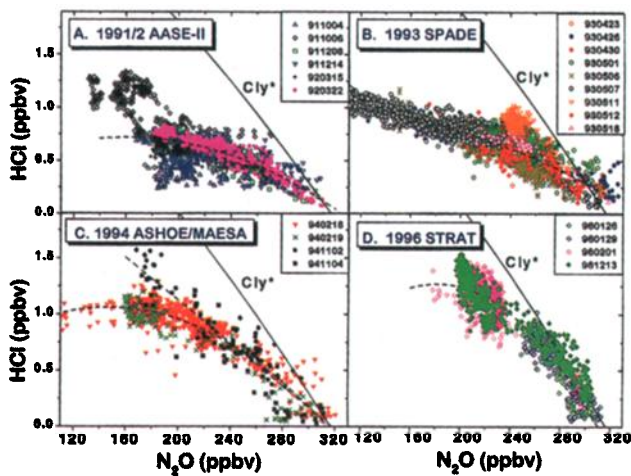


Figure 1. HCl vs. N_2O from 1991 through 1996, compared with expected total inorganic chlorine (Cl_y) [Woodbridge *et al.*, 1995]. Dashed lines are polynomial fits to the data, where the flights of 4 and 6 Oct. 1991, and those of 1 and 11 May 1993 are not included.

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/Cl_y ratios are seen in Fig. 4 to be higher than the 1992–96 fit. Tracer correlations indicate that

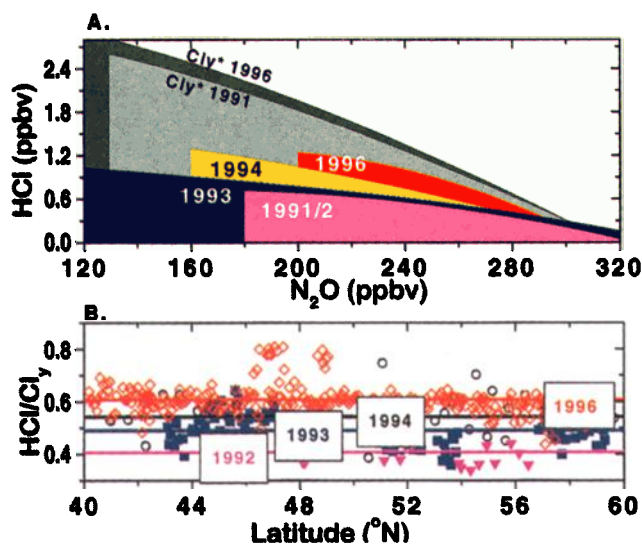


Figure 2. A. Superposition of the polynomial fits to the ALIAS HCl vs. N_2O mixing ratios, showing the apparent time evolution. B. Measured HCl/Cl_y vs. latitude over the range 40–60 °N for data constrained by: pressure \leq 67 mbar, $N_2O \leq$ 260 ppbv, $ClO \leq$ 150 pptv, and $1500 \leq O_3 \leq$ 2500 ppbv. Solid lines are average values over the given latitude range.

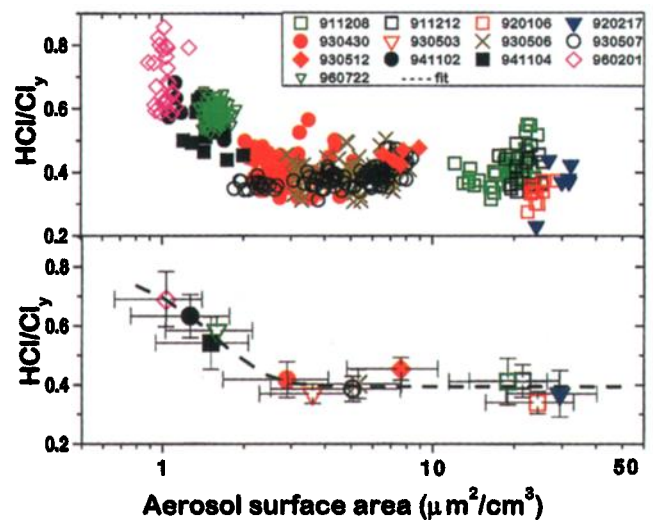


Figure 3. Measured HCl/Cl_y vs. aerosol SA concentration. All data are constrained as in Fig. 2. The lower panel shows the flight-average values and an exponential least-squares fit to these points. Error bars represent the root-square-sum of the 1σ deviation from the mean and the measurement accuracy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

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/Cl_y 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 \leq 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. N_2O correlation plot seen for October

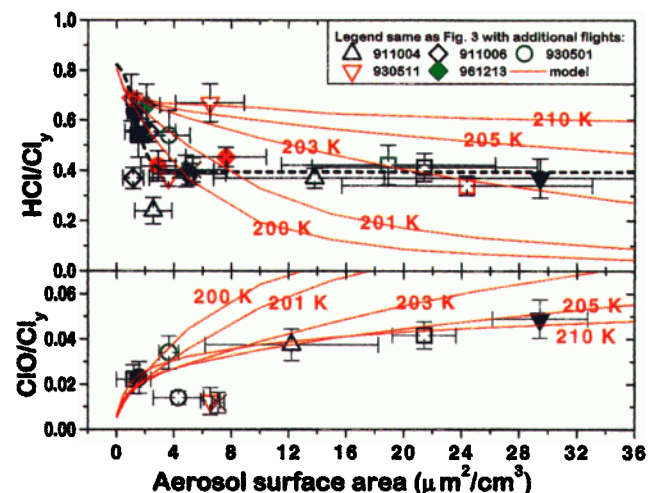


Figure 4. Comparison between theory and measurements. Flight-average values of HCl/Cl_y and ClO/Cl_y vs. aerosol SA are constrained as in Fig. 3. In addition to the flights of Fig. 3, flights of 4 and 6 Oct. 1991, 1 and 11 May 1993, and 13 Dec. 1996, are included. Calculated values at 18 km are plotted 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 ClO/Cl₂ 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 O₃ amount by a small correction term generated from the observed dependence of ClO/Cl₂ 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 SA concentrations of ~2–6 μm²/cm³ due to higher NO_x values. When dependence on NO_x is taken into account, the consistency in the ClO/Cl₂ measurements is very good. The model results do show that low HCl/Cl₂ values can be expected in a high aerosol environment at only moderately low (<203 K) temperatures. Lower HCl/Cl₂ 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/Cl₂ and HCl/Cl₂ still remains, in that the temperatures needed to match the HCl/Cl₂ observations are somewhat lower than those needed for ClO/Cl₂. 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 HClO₄ [Jaeglé et al., 1995] may be contributing.

Acknowledgements. The authors thank team members of the aircraft missions, and acknowledge helpful discussions with Susan Solomon. Part of the research described in this paper was carried out by the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

References

- Avallone, L.M., et al., *In situ* measurements of ClO at midlatitudes: is there an effect from Mt. Pinatubo?, *Geophys. Res. Lett.* 20, 2519–2522, 1993.
- Baumgardner, D., J.E. Dye, B.W. Gandrud, and R.G. Knollenberg, Interpretation of measurements made by the forward scattering spectrometer probe (FSSP-300) during the airborne Arctic stratospheric expedition, *J. Geophys. Res.* 97, 8035–8046, 1992.
- Chang, A.Y., et al., A comparison of measurements from ATMOS and instruments aboard the ER2 aircraft: halogenated gases, *Geophys. Res. Lett.* 23, 2393–2396, 1996.
- Dessler, A.E., et al., Correlated observations of HCl and ClONO₂ from UARS and implications for stratospheric chlorine partitioning, *Geophys. Res. Lett.* 22, 1721–1724, 1995.
- Dessler, A.E., et al., Lower stratospheric chlorine partitioning during the decay of the Mt. Pinatubo aerosol, *Geophys. Res. Lett.* 24, 1623–1626, 1997.
- Fahey, D.W., et al., *In situ* measurements constraining the role of sulfate aerosols in mid-latitude ozone depletion, *Nature*, 363, 509–514, 1993.
- Fahey, D.W., et al., Polar ozone (Chapter 3), WMO, Scientific Assessment of Ozone Depletion: 1994, Report No. 37, World Meteorological Organization, Geneva, 1995.
- Hanson, D.R., A.R. Ravishankara, and S. Solomon, Heterogeneous reactions in sulfuric acid aerosols: a framework for model calculations, *J. Geophys. Res.*, 99, 3615–3629, 1994.
- Hofmann, D.J., and S. Solomon, Ozone destruction through heterogeneous chemistry following the eruption of El Chichón, *J. Geophys. Res.*, 94, 5029–5041, 1989.
- Jaeglé, L., Y.L. Yung, G.C. Toon, B. Sen, and J.F. Blavier, Balloon observations of organic and inorganic chlorine in the stratosphere: the role of HClO₄ production on sulfate aerosols, *Geophys. Res. Lett.* 23, 1749–1752 (1996).
- Jones, R.E. et al., in Scientific Assessment of Ozone Depletion: 1994, Ch.4 Tropical and Midlatitude Processes, WMO Global Ozone Research and Monitoring Project, Report 37, 1994.
- Jónsson, H.H., et al., Evolution of the stratospheric aerosol in the N.hemisphere following the June 1991 volcanic eruption of Mt. Pinatubo, *J. Geophys. Res.* 101, 1553–1570, 1996.
- Koike, M.Y., et al., Impact of Pinatubo aerosols on the partitioning between NO₂ and HNO₃, *Geophys. Res. Lett.* 21, 597–600, 1994.
- Mankin, W.G., M.T. Coffey, and A. Goldman, Airborne observations of SO₂, HCl, and O₃ in the stratospheric plume of the Pinatubo volcano in July 1991, *Geophys. Res. Lett.* 19, 179–182, 1992.
- McCormick, M.P., L.W. Thomason, and C.R. Trepte, Atmospheric effects of the Mt Pinatubo eruption, *Nature* 373, 399–404, 1995.
- Michelsen, H.A., et al., Stratospheric chlorine partitioning: constraints from shuttle-borne measurements of HCl, ClONO₂, and ClO, *Geophys. Res. Lett.* 23, 2361–2364, 1996.
- Michelsen, H.A., et al., Heterogeneous chlorine/nitrogen chemistry at temperatures above 200 K, submitted to *Nature*, 1997a.
- Michelsen, H.A., et al., in preparation, *Geophys. Res. Lett.* 1997b.
- Podolske, J.R., and M. Loewenstein, Airborne tunable diode laser spectrometer for trace gas measurements in the lower stratosphere, *Appl. Opt.* 32, 5324–5330, 1993.
- Proffitt, M.H., and R.J. McLaughlin, Fast response dual beam UV absorption ozone photometer suitable for use on stratospheric balloons, *Rev. Sci. Instr.* 54, 1719–1728, 1983.
- Salawitch, R.J., et al., The distribution of hydrogen, nitrogen, and chlorine radicals in the stratosphere: implications for changes in O₃ due to emission of NO_x from supersonic aircraft, *Geophys. Res. Lett.* 21, 2547–2550, 1994.
- Solomon, S., R.W. Sanders, R.R. Garcia, and J.G. Keys, Increased chlorine dioxide over Antarctica caused by volcanic aerosols from Mt. Pinatubo, *Nature* 363, 245–248, 1993.
- Solomon, S. et al., The role of aerosol variations in anthropogenic ozone depletion at N. midlatitudes, *J. Geophys. Res.* 101, 6713–6727 (1996).
- Stimpfle, R.M., et al., The response of ClO radical concentrations to variations in NO₂ radical concentrations in the lower stratosphere, *Geophys. Res. Lett.* 21, 2543–2546, 1994.
- Toohey, D.W., et al., The seasonal evolution of reactive chlorine in the northern hemisphere stratosphere, *Science* 261, 1134–1136, 1993.
- Webster, C.R., et al., Chlorine chemistry on polar stratospheric cloud particles in the Arctic winter, *Science* 261, 1130–1133, 1993.
- Webster, C.R., R.D. May, M. Allen, and L. Jaeglé, Balloon profiles of stratospheric NO₂ and HNO₃ for testing the heterogeneous hydrolysis of N₂O₅ on sulfate aerosols, *Geophys. Res. Lett.* 21, 53–56, 1994a.
- Webster, C.R., et al., Hydrochloric acid and the chlorine budget of the lower stratosphere, *Geophys. Res. Lett.* 21, 2575–2578, 1994b.
- Webster, C.R., R.D. May, C.A. Trimble, R.G. Chave, and J. Kendall, Aircraft (ER-2) laser infrared absorption spectrometer (ALIAS) for *in situ* stratospheric measurements of HCl, N₂O, CH₄, NO₂, and HNO₃, *Applied Optics* 33, 454–472, 1994c.
- Wilson, J.C., J.H. Hyun, and E.D. Blackshear, The function and response of an improved stratospheric condensation nucleus counter, *J. Geophys. Res.* 88, 6781, 1983.
- Woodbridge, E.L., et al., Estimates of total organic and inorganic chlorine in the lower stratosphere from *in situ* measurements during AASE II, *J. Geophys. Res.* 100, 3057–3064, 1995.

(Received March 13, 1997; revised August 20, 1997; accepted October 7, 1997.)