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Chlorine activation and ozone destruction in the northern lowermost stratosphere

J. Lelieveld,¹ A. Bregman,¹ H. A. Scheeren,¹ J. Ström,² K. S. Carslaw,³
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Abstract. We report aircraft measurements from the Stratosphere-Troposphere Experiments by Aircraft Measurements (STREAM) II campaign, performed during February 1995 from Kiruna, northern Sweden, near 67°N latitude. We have measured trace species, e.g., O₃, nitrogen compounds, HCl, hydrocarbons, CO, ice particles, and aerosols, to characterize the chemical conditions of the lowermost stratosphere at altitudes up to ~12.5 km. From the observation of anomalously high CO/C₂H₆ ratios, caused by enhanced C₂H₆ breakdown, we derive that heterogeneous chlorine activation has occurred. This has liberated a diurnal mean Cl concentration up to 1.0×10^4 atoms cm⁻³, which efficiently destroys ozone. We also infer that much of the Cl activation has taken place on ice crystals above the tropopause. The measured crystal number densities were typical of thin cirrus. Model calculations suggest that heterogeneous chlorine conversion on ice crystals, in addition to that on liquid aerosols, may contribute significantly to ozone destruction in the middle- and high-latitude lowermost stratosphere.

1. Introduction

Ozonesonde measurements over Europe and Canada show a negative ozone trend of ~0.5–1%/yr in the lower stratosphere during the past decades [Logan, 1994; Bojkov and Fioletov, 1997; World Meteorological Organization, (WMO), 1998]. The trend is about twice as large in winter and spring than in summer and fall. Stratospheric ozone depletion and polar ozone hole development can be unequivocally attributed to chlorofluorocarbon breakdown and consequent chlorine activation, the latter being enhanced by heterogeneous processes on cloud and aerosol particles [WMO, 1995]. However, important uncertainties persist. In particular, the contribution by local ozone destruction at middle latitudes relative to transport of ozone-depleted air from the poles is unclear. Especially for the lowermost stratosphere (i.e., the region between the potential temperature level $\theta = 380$ K (~15 km altitude) and the extratropical tropopause), interactions between transport and chemical processes are poorly understood. The lowermost stratosphere is not only the final transit of air from the Brewer-Dobson circulation, but it is also affected by two-way cross-tropopause exchange [Hoerling et al., 1993; Lamarque and Hess, 1994]. This introduces relatively short-lived tropospheric pollutants into the lowermost stratosphere, while aircraft exhausts bring about additional perturbations [Bregman et al., 1997a; Lelieveld et al., 1997; Brasseur et al., 1998].

Recently, it has been hypothesized that cirrus clouds play a role in chlorine activation in the extratropical tropopause re-

gion [Borrmann et al., 1996, 1997; Solomon et al., 1997]. Lidar observations by Reichardt et al. [1996] showed pronounced ozone minima associated with ice clouds near the tropopause over northern Germany. These might be explained by either small-scale dynamical processes or chemical ozone loss. Heterogeneous reactions of the chlorine reservoir species ClONO₂ and HCl on ice crystals liberate reactive chlorine that catalytically destroys ozone. These reactions can also take place on aerosol particles. ER-2 aircraft measurements in the midlatitude lowermost stratosphere over the United States in January 1992 [Borrmann et al., 1997] and in April 1993 [Keim et al., 1996] showed strongly enhanced ClO mixing ratios, associated with Mount Pinatubo sulfate aerosols. Furthermore, cross-tropopause exchange carries water vapor from the troposphere into the lowermost stratosphere [Dessler et al., 1995], which contributes to the growth of aerosols and enhances the effects of heterogeneous chemistry. In addition to high levels of ClO and HO₂ due to Pinatubo aerosol related chemistry, Keim et al. [1996] observed strongly reduced NO/NO_x ratios, attributed to nighttime heterogeneous conversion of NO_x to HNO₃. This significantly decreased the potential of these air masses to deactivate chlorine by ClONO₂ formation.

This paper addresses the possible impact of heterogeneous chemistry on ice crystals in the lowermost stratosphere during late winter. We have performed aircraft measurements that provide strong indications that such particles occur in air masses that travel between middle latitudes and the Arctic at 10–12.5 km altitude. The associated heterogeneous processes contribute to ozone loss. Section 2 describes the materials and methods, i.e., the aircraft campaign, the instrumentation, and the model used to support analyses of the results. In section 3 we present empirical evidence of heterogeneous chlorine activation on ice particles on the basis of simultaneous measurements of carbon monoxide and ethane, the latter being selectively destroyed by chlorine atoms. We support these assertions by model calculations in section 4. Conclusions are presented in section 5.

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Table 1. Citation Aircraft Instrumentation During the STREAM II Campaign

Species Measured	Technique	Research Group ^a
CH ₄ , CO, N ₂ O	tunable diode laser spectrometer	MPI for Chemistry, Mainz
HNO ₃ , HCl, HCN, SO ₂ , (CH ₃) ₂ CO, CH ₃ CN	ion-molecule reaction mass spectrometer	MPI for Nuclear Physics, Heidelberg
Nonmethane hydrocarbons	gas chromatograph (canister samples)	IMAU, Utrecht University
NO _y	chemiluminescence (gold converter)	MPI for Chemistry, Mainz
CO ₂	infrared analyzer	MPI for Chemistry, Mainz
O ₃	chemiluminescence	IMAU, Utrecht University
F-11, F-12, N ₂ O	in situ gas chromatograph	Institute for Meteorology and Geophysics, Frankfurt University
Aerosols (7 nm < D < 1 μm)	CN counters, optical counter	MISU, Stockholm University
Ice crystals (D > 5 μm)	counterflow virtual impactor	MISU, Stockholm University

^aMPI, Max-Planck-Institute; IMAU, Institute for Marine and Atmospheric Research, Utrecht University; MISU, Meteorological Institute, Stockholm University.

2. Aircraft Campaign and Methods

The measurements have been performed in February 1995 with a Cessna Citation-II twinjet aircraft, as part of the second phase of the Stratosphere-Troposphere Experiments by Aircraft Measurements (STREAM) project. Recent measurement results from the STREAM project have been reported by Arnold *et al.* [1997, 1998], Bregman *et al.* [1997a, b], Fischer *et al.* [1997], Lelieveld *et al.* [1997], de Reus *et al.* [1998], Schneider *et al.* [1997], Schneider [1998], Schröder and Ström [1997], and Waibel *et al.* [1998]. An overview of the species measured and the techniques employed is given in Table 1.

The STREAM II measurement campaign was coordinated within the Second European Stratospheric Arctic and Midlatitude Experiment (SESAME), supported by the European Union. Four flights were carried out from Kiruna, Sweden (67.5°N and 20.15°E), on February 9, 18, 21, and 24, 1995. Flight planning was based on European Centre for Medium-Range Weather Forecasts (ECMWF) forecasts. From these, potential vorticity maps were derived to provide insight in the position of the tropopause. In this study we focus mostly on the flight performed on February 18, 1995, at ~66°–68°N, from Kiruna to northern Finland. The flight pattern in the stratosphere involved 15–30 min tracks at altitude intervals of 0.5–1 km between ~8 and 12.5 km altitude ($\theta \approx 320$ –370 K). The meteorological situation on February 18, 1995, at northern middle and polar latitudes in the lowermost stratosphere was determined by a low-pressure system west of Greenland. In the flight region near Kiruna, being at a relatively large distance from major synoptic disturbances, the tropopause was rather flat, and wind speeds were modest (Figure 1). Figure 1 also shows the flight track from Kiruna.

2.1. NMHC Sampling and Analyses

Air samples for nonmethane hydrocarbon (NMHC) analysis were collected in 2.5 L electropolished stainless steel bottles. The canisters were cleaned by heating them at 150°C while flushing with clean N₂ for 12–15 hours. After cleaning, the canisters were filled with clean He and analyzed for contamination. On board the aircraft a MB-602 metal bellows pump was used to flush the system (5 min) prior to the collection of an air sample (0.5–3 min depending on the outside air pressure) to an overpressure of maximum 2.3 bars. Depending on atmospheric pressure, filling took 15–165 s (at 3 km and 12.5 km altitude, respectively), which corresponds to ~2.5–25 km of flight track. Within a day after each flight the canisters were sent to the laboratory and analyzed within 1 week after collec-

tion for hydrocarbons by gas chromatography (GC) equipped with flame ionization detection (FID).

The principle of the analytical system was adapted from Penkett *et al.* [1993]. Prior to analysis, a 1–2 L air sample was preconcentrated on a liquid nitrogen cold trap packed with glass beads at a freezing temperature between 88 and 90 K in the N₂ vapor just above the liquid level (sample flow 33.33 mL/min). The cold trap temperature was monitored by a PT-100 temperature sensor, which controlled a small heater in the nitrogen liquid. The trap was then warmed with boiling water and flushed for 30 s with He carrier gas releasing the condensed hydrocarbons onto the column.

Analysis took place on HP 5890 gas chromatograph with a Al₂O₃/KCl capillary column (50 m × 0.53 mm) equipped with a FID using He as carrier gas (12 mL/min). Analysis took 40 min using the following temperature program: a start temperature of 35°C for 4 min was followed by a 6°C increase per minute to 210°C and ended at 12 min at 210°C. The GC-FID analysis had a detection limit of 1 part per trillion by volume (pptv). Standardization was performed with a commercial standard mixture of aliphatic hydrocarbons (Scott, C2-C5 nonmethane hydrocarbons at 20 ppbv with a 10% absolute accuracy). The total uncertainty is defined as the sum of the precision of the analysis and the absolute accuracy of the calibration gas, as certified by the supplier ($\pm 10\%$). The precision of the ethane analysis was $\pm 6\%$ as determined by the reproducibility of the air sample analysis and preconcentration step.

2.2. Measurements of NO_y, HNO₃, and HCl

The NO_y measurement technique is based on the gold-catalyzed reduction of nitrogen oxides (besides N₂O) to NO in the presence of CO (1%) in a heated Au tube [Fahey *et al.*, 1985]. The subsequent NO measurements were performed with a modified chemiluminescence detector (TECAN CLD 770 AL). The 70 cm long gold tube (5 mm inside diameter (ID), 6 mm outside diameter (OD)) was heated to 573 K over a 20 tube section near the center [Fischer *et al.*, 1997]. The outside air was sampled directly into the gold tube, which is mounted onto the aircraft fuselage in a vacuum shielded stainless steel support tube tilted 45° into the flight direction. The tip of the gold tube is also tilted by 45° so that the air is sampled opposite to the flight direction. Prior to the flights, the converter was heated up to 573 K and flushed with synthetic air for at least 2 hours. During the flights the converter and the CLD were calibrated with NO (Linde AG, 2.2 ppmv $\pm 5\%$ NO

Figure 1. Latitude-altitude cross section between 60°N, 25°E and 75°N, 25°E, showing the flight track on February 18, 1995 (thick solid line). Also shown are isopleths of wind speed (dashed line, in m s^{-1}) and potential vorticity (PV) (in potential vorticity units (PVU) = $10^{-6} \text{ K m}^2 \text{ kg}^{-1} \text{ s}^{-1}$). The tropopause is indicated by the 3–4 PVU shaded region.

in N_2) and NO_2 (Linde AG, $11.3 \text{ ppmv} \pm 10\%$ in synthetic air), diluted in synthetic air to 9.36 ppbv NO and 22.8 ppbv NO_2 . The conversion efficiency for NO_2 was $80 \pm 5\%$. The conversion efficiency of HNO_3 , as determined in the laboratory, was 75% . From the reproducibility of NO_2 calibrations the precision is estimated at 20% . Including the uncertainty in the calibration gas standards leads to a combined estimated accuracy of $\pm 25\%$.

The HNO_3 and HCl measurements were performed with an Automatic Airborne Mass-Spectrometer (AAMAS) based on Ion-Molecule-Reaction Mass-Spectrometry [Möhler *et al.*, 1993; Arnold and Spreng, 1994]. Other gases measured by this technique, such as SO_2 , HCN , acetone, and acetonitrile, are not presented here. The air is sampled by a 40 mm (ID) stainless steel tube. At cruising speed this provides an air flow of $\sim 35 \text{ m/s}$, so that the residence time of trace species inside the tube is only $\sim 90 \text{ ms}$. The temperature inside the tube is $\sim 250 \text{ K}$. The AAMAS instrument consists of three major components: a cryogenically pumped (liquid Neon cooled) quadrupole mass spectrometer (MS), an ion-flow tube reactor, and an ion source. The source ions, mostly $\text{H}^+(\text{H}_2\text{O})$ and CO_3^+ , are injected into the flow tube reactor where they react with trace gases in the ambient air stream. The trace gas concentration is determined with high sensitivity by the quadrupole MS from the ratio of product-to-educt ions. The time resolution is 5–15 s (depending on the number of gases selected and the ambient concentrations). The detection limit is 10 pptv or less for a time resolution of 13 s. The uncertainty and precision are about

$\pm 40\%$ and $\pm 20\%$, respectively. The uncertainty is largely determined by the accuracy at which the rate coefficients have been determined; the precision is dependent on the count rate statistics.

2.3. Measurements of O_3 , CO , and N_2O

Ozone was measured with a chemiluminescence monitor (Bendix 8002), on the basis of the reaction with ethylene [Bregman *et al.*, 1997a, b]. The instrument has been modified to measure pressure independently [Gregory *et al.*, 1983]. The measurement response time was 1 Hz. Gas phase calibrations based on the reaction with NO have been performed before and after the campaign. During the field phase the instrument was checked with an external ozone generator before and after each flight. The overall precision was $\pm 2\%$, and the accuracy was $\pm 5\%$, mainly determined by fluctuations of the mercury lamp in the calibration device.

Carbon monoxide and N_2O have been measured by Tunable Diode Laser Absorption Spectroscopy (TDLAS) [Wienhold *et al.*, 1994; Fischer *et al.*, 1997]. These measurements are based on the high spectral brightness and narrow tunable emission bandwidth of two midinfrared lead-salt diode lasers. By pumping the atmospheric samples rapidly through a low-pressure ($\sim 30 \text{ hPa}$) cell the width of the pressure-broadened line is reduced, and overlap with absorption by other species is minimized. The sensitivity is enhanced by multiple reflections of the laser beams using modified white optics [Roths *et al.*, 1996]. During the STREAM campaign the instrument measured CO

and N_2O simultaneously at a time resolution of 1 s. Every 15 min in situ calibrations were performed by replacing the ambient air with known secondary standards (BOC 192 ppbv $\pm$ 2% CO , 317 ppbv $\pm$ 2% N_2O in synthetic air). The overall accuracy is determined by the accuracy of the standards used. The precision has been estimated by the standard deviations of the calibrations during the flight, which were about $\pm$ 2%. During the STREAM 1997 campaign a comparison of the TDLAS measurements of N_2O with those by an airborne gas chromatograph has been performed [Bujok, 1998]. The GC time resolution was 2 min, its in-flight precision was about $\pm$ 5%, and the accuracy was about $\pm$ 1.5%. The in-flight comparison indicated agreement between both instruments within 2–3%.

2.4. Aerosol and Cloud Measurements

Two complementary air inlets were used to sample aerosols and cloud elements, i.e., cirrus crystals in the tropopause region [Schröder and Ström, 1997; Ström and Ohlsson, 1998]. One is the supermicrometer inlet of the Counterflow Virtual Impactor (CVI), which samples cloud elements with an aerodynamic diameter $>5\text{ }\mu\text{m}$ [Noone et al., 1993]. The other is a backward directed 0.25 inch stainless steel submicrometer inlet tapered to a 2.2 mm opening. The upper cutoff diameter for this inlet is estimated at $1\text{ }\mu\text{m}$. The CVI inertially separates the larger particles, and the evaporated residual aerosols are sampled downstream by two TSI-3760 condensation particle counters (CPCs) modified for aircraft use [Schröder and Ström, 1997]. By assuming that each evaporated cirrus crystal leaves only one particle, these measurements provide an indication of the number concentration of crystals with a diameter larger than the lower cut size of the CVI. The size distribution of the residual particles between 0.1 and $3.5\text{ }\mu\text{m}$ diameter was measured by a PMS PCAS-X-P Optical Particle Counter (OPC) working alternately on both inlets. A dual-beam Lyman α hygrometer [Zuber and Wütt, 1987] was used to measure the water evaporated from the cloud elements. This corresponds to the condensed water content of the cloud since only very little water is contained in the cloud elements with a diameter $<5\text{ }\mu\text{m}$.

The accumulation mode ambient particles were also measured by the OPC. It was calibrated using an ammonium sulfate submicron size aerosol and latex spheres for particle diameters exceeding $1\text{ }\mu\text{m}$. After excluding the erroneous first channel, the instrument classifies the size distribution of aerosols in 30 bins between 0.12 and $3.5\text{ }\mu\text{m}$. The OPC operated with a sample flow between 15 and $60\text{ cm}^3/\text{min}$, depending on the ambient pressure. Smaller particles were measured by two CPCs with different lower size detection limits (50% cutoffs). The CPCs used were of the type TSI-3760, operating at a volumetric flow of 1.5 L/min. The instruments detected total particle concentrations with diameters above 7 nm (10% efficiency at 5.5 nm) and 18 nm (10% efficiency at 12 nm), respectively. The laboratory and in-flight calibration procedure has been comprehensively described by Schröder and Ström [1997]. The difference between the measurements of the CPCs with the 7 and 18 nm cutoff sizes provided a measure of the ultrafine or Aitken particle concentration.

2.5. Modeling

To support the measurement analyses, back-trajectories have been calculated on the basis of ECMWF analyzed meteorological fields, applying a time resolution of 6 hours and a

spatial resolution of 0.5° latitude/longitude (T213, 31 levels) [Scheele et al., 1996]. Since the grid points and time periods of the ECMWF data do not exactly coincide with the flight data, a spatial interpolation is applied that is linear in the horizontal and linear with the logarithm of pressure in the vertical direction. The computed trajectories are fully three-dimensional, following the recommendations by Stohl et al. [1995, 1998]. The model has been tested in applications near the tropopause region, in particular for its ability to reproduce trajectories in small-scale flow patterns in and outside tropopause foldings [Scheele et al., 1996].

We calculated 30 day back-trajectories starting at locations along the flight tracks. For February 18, 1995, trajectories were calculated at 10 min intervals. Note that back-trajectories more than 1–2 weeks prior to their origin are associated with significant uncertainties, so that especially the first weeks (mid-January to early February 1995) should be conceived as possible air mass trajectories rather than actual ones. Figure 2 presents two typical trajectories, showing extensive meridional excursions between $\sim 40^\circ\text{N}$ and the North Pole, and large pressure and temperature variations over several day periods. The air sampled along the flight track on February 18 encircled the globe several times during the 30 day period prior to the measurements.

The chemical part of the model, i.e., used as a box model, was originally developed by Crutzen et al. [1992], Müller and Crutzen [1993], and Müller et al. [1994] and has been applied previously by Bregman et al. [1997a, b]. The model uses a Gear method to integrate the coupled set of differential equations [Curtis and Sweetenham, 1987]. Photolysis rate coefficients are calculated with an updated version of the radiative transfer model by Lary and Pyle [1991]. It includes the temperature dependence of the UV cross sections of HNO_3 and recent revisions of the $\text{O}(^1\text{D})$ quantum yield from O_3 photodissociation. The model has been updated with a full code for bromine reactions. Furthermore, the model has been extended with a representation of ethane and propane chemistry, as these gases are sufficiently long lived to mix into the lowermost stratosphere and contribute, for example, to peroxyacetylnitrate (PAN) and acetone formation.

Ternary and binary reaction rate coefficients have been adopted from the work of DeMore et al. [1997]. The model includes heterogeneous reactions on liquid and solid particles. The composition and volume of liquid $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ aerosols are calculated using the analytic expression of Carslaw et al. [1995]. The solubilities of HCl and HOCl are calculated according to Luo et al. [1995] and Huthwelker et al. [1995]. Reactive uptake coefficients, i.e., γ values, have been parameterized according to Hanson and Ravishankara [1994]. The model accounts for aerosol phase transitions as described by Carslaw et al. [1997]. It has been assumed that $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ aerosols freeze completely to form nitric acid trihydrate (NAT) and sulfuric acid tetrahydrate (SAT) at the NAT equilibrium temperature. These phase transitions are still not completely understood, which introduces uncertainties in the calculations. However, the low temperatures required to form NAT only rarely occur in the lowermost stratosphere, so that the aerosol particles are liquid during most of the time. In our model, NAT forms at a supersaturation of 10. The formation threshold is temperature and pressure dependent. We also tested a supersaturation of 1 and a temperature reduction of 15 K. Even under these conditions, NAT formation only occurs

Figure 2. Thirty day back-trajectories, calculated from European Centre for Medium-Range Weather Forecasts (ECMWF) analyses, ending at the flight track on February 18, 1995, at (right) 216 hPa (67.4°N, 26.7°E and (left) 196 hPa (67.2°N, 26.2°E). The trajectories show 30°–40° latitude excursions, indicating rapid north-south traverses. Variations of temperature by ~30 K and of pressure up to 90 hPa thus occur on timescales of several days.

once in our simulations and contributes marginally to chlorine activation. However, in section 4 we will assume the presence of water ice crystals during several 2 hour periods and show that this significantly contributes to chlorine activation. We emphasize that this postulate, although supported by our observations, is to a large degree arbitrary and should be conceived as the basis of a sensitivity study. As yet the theory to explain ice crystal presence in the lowermost stratosphere is incomplete.

The STREAM measurements have been used to constrain the model and provide boundary conditions, notably for O_3 , CO , C_2H_6 , $(CH_3)_2CO$, NO_x , and HCl . Water vapor was derived from a series of N_2O/H_2O ratio measurements in the middle-latitude stratosphere (C. Schiller, personal communication, 1998), indicating a H_2O mixing ratio of ~10 ppmv, consistent with the measurements by Dessler *et al.* [1995]. For those species for which no measurements were available the output of a global 3-D chemistry-transport model have been adopted (M. van den Broek *et al.*, manuscript in preparation, 1999). The use of STREAM measurements as boundary conditions means that for C_2H_6 , for example, the model has been initialized with a “background” C_2H_6 mixing ratio based on the

measurement results described in section 3. The same applies to O_3 and HCl , which are consistent with our 3-D model calculations. The initial O_3 mixing ratio used in the box model was based on the mean O_3 level encountered at the highest flight tracks. The model results (e.g., through the Cl/ClO ratio) are not very sensitive to this condition. However, the results are quite sensitive to the assumed total chlorine level. The partitioning between active chlorine and chlorine reservoir species is largely determined by the ice surface and radiation intensity. The comparison between calculated and measured HCl provides an important test to the model. We performed sensitivity runs to study the effect of the $HCl/ClONO_2$ ratio. The results are sensitive to this ratio. If we assume that all reservoir chlorine is HCl , the Cl activation is less. However, the $HCl/ClONO_2$ ratio converges toward the one we assumed in section 4, and if we extend the run by another week, the same result is obtained. The amount of $ClONO_2$ is largely controlled by the availability of NO_x . The latter, in turn, is controlled by HNO_3 photolysis. As the trajectories move rather far south, HNO_3 photolysis is quite important. Therefore, although we did not measure $ClONO_2$, both the HCl and the HNO_3 measurements help to constrain this variable.

Table 2. Observed CO and C₂H₆ Mixing Ratios Near the Tropopause

Campaign	Date	Altitude, km	C ₂ H ₆ , pptv	CO, ppbv	CO/C ₂ H ₆ , ppbv/pptv
STREAM II 65°–70°N	Feb. 9, 1995	10.5	827 (149)	85 (2.5)	0.10
	Feb. 18, 1995	9.0	517 (93)	113 (3.4)	0.22
STREAM III 65°–70°N	March 25, 1997	11.9	326 (52)	57 (1.7)	0.17
	March 25, 1997	9.1	1023 (163)	131 (3.9)	0.13
West Coast United States 30°N ^a	April 1985	9–13	1286	129	0.10
West Coast United States 39°–48°N ^a	April 1985	11–13	804	75	0.09
Alaska 61°N ^a	April 1985	8.3	2432	176	0.07
AASE-II 70°–90°N ^b	winter 1992	<12	1563	134	0.09
AASE-II 40°–60°N ^b	winter 1992	<12	1348	131	0.10
PEM-West A 20°–40°N ^c	Sept.–Oct. 1991	8–12	958	127	0.13
PEM-West B 20°–60°N ^c	Feb.–March 1994	7–12	874	112	0.13
Arithmetic mean			1132	120	0.11

Uncertainty ranges are indicated in parentheses.

^aGreenberg *et al.* [1990].

^bAnderson *et al.* [1993].

^cTalbot *et al.* [1996, 1997].

3. Observations of CO/Ethane Ratio

Ethane efficiently reacts with chlorine radicals, whereas CO does not. We make use of these different reactivities to estimate reactive chlorine loadings of air parcels in the lowermost stratosphere. This is feasible since the emissions of CO and C₂H₆ are highly correlated [Olivier *et al.*, 1994], and the lifetimes of both gases due to destruction by OH are of similar magnitude. The relevant reactions are

These reaction rate constants have been adopted from DeMore *et al.* [1997]. P_{atm} is the air pressure in atmospheres and T is the temperature. Of course, CO is also produced from CH₄ oxidation, but this merely influences the CO concentration on timescales of several months or more, hence outside the scope of our argument. If we assume an upper tropospheric and lower stratospheric OH concentration of 3×10^5 molecules cm⁻³, a mean pressure level of 200 hPa, and a temperature of 220 K, we obtain an OH-controlled CO and C₂H₆ lifetime of ~0.6 and 1.5 years, respectively. If we would add CO production from CH₄ oxidation, the rate of change of CO and C₂H₆ is even more similar. Hence, during transport in the lowermost stratosphere the CO/C₂H₆ ratio changes very little as a result of OH breakdown alone.

Next we need to assess the CO and C₂H₆ mixing ratios that occur in the tropopause region in the absence of reactive chlorine (referred to as background CO/C₂H₆). Furthermore, we note that C₂H₆ can only be used as an indicator of reactive chlorine presence if the differences in CO/C₂H₆ between the background and chlorine perturbed conditions are significant, i.e., well outside the range expected on the basis of OH chemistry alone. Table 2 provides some insight in CO/C₂H₆ ratios in the tropopause region, in part based on measurements by other groups. It appears that CO/C₂H₆ is not very variable with

a mean of ~0.11 ppbv/pptv ($\sigma = 0.04$ ppbv/pptv), hardly dependent on location and season and in line with the above assumptions about CO and C₂H₆ lifetimes and sources. Pure stratospheric air at high latitudes, of course, does not contain C₂H₆. Pure stratospheric CO (controlled by CH₄ oxidation), as observed during the STREAM flights since 1993, averages ~20 ppbv. The lowest CO level, measured on March 21, 1997, at 13 km altitude, was 14 ppbv, whereas N₂O was 265 ppbv, and C₂H₆ was below the detection limit. Any ethane detected in the high-latitude lower stratosphere and CO in excess of ~20 ppbv must therefore originate from mixing with tropospheric air.

Mixing ratios of CO in the free troposphere (at O₃ < 200 ppbv) during the 1995 STREAM campaign averaged 155 ppbv, and mixing ratios of ethane averaged 801 pptv. Thus the mean free tropospheric CO/C₂H₆ ratio was 0.19 ppbv pptv⁻¹. This is higher than the arithmetic mean of 0.11 derived from Table 2, but we will see later in this section that this difference is only small compared to that with Cl perturbed air masses in the lowermost stratosphere.

In the lowermost stratosphere (at O₃ > 200 ppbv), CO mixing ratios averaged 50 ppbv, and those of ethane averaged 234 pptv; thus the mean CO/C₂H₆ ratio was 0.21. This result agrees well with the Pacific Exploratory Mission (PEM) West B measurements reported by Singh *et al.* [1997] performed in the midlatitude lowermost stratosphere (37°–57°N), indicating a mean CO mixing ratio of 45 ppbv and C₂H₆ of 170 pptv and hence a CO/C₂H₆ ratio of 0.26 ppbv/pptv. In general, CO/C₂H₆ ratios in the lowermost stratosphere are somewhat higher than in the upper troposphere, which is no surprise considering the contribution by downward transport of C₂H₆-depleted air at high latitudes.

The measurements on February 18, 1995 (at O₃ > 200 ppbv), show that O₃ typically varied up to 500 ppbv, N₂O from 270 to 290 ppbv, CO from 40 to 70 ppbv (Figure 3), and HNO₃ and NO_y from 2 to 8 ppbv. Although the presence of ethane and excess CO (>20 ppbv) suggests tropospheric influences, N₂O and O₃ levels are indicative of air that is traditionally defined as stratospheric; that is, N₂O ≤ 300 ppbv and O₃ ≥ 200 ppbv (Table 3). Aerosol particle levels ($D < 1 \mu\text{m}$) were somewhat higher than stratospheric background levels, providing a surface area of $S \approx 1\text{--}5 \mu\text{m}^2/\text{cm}^3$ (Figure 4). Note that this represents the dry aerosol after sampling, whereas the

ambient particles may have had a surface area up to a factor of 2 larger.

Figure 5 shows $\text{CO}/\text{C}_2\text{H}_6$ ratios observed during STREAM and other campaigns in the vicinity of the tropopause and in the lowermost stratosphere. It also shows several anomalous $\text{CO}/\text{C}_2\text{H}_6$ values observed during other measurement flights in February 1995. On February 18, 1995, between 10 and 12.5 km altitude (300–270 ppbv N_2O) the mean $\text{CO}/\text{C}_2\text{H}_6$ ratio was close to unity, suggesting that ethane was depleted by a factor of 5–10 (Table 3). During one altitude track, at 216 hPa, the $\text{CO}/\text{C}_2\text{H}_6$ ratio reached a value of 1.52 ppbv/pptv. In section 4 we will focus on this observation, providing a quantitative explanation based on model calculations. First, however, we estimate the mean Cl loading based on the empirically derived $\text{CO}/\text{C}_2\text{H}_6$ enhancement.

The change of $\text{CO}/\text{C}_2\text{H}_6$ in time is calculated by

$$\frac{[\text{CO}]_t}{[\text{C}_2\text{H}_6]_t} = \frac{[\text{CO}]_0 \exp(-k_1[\text{OH}]t)}{[\text{C}_2\text{H}_6]_0 \exp(-k_2[\text{OH}]t) \exp(-k_3[\text{Cl}]t)} \quad (1)$$

The ratio $[\text{CO}]_t/[\text{C}_2\text{H}_6]_t = C_t$ can be derived from the “anomalous” measurements, for example, ~ 1 ppbv/pptv for February 18, 1995 (Table 3); the ratio $[\text{CO}]_0/[\text{C}_2\text{H}_6]_0 = C_0$ follows from the background measurements for which we adopt 0.2 ppbv/pptv. The diurnal mean hydroxyl and chlorine concentrations are $[\text{OH}]$ and $[\text{Cl}]$, respectively (in molecules or atoms cm^{-3}). Since the reaction rates of CO and C_2H_6 with OH are relatively slow, the ratio $\{\exp(-k_1[\text{OH}]t)/\{\exp(-k_2[\text{OH}]t)\}$ remains close to 1 for at least a month during transport in the lowermost stratosphere. Thus (1) simplifies to

$$C_t = \frac{C_0}{\exp(-k_3[\text{Cl}]t)}$$

so that

$$[\text{Cl}] = \ln \frac{C_0}{C_t} \frac{1}{-k_3 t}$$

Table 4 presents some $[\text{Cl}]$ estimates based on time periods of 10 and 30 days. It thus appears that the anomalous $\text{CO}/\text{C}_2\text{H}_6$ ratios measured on February 18, 1995, can be explained by assuming a diurnal mean chlorine loading of $[\text{Cl}] \approx 10^4$ atoms cm^{-3} over a period of 30 days prior to the measurements. If the period during which chlorine activation has taken place would have been much shorter, e.g., 10 days, average Cl concentrations should have reached up to $[\text{Cl}] \approx 3 \times 10^4$ atoms cm^{-3} . If the air parcels would have been exposed to reactive chlorine over periods exceeding a month or more, proportionally lower $[\text{Cl}]$ would be needed. Typical exchange times between the lowermost stratosphere and upper troposphere are of the order of 2 months [Lelieveld et al., 1997], in which case a Cl concentration of $\sim 5 \times 10^3$ atoms cm^{-3} would be required to explain our anomalous $\text{CO}/\text{C}_2\text{H}_6$ observations.

4. Chlorine Activation on Ice Crystals

The trajectory-chemistry model, as described in section 2.5, was applied to analyze the lowermost stratosphere measurements on February 18, 1995. The 216 hPa trajectory (11.1 km altitude; see section 2) and our aircraft measurements of trace species have been used to provide boundary conditions for the chemistry simulations. Concentrations of relevant species that have not been measured were adopted from a 3-D chemistry-transport model. Potential vorticity averaged 7.0 potential vor-

Figure 3. Measurement results as a function of time (UTC) from the flight over northern Sweden on February 18, 1995. (top) O_3 and N_2O (ppbv), (middle) CO (ppbv) and C_2H_6 (pptv), and (bottom) HNO_3 (ppbv), HCl (pptv), and ECMWF calculated potential vorticity (PVU).

ticity units (PVU), and we observed on average 280 ppbv O_3 and 272 ppbv N_2O . Although the air parcels sometimes descended by several kilometers, they remained within the stratosphere for at least 30 days prior to the measurements, as potential vorticity values did not drop below ~ 4 PVU (Figure 2).

The 216 hPa trajectory depicted in Figure 2 shows that large, up to 40° latitude, excursions occurred several times before the air arrived at the measurement location near 67°N . The associated pressure increases at middle latitudes, up to 280 hPa, demonstrate that air parcels moved to much lower altitudes, associated with synoptic disturbances. As we will show, the presence of significant number densities of ice crystals, causing

Table 3. Pressure, Potential Vorticity (PV), and Trace Gases Observed on February 18, 1995, at 66°–68°N Latitude in the Lowermost Stratosphere

Altitude, km	Pressure, hPa	PV, PVU ^a	O ₃ , ppbv	N ₂ O, ppbv	HNO ₃ , ppbv	HCl, ppbv	C ₂ H ₆ , pptv	CO, ppbv	CO/C ₂ H ₆ , ppbv/pptv
9.9	260	5.9	219 (11)	284 (8.5)	2.93 (1.1)	0.53 (0.2)	229 (41)	68 (2.0)	0.30
10.5	238	6.3	240 (12)	300 (9)	3.21 (1.3)	0.52 (0.2)	92 (17)	67 (2.0)	0.73
11.1	216	7.0	280 (14)	272 (8)	4.23 (1.7)	0.51 (0.2)	29 (5)	44 (1.3)	1.52
11.7	196	8.6	344 (17)	292 (9)	3.23 (1.3)	0.46 (0.2)	40 (7)	54 (1.6)	1.35
12.3	177	9.5	468 (23)	280 (8.5)	4.62 (1.8)	0.45 (0.2)	45 (8)	47 (1.4)	1.04

Uncertainty ranges are indicated in parentheses.

^aPVU = 10⁻⁶ Km² kg⁻¹ s⁻¹.

heterogeneous conversion of chlorine reservoir species, can explain the relatively large amounts of reactive chlorine that occurred in the lowermost stratosphere, causing strongly enhanced CO/C₂H₆ ratios.

Extratropical cirrus clouds usually form in the upper troposphere in association with cyclonic storms. It has been observed, however, also from our own aircraft measurements (J. Ström et al., manuscript in preparation, 1999), that deep convective towers sometimes penetrate the tropopause, releasing cloud elements into the lowermost stratosphere and moistening the air [Poulida et al., 1996]. Lidar observations have confirmed the presence of cirrus above the tropopause [Ansmann et al., 1993; Sassen, 1991; Winker and Vaughan, 1994], as dis-

cussed by Solomon et al. [1997]. However, the lidar laser beams only pass through the atmosphere under relatively optically thin conditions, while it is likely that thick clouds form in cyclonic weather conditions. Therefore surface lidars conceivably underestimate the presence of stratospheric ice clouds.

Subvisible cirrus was also observed by the ER-2 aircraft at 11–12 altitude during the spring 1996 Subsonic Aircraft Contrail and Cloud Effects Special Study (SUCCESS) campaign over the central United States [Smith et al., 1998]. One possible explanation of such clouds in the lowermost stratosphere is that cross-tropopause exchange moistens the lowermost stratosphere while buoyancy waves generated by convection cause local supersaturation and ice cloud formation. Smith et al. [1998] mention the possibility that some subvisible cirrus clouds may be the residuals of contrails that have formed from

Figure 4. Aerosol surface area S up to 12 km altitude on February 18, 1995. The associated particle number concentration (not shown) varied from $N \approx 1000 \text{ cm}^{-3}$ in the upper troposphere to $N \approx 10 \text{ cm}^{-3}$ at 12 km. The high peak in S near the tropopause coincides with a maximum in the concentration of small particles ($N \approx 2500 \text{ cm}^{-3}$ for $D > 0.007 \text{ μm}$), suggesting new particle formation [de Reus et al., 1998].

Figure 5. Ratios of CO/C₂H₆ as a function of the N₂O mixing ratio, observed during the Stratosphere-Troposphere Experiments by Aircraft Measurement (STREAM) campaigns in February 1995 and March 1997. For comparison, results from Pacific Exploratory Mission (PEM)-West B at 20–40°N [Talbot et al., 1997] and Airborne Arctic Stratospheric Experiment (AASE) II at 40–60°N and 70–90°N [Anderson et al., 1993] are also shown. The dashed line indicates the expected average CO/C₂H₆ ratio due to destruction by OH alone.

Table 4. Estimated Diurnal Mean Chlorine Concentrations in the Lowermost Stratosphere Needed to Explain the Anomalous CO/C₂H₆ Observations

Date	O ₃ , ppbv	CO, ppbv	C ₂ H ₆ , pptv	CO/C ₂ H ₆ , ppbv/pptv	Cl, <i>t</i> = 10 days	Cl, <i>t</i> = 30 days
Feb. 18, 1995	219 (11)	68 (2.0)	229 (41)	0.30	9.2×10^3	3.1×10^3
Feb. 18, 1995	240 (12)	67 (2.0)	92 (17)	0.73	2.9×10^4	9.8×10^3
Feb. 18, 1995	280 (14)	44 (1.3)	29 (5)	1.52	4.6×10^4	1.5×10^4
Feb. 18, 1995	344 (17)	54 (1.6)	40 (7)	1.35	4.3×10^4	1.4×10^4
Feb. 18, 1995	468 (23)	47 (1.4)	45 (8)	1.04	3.7×10^4	1.2×10^4
Feb. 21, 1995	478 (24)	45 (1.4)	12 (2)	3.7	6.6×10^4	2.2×10^4
Feb. 24, 1995	260 (13)	67 (2.0)	185 (33)	0.36	1.3×10^4	4.4×10^3
Feb. 24, 1995	402 (20)	46 (1.4)	76 (14)	0.60	2.5×10^4	8.3×10^3
Feb. 24, 1995	438 (22)	45 (1.4)	12 (2)	3.7	6.6×10^4	2.2×10^4

Uncertainty ranges are indicated in parentheses. Chlorine concentrations are in atoms/cm³.

aircraft exhausts and that these particles can remain buoyant in the stable tropopause region. We emphasize, however, that these explanations are speculative and more studies are needed.

Evidence of stratospheric cirrus is also offered by our measurements on February 18, 1995. Figure 6 shows the CVI results, which confirm the presence of relatively large particles above the tropopause. The CVI inertially separates the smaller aerosols from hydrometeors with an aerodynamic diameter >5 μm [Ström and Ohlsson, 1998]. Figure 6 shows a low-level cloud at 2.5 km above sea level and cirrus clouds near the tropopause at ~7.5 km. It also shows that the stratosphere contained ice crystals at least up to the top flight level at 12 km altitude. The crystal densities, up to ~0.4 cm⁻³, occurred very intermittently along the flight track, and the cloud structure

Figure 6. Particle number densities ($D > 5 \mu\text{m}$) measured with the counterflow virtual impactor (CVI) on February 18, 1995. Particle counts up to ~7.5 km altitude show upper tropospheric cirrus clouds. Particle counts above the tropopause, up to 12 km, indicate thin cirrus clouds in the lowermost stratosphere. The mechanism of formation of these clouds is not well understood.

appeared to be layered. Similarly, ice clouds were observed on February 9, 1995, only up to 9.5 km altitude, however, although crystal number densities were about a factor of 10 higher.

Next we need some reasonable assumptions for ice clouds in our model calculations. A simulation in which ice crystal presence is neglected does not reproduce the observed CO/C₂H₆ ratio. Although moistening of the lowermost stratosphere by tropospheric influences at midlatitudes (~10 ppmv) contributes to aerosol growth and heterogeneous chlorine activation, the amount of reactive chlorine is not sufficient to rapidly oxidize C₂H₆. The observed CO/C₂H₆ ratio can only be reproduced if we assume a significant crystal presence so that much of the chlorine is activated. The combination of an ice surface area for heterogeneous reactions and the relatively intense solar radiation at middle latitudes (compared to wintertime Arctic conditions) very efficiently activates chlorine from HCl and ClONO₂. Furthermore, model calculations suggest that it does not make much of a difference whether we assume a single cirrus cloud persisting over a whole day or that ice clouds arise for a few hours during multiple intervals during the 30 day period considered.

For the model calculations presented in Figure 7 we adopted five 2 hour cirrus cloud events starting at the highest pressures along the back-trajectory that ends at 216 hPa (see also Figure 2). We assumed a crystal surface area of $1\text{--}1.5 \times 10^3 \mu\text{m}^2 \text{cm}^{-3}$, which represents a thin cirrus cloud that contains up to 0.4 particles cm⁻³ with an average diameter of ~10–20 μm. The model results indicate that this leads to significant chlorine activation and consequent ethane destruction, consistent with the results empirically derived in section 3. For example, the calculated mean Cl concentration is $\sim 1.0 \times 10^4 \text{ atoms cm}^{-3}$. The amount of HCl (~0.5 ppbv) that is calculated at the time of aircraft measurements on February 18, 1995, is consistent with our observations [Bürger, 1995; Schneider, 1998] (Figure 3).

To demonstrate that ice crystals are needed to explain our measurements, we show some sensitivity calculations. We drastically reduced the temperature by 15 K during the same periods for which we assumed ice crystals in Figure 7. Thus we enhanced liquid aerosol growth, but we precluded ice formation. Figure 8 shows that although significant chlorine activation can take place on liquid aerosols, it brings about a much lower CO/C₂H₆ ratio. If we further reduce the temperature to below the frost point (still precluding cirrus formation), i.e., by 20–25 K, Cl activation becomes much stronger and the effect is close to that of cirrus. Although we cannot exclude this possibility, our observations point to thin cirrus presence

Figure 7. Model calculated trace gas mixing ratios and particle surface area pertaining to the measurement flight in the lowermost stratosphere on February 18, 1995. The 216 hPa 30 day back-trajectory (see also Figure 2) and aircraft measurements of trace species have been used to provide initial and boundary conditions. The back-trajectory ends at the time and location of the measurements. We assumed ice cloud presence during five periods of 2 hours. This illustrates the conditions required to activate about 1.0×10^4 atoms cm^{-3} of Cl.

rather than very large temperature excursions and associated aerosol growth.

Furthermore, the calculations that include ice clouds show that chlorine activation contributes to rapid O_3 breakdown (Figure 7). The chemical mechanism is comparable to O_3 loss on polar stratospheric clouds that can form at higher altitudes in the Arctic stratosphere, for example, from cooling by mountain-induced gravity waves [Carslaw *et al.*, 1998]. Our calculations suggest that more than 20% of the ozone could be lost over a 30 day period. Considering the magnitude of the O_3 trend in the lowermost stratosphere [e.g., Bojkov and Fioletov, 1997], it is unlikely that such strong O_3 losses occur over the whole winter and early spring period, and it underscores that our observations of enhanced $\text{CO}/\text{C}_2\text{H}_6$ ratios represent unusual conditions. Nevertheless, these results point to an important mechanism that can cause chlorine activation. Even if such conditions occur only occasionally, they are likely to contribute to significant chemical O_3 loss in the middle- and high-latitude lowermost stratosphere.

A previous analysis of the 1995 STREAM measurements of NO_y , O_3 , and N_2O by Fischer *et al.* [1997] has shown that ozone concentrations in the lowermost stratosphere were substantially lower than those expected in unperturbed stratospheric

air. For example, $\text{O}_3/\text{N}_2\text{O}$ ratios were much reduced compared to those measured previously, a strong indication of chemical ozone loss in the Arctic winter of 1994–1995. Indeed, the 1994–1995 Arctic winter was so cold that polar stratospheric clouds have formed relatively frequently, which enhanced heterogeneously catalyzed ozone loss within the vortex. Satellite measurements have confirmed that strong ozone destruction occurred in the Arctic winter of 1994–1995, with local reductions by more than 50% and a column O_3 loss of ~ 100 Dobson unit (DU) [Müller *et al.*, 1996]. Our analysis is complementary in the sense that some ozone loss can also occur during transport from the vortex to lower altitudes and latitudes in the lowermost stratosphere where stratospheric and tropospheric air are mixed.

Finally, our analysis does not preclude the possibility that chlorine activation occurs in the upper troposphere. Especially the first part of the trajectories, as presented in Figure 2, is associated with uncertainties, so that it is conceivable that they have reached higher pressure levels and thus crossed the tropopause. We argue, however, that chlorine activation can also occur above the tropopause. As indicated by our observations, the HCl amount and the light intensity are sufficient to activate chlorine, provided that a surface is available for het-

Figure 8. Model-calculated reactive chlorine, assuming that no ice was formed. However, we strongly reduced the temperature by 15 K during the 2 hour periods for which we assumed ice cloud presence in Figure 7. This significantly enhances chlorine activation on liquid aerosols (S_{liquid} is aerosol surface area in $\mu\text{m}^2/\text{cm}^3$), but not sufficient to explain the observed anomalous $\text{CO}/\text{C}_2\text{H}_6$ ratios.

ogeneous reactions to occur. Our observations further suggest that such surfaces are available, in the form of aerosols and thin cirrus. Future work must help to quantify to what extent these heterogeneous chemical pathways contribute to ozone loss in the middle- and high-latitude lowermost stratosphere.

5. Conclusions

Aircraft measurements performed in February 1995 over northern Sweden show that very high $\text{CO}/\text{C}_2\text{H}_6$ ratios can occur in the lowermost stratosphere. These can be explained by assuming a significant level of reactive chlorine. From both empirical evidence and model calculations, we derive that chlorine levels may have been of the order of $[\text{Cl}] \approx 1.0 \times 10^4 \text{ atoms cm}^{-3}$. This reduces the C_2H_6 lifetime from ~ 1.5 years (as determined by OH) to several weeks, whereas it does not affect the CO lifetime (~ 0.6 years). Our model calculations suggest that this Cl level had to be caused by heterogeneous chlorine activation from HCl and ClONO_2 . Nevertheless, it remains difficult to unambiguously determine where the chlorine has been activated. The aerosol measurements do not support the possibility of strongly enhanced levels of submi-

crometer size particles. However, our CVI measurements show significant number densities of large particles ($D > 5 \mu\text{m}$) well above the tropopause. We believe that these particles represent thin cirrus clouds. In the model calculations we have assumed that such ice particle events also occurred several times in the 30 day period previous to our measurements.

Our measurements and model results confirm the suggestion by *Bormann et al.* [1996, 1997] and *Solomon et al.* [1997] that cirrus can contribute to heterogeneous chlorine activation and consequent ozone destruction. Moreover, our measurements and model calculations indicate that ice clouds can occur above the tropopause and thus contribute to ozone loss in the middle- and high-latitude lowermost stratosphere. This effect adds to heterogeneous chlorine activation by aerosol particles, which can also be significant. We note that sedimentation of ice crystals could also play a role in the altitude repartitioning of HNO_3 [*Fischer et al.*, 1997], although we did not obtain evidence for this during the current measurements. Our model calculations indicate that aerosols activate less than half the amount of chlorine needed to explain our observations, even if we assume very strong cooling. Moistening of the lowermost stratosphere by exchange with the troposphere, in combination

with local cooling from wave activity by extratropical storms, provides a possible mechanism that leads to both ice cloud formation and aerosol growth above the tropopause.

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References

- Anderson, B. E., J. E. Collins, G. W. Sachse, G. W. Whiting, D. R. Blake, and F. S. Rowland, AASE-II observations of trace carbon species distributions in the mid to upper troposphere, *Geophys. Res. Lett.*, **20**, 2539–2542, 1993.
- Ansmann, A., et al., Lidar network observations of cirrus morphological and scattering properties during the International Cirrus Experiment 1989: The 18 October, 1989 study and statistical analysis, *J. Appl. Meteorol.*, **32**, 1608–1622, 1993.
- Arnold, F., and S. Spreng, Balloon-borne mass spectrometer measurements of HCl and HF in the winter Arctic stratosphere, *Geophys. Res. Lett.*, **21**, 1255–1258, 1994.
- Arnold, F., V. Bürger, B. Droste-Franke, F. Grimm, A. Krieger, J. Schneider, and T. Stulp, Acetone in the upper troposphere and lower stratosphere: Impact on trace gases and aerosols, *Geophys. Res. Lett.*, **24**, 3017–3020, 1997.
- Arnold, F., V. Bürger, K. Gollinger, M. Roncossek, J. Schneider, and S. Spreng, Observations of nitric acid perturbations in the winter Arctic stratosphere: Evidence for PSC sedimentation, *J. Atmos. Chem.*, **30**, 3–10, 1998.
- Bojkov, R. D., and V. E. Fioletov, Changes of the lower stratospheric ozone over Europe and Canada, *J. Geophys. Res.*, **102**, 1337–1347, 1997.
- Borrmann, S., S. Solomon, J. E. Dye, and B. Luo, The potential of cirrus clouds for heterogeneous chlorine activation, *Geophys. Res. Lett.*, **23**, 2133–2136, 1996.
- Borrmann, S., S. Solomon, L. Avallone, D. Toohey, and D. Baumgardner, On the occurrence of ClO in cirrus clouds and volcanic aerosol in the tropopause region, *Geophys. Res. Lett.*, **24**, 2011–2014, 1997.
- Brasseur, G. P., R. A. Cox, D. Hauglustaine, I. S. A. Isaksen, J. Lelieveld, D. H. Lister, R. Sausen, U. Schumann, A. Wahner, and P. Wiesen, European scientific assessment of the atmospheric effects of aircraft emissions, *Atmos. Environ.*, **32**, 2327–2422, 1998.
- Bregman, A., et al., In situ trace gas measurements in the summer lower stratosphere during STREAM: Implications for O₃ production, *J. Atmos. Chem.*, **26**, 275–310, 1997a.
- Bregman, A., M. van den Broek, K. S. Carslaw, R. Müller, T. Peter, R. Scheele, and J. Lelieveld, Ozone depletion in the late winter lower Arctic stratosphere: Observations and model results, *J. Geophys. Res.*, **102**, 10,815–10,828, 1997b.
- Bujok, O., In situ Messungen langlebiger Spurengase in der unteren Stratosphäre: Entwicklung und Anwendung einer flugzeuggestützten gaschromatographischen Nachweismethode, Ph.D. thesis, Univ. of Bonn, Bonn, Germany, 1998.
- Bürger, V., Messungen atmosphärischer Spurengase mit einem flugzeuggestützten Massenspektrometer: Erkenntnisse zu vertikalen Umverteilung stratosphärischer Salpetersäure und zur Bildung stratosphärischer Wolken, diplom thesis, Heidelberg Univ., Heidelberg, Germany, 1995.
- Carslaw, K. S., B. P. Luo, and T. Peter, An analytic expression for the composition of aqueous HNO₃-H₂SO₄ stratospheric aerosols including gas phase removal of HNO₃, *Geophys. Res. Lett.*, **22**, 1877–1880, 1995.
- Carslaw, K. S., T. Peter, and R. Müller, Uncertainties in reactive uptake coefficients for solid stratospheric particles, 2, Effect on ozone depletion, *Geophys. Res. Lett.*, **24**, 1747–1750, 1997.
- Carslaw, K. S., M. Wirth, A. Tsias, B. P. Luo, A. Dörnbrack, M. Leutbecher, H. Volkert, W. Renger, J. T. Backmeister, E. Reimer, and T. Peter, Increased stratospheric ozone depletion due to mountain-induced atmospheric waves, *Nature*, **391**, 675–678, 1998.
- Crutzen, P. J., R. Müller, C. Brühl, and T. Peter, On the potential importance of the gas phase reaction CH₃O₂ + ClO → ClOO + CH₃O and the heterogeneous reaction HOCl + HCl → H₂O + Cl₂ in “ozone hole” chemistry, *Geophys. Res. Lett.*, **19**, 1113–1116, 1992.
- Curtis, A. R., and W. P. Sweetenham, *Facsimile/CheckMat Users Manual*, 135 pp., Comput. Sci. and Syst. Div., Harwell Lab., Oxford, England, 1987.
- DeMore, W. B., et al., Chemical kinetics and photochemical data for use in stratospheric modeling, *Evaluation No. 12*, NASA Jet Propul. Lab., Pasadena, Calif., 1997.
- de Reus, M., J. Ström, M. Kulmala, L. Pirjola, J. Lelieveld, C. Schiller, and M. Zöger, Airborne aerosol measurements in the tropopause region and the dependence of new particle formation on preexisting particles, *J. Geophys. Res.*, **103**, 31,097–31,105, 1998.
- Dessler, A. E., E. J. Hints, E. M. Weinstock, J. G. Anderson, and K. R. Chan, Mechanisms controlling water vapor in the lower stratosphere: “A tale of two stratospheres,” *J. Geophys. Res.*, **100**, 23,167–23,172, 1995.
- Fahey, D. W., C. S. Eubank, G. Hübler, and F. C. Fehsenfeld, Evaluation of a catalytic reduction technique for the measurement of total reactive nitrogen NO_y in the atmosphere, *J. Atmos. Chem.*, **3**, 435–468, 1985.
- Fischer, H., et al., Observations of high concentrations of total reactive nitrogen (NO_y) and nitric acid (HNO₃) in the lower Arctic stratosphere during the STREAM II campaign in February 1995, *J. Geophys. Res.*, **102**, 23,559–23,571, 1997.
- Greenberg, J. P., P. R. Zimmerman, and P. Haagenson, Tropospheric hydrocarbon and CO profiles over the U.S. West Coast and Alaska, *J. Geophys. Res.*, **95**, 14,015–14,026, 1990.
- Gregory, G. L., C. H. Hudgins, and R. A. Edahl, Laboratory evaluation of an airborne ozone instrument that compensates for altitude/sensitivity effects, *Environ. Sci. Technol.*, **17**, 100–103, 1983.
- Hanson, D. R., and A. R. Ravishankara, Reactive uptake of ClONO₂ onto sulfuric acid due to reaction with HCl and H₂O, *J. Phys. Chem.*, **98**, 5728–5735, 1994.
- Hoerling, M. P., T. K. Schaack, and A. J. Lenzen, A global analysis of stratospheric-tropospheric exchange during northern winter, *Mon. Weather Rev.*, **121**, 162–172, 1993.
- Huthwelker, T., T. Peter, B. P. Luo, S. L. Clegg, K. S. Carslaw, and P. Brimblecombe, Solubility of HOCl in water and aqueous H₂SO₄ at stratospheric temperatures, *J. Atmos. Chem.*, **21**, 81–95, 1995.
- Keim, E. R., et al., Observations of large reductions in the NO/NO_y ratio near the midlatitude tropopause and the role of heterogeneous chemistry, *Geophys. Res. Lett.*, **23**, 3223–3226, 1996.
- Lamarque, J. F., and P. G. Hess, Cross-tropopause mass exchange and potential vorticity budget in a simulated tropopause folding, *J. Atmos. Sci.*, **51**, 2246–2269, 1994.
- Lary, D. J., and J. A. Pyle, Diffuse radiation, twilight and photochemistry, *J. Atmos. Chem.*, **13**, 373–406, 1991.
- Lelieveld, J., F. Arnold, B. Bregman, V. Bürger, P. Crutzen, H. Fischer, P. Siegmund, P. van Velthoven, and A. Waibel, Chemical perturbation of the lowermost stratosphere through exchange with the troposphere, *Geophys. Res. Lett.*, **24**, 603–606, 1997.
- Logan, J. A., Trends in the vertical distribution of ozone: An analysis of ozonesonde data, *J. Geophys. Res.*, **99**, 25,553–25,585, 1994.
- Luo, B. P., K. S. Carslaw, T. Peter, S. L. Clegg, Vapour pressures of H₂SO₄-HNO₃-HCl-HBr-H₂O solutions to low stratospheric temperatures, *Geophys. Res. Lett.*, **22**, 247–250, 1995.
- Möhler, O., T. Reiner, and F. Arnold, A novel aircraft-based tandem mass spectrometer for atmospheric ion and trace gas measurements, *Rev. Sci. Instrum.*, **64**, 1199–1207, 1993.
- Müller, R., and P. J. Crutzen, Chlorine activation mechanisms during the polar night, *J. Geophys. Res.*, **98**, 20,483–20,490, 1993.
- Müller, R., et al., Chlorine chemistry and the potential for ozone destruction in the Arctic stratosphere in the winter 1991/1992, *Geophys. Res. Lett.*, **21**, 1427–1430, 1994.
- Müller, R., P. J. Crutzen, J.-U. Groö, C. Brühl, J. M. Russell III, and A. F. Tuck, Chlorine activation and ozone depletion in the Arctic vortex: Observations by the Halogen Occultation Experiment on the Upper Atmosphere Research Satellite, *J. Geophys. Res.*, **101**, 12,531–12,554, 1996.
- Noone, K. B., K. J. Noone, J. Heintzenberg, J. Ström, and J. A. Ogren, In situ observations of cirrus cloud microphysical properties using the counterflow virtual impactor, *J. Atmos. Oceanic Technol.*, **10**, 294–303, 1993.
- Olivier, J. G. J., A. F. Bouwman, C. W. M. van der Maas, and J. J. M.

- Berdowski, Emission data base for global atmospheric research, *Environ. Monit. Assess.*, **31**, 93–106, 1994.
- Penkett, S. A., N. J. Blake, P. Lightman, A. R. W. Marsh, and P. Anwyll, The seasonal variation of nonmethane hydrocarbons in the free troposphere over the North Atlantic Ocean: Possible evidence for extensive reactions of hydrocarbons with the nitrate radical, *J. Geophys. Res.*, **98**, 2865–2885, 1993.
- Poulida, O., R. R. Dickerson, and A. Heymsfield, Stratosphere-troposphere exchange in a midlatitude mesoscale convective complex, 1, Observations, *J. Geophys. Res.*, **101**, 6823–6836, 1996.
- Reichardt, J., A. Ansmann, M. Serwazi, C. Weitkamp, and W. Michaelis, Unexpectedly low ozone concentration in midlatitude tropospheric ice clouds: A case study, *Geophys. Res. Lett.*, **23**, 1929–1932, 1996.
- Roths, J., T. Zenker, U. Parchatka, F. Wienhold, and G. W. Harris, FLAIR, a four laser infrared spectrometer for atmospheric trace gas measurements, *Appl. Opt.*, **35**, 7075–7084, 1996.
- Sassen, K., Corona-producing cirrus cloud properties derived from polarization lidar and photographic analysis, *Appl. Opt.*, **30**, 3421–3552, 1991.
- Scheele, M. P., P. C. Siegmund, and P. F. J. van Velthoven, Sensitivity of trajectories to data resolution and their dependence on the starting point: In or outside a tropopause fold, *Meteorol. Appl.*, **3**, 267–273, 1996.
- Schneider, J., Aircraft-based mass spectrometric measurements of trace gas distributions in the tropopause region: Implications for stratosphere-troposphere exchange, ozone chemistry and global biomass burning, PhD thesis, Ruprecht-Karls-Univ. of Heidelberg, Heidelberg, Germany, 1998.
- Schneider, J., V. Bürger, and F. Arnold, Methyl cyanide and hydrogen cyanide measurements in the lower stratosphere: Implications for methyl cyanide sources and sinks, *J. Geophys. Res.*, **102**, 25,501–25,506, 1997.
- Schröder, F., and J. Ström, Aircraft measurements of sub-micrometer aerosol particles (>7 nm) in the midlatitude free troposphere and the tropopause region, *Atmos. Res.*, **44**, 333–356, 1997.
- Singh, H. B., Y. Chen, G. L. Gregory, G. W. Sachse, R. Talbot, D. R. Blake, Y. Kondo, J. D. Bradshaw, B. Heikes, and D. Thornton, Trace chemical measurements from the northern midlatitude lowermost stratosphere in early spring: Distributions, correlations, and fate, *Geophys. Res. Lett.*, **24**, 127–130, 1997.
- Smith, W. L., S. Ackerman, H. Revercomb, H. Huang, D. H. DeSlover, W. Feltz, L. Gumley, and A. Collard, Infrared spectral absorption of nearly invisible cirrus clouds, *Geophys. Res. Lett.*, **25**, 1137–1140, 1998.
- Solomon, S., S. Borrmann, R. R. Garcia, R. Portmann, L. Thomason, L. R. Poole, D. Winker, and M. P. McCormick, Heterogeneous chlorine chemistry in the tropopause region, *J. Geophys. Res.*, **102**, 21,411–21,429, 1997.
- Stohl, D. D., and P. Seibert, Accuracy of trajectories as determined from the conservation of meteorological tracers, *Q. J. R. Meteorol. Soc.*, **24**, 1465–1484, 1998.
- Stohl, D. D., G. Wotawa, P. Seibert, and H. Kromp-Kolb, Interpolation errors in wind fields as a function of spatial and temporal resolution and their impact on different types of kinematic trajectories, *J. Appl. Meteorol.*, **34**, 2149–2165, 1995.
- Ström, J., and S. Ohlsson, Real-time measurements of absorbing material in contrail ice using a counterflow virtual impactor, *J. Geophys. Res.*, **103**, 8737–8741, 1998.
- Talbot, R. W., et al., Chemical characteristics of continental outflow from Asia to the troposphere over the western Pacific Ocean during September–October 1991: Results from PEM-West A, *J. Geophys. Res.*, **101**, 1713–1725, 1996.
- Talbot, R. W., et al., Chemical characteristics of continental outflow from Asia to the troposphere over the western Pacific Ocean during February–March 1994: Results from PEM-West B, *J. Geophys. Res.*, **102**, 28,255–28,274, 1997.
- Waibel, A. E., H. Fischer, B. Lee, J. Lelieveld, P. C. Siegmund, J. Ström, and F. G. Wienhold, Highly elevated CO concentrations in the upper troposphere and lower stratosphere at northern midlatitudes during the STREAM-II summer campaign in 1994, *Chemosphere*, in press, 1999.
- Wienhold, F. G., T. Zenker, and G. W. Harris, A dual channel two tone modulation tunable diode laser spectrometer for ground based and airborne trace gas measurements, *Proc. SPIE Int. Soc. Opt. Eng.*, **2112**, 31–41, 1994.
- Winker, D. M., and M. A. Vaughan, Vertical distribution of clouds over Hampton, Virginia, observed by lidar under the ECLIPS and FIRE ETO programs, *Atmos. Res.*, **34**, 117–133, 1994.
- World Meteorological Organization (WMO), Scientific assessment of ozone depletion: 1994, Geneva, Switzerland, 1995.
- World Meteorological Organization (WMO), Global Ozone Research and Monitoring Project Report, *Rep. 43*, Geneva, Switzerland, 8.1–8.42, 1998.
- Zuber, A., and G. Witt, Optical hygrometer using differential absorption of hydrogen Lyman-alpha radiation, *Appl. Opt.*, **26**, 3083–3098, 1987.
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