

Aircraft measurements of ClO and HCl during EASOE 1991/92

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Abstract. As part of the European Arctic Stratospheric Ozone Experiment (EASOE), performed in the winter period 1991/92, stratospheric chlorine monoxide (ClO) and hydrochloric acid (HCl) have been observed using the Submillimeter Atmospheric Sounder (SUMAS). The instrument measures the thermal emission of the atmosphere in the frequency range 620-650 GHz. Due to strong tropospheric water vapor absorption in this frequency range the radiometer has to be operated on-board a high-flying aircraft. During EASOE several flight missions were performed over northern Europe in the periods 10-13 December 1991, 5-14 February 1992 and 7-13 March 1992 using the research aircraft FALCON operated by the German Air and Space Organization (DLR). We report on two flights in February and two in March. From a first analysis it is found that the HCl column content as observed during the March flight, increased by about 20-30 % compared to the results for the mid-February flight. On the other hand, high ClO amounts, particularly at lower altitudes, were observed in February. From the observed trends for the ClO and HCl abundances we assume that some HCl had been converted to reactive chlorine indicating a chemically disturbed Arctic vortex in February.

Introduction

There is clear evidence that stratospheric ozone can be destroyed effectively with chlorine as a catalyst [Solomon, 1990]. Measurements in the Antarctic "ozone hole" have shown an anomalously high concentration of the ClO radical well correlated with low ozone values [deZafra *et al.*, 1987; Solomon *et al.*, 1987; Anderson *et al.*, 1989]. This rapid ozone loss during austral spring is believed to be caused largely by the ClO dimer mechanism [Molina and Molina, 1987] whereas the increased ClO levels result from heterogeneous reactions occurring on the surfaces of polar stratospheric clouds (PSC's).

Stratospheric ozone loss in the Arctic and at mid-latitudes is an established fact [WMO, 1988], but the question to what extent the Arctic winter atmosphere may suffer an ozone loss similar to Antarctica is still an unsolved problem. Measurements of ClO, a good tracer to detect chemically perturbed regions, and of HCl, one of the major chlorine reservoirs, are essential to a better understanding of the Arctic ozone chemistry.

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Our instrument detects the thermal emission from the rotational transitions of H^{35}Cl at 625.917 GHz and ^{35}ClO at 649.448 GHz. As the pressure broadened line profiles are spectrally resolved, the measurements provide information on the vertical volume-mixing-ratio (VMR) profiles. Due to strong water vapor absorption in the frequency range of interest, the observations have to be performed from a high-flying aircraft leaving the tropospheric fraction of approximately 95 % of the total water vapor content below flight altitude. Two different radiometer front-ends for SUMAS were used alternately during EASOE, one tuned to measure HCl and, with only minor adjustments, ozone, and the other being optimized for ClO measurements. However, it was not possible to operate both radiometers simultaneously.

In this paper we focus on a comparison of ClO and HCl abundances in February and March. The results of four flights are discussed in detail.

Technical Information on Sensor

Both radiometers are heterodyne detection systems converting the incoming atmospheric signal to an intermediate frequency (if) band, located in the 10-12 GHz range. The if signal, at an instantaneous bandwidth of 1.2 GHz, is spectrally analyzed by the backend spectrometer consisting of a filterbank and a 40 MHz-bandwidth Chirp Transform Spectrometer (CTS) [Hartogh and Hartmann, 1992]. Details of the receiver design can be found in [Nett *et al.*, 1990 and 1991a,b]. Table 1 summarizes the technical data of the HCl and the ClO receivers.

The atmospheric signal enters the SUMAS system, at an elevation angle of +15°, through a pressure window in the aircraft fuselage fabricated of high-density polyethylene. The instrument is calibrated by coupling the input alternately to two blackbodies, one at ambient and one at liquid nitrogen temperature, respectively. An individual calibrated spectrum is obtained every 9 seconds.

Flights

The operations base during the EASOE campaign was Kiruna, Sweden. In addition to the transfer flights between Munich and Kiruna 12 local flights, with ClO measured on eight flights, were performed over northern Scandinavia. A typical flight took about 2.5 hours and covered a flight distance of about 2,000 km. Taking into account climb and descent phases the actual measuring time at cruising altitude (10-13 km) is reduced to about two hours. Aircraft data such as altitude, geographic position and outside air

TABLE 1: Specifications of SUMAS.

Receiver	HCl/O ₃	ClO
Signal frequencies	H ³⁵ Cl (625.9 GHz) O ₃ (647.8 GHz)	³⁵ ClO (649.4 GHz)
Mixing element	quasi-optical Schottky-diode mixer (uncooled)	Schottky-diode wave guide mixer (80K)
Sideband suppression	> 20 dB	
Bandwidth	1.2 GHz	
Backend Spectrometer	28 channel filterbank 10 x 80 MHz, 8 x 40 MHz, 10 x 8 MHz 40 MHz CTS with 25 KHz resolution	
System noise Temperature (ssb)	<10,000 K	<5,000 K

temperature are supplied during the flight operation by the FALCON on-board computer and stored, along with additional house-keeping data, on a magnetic tape. Quick-look information is available from the experiment computer during flight.

During the Arctic winter 1991/92 stratospheric temperatures cold enough to produce PSCs were observed only from mid-December into January. In early January enhanced ClO values were detected over northern Europe and Asia by the MLS experiment on-board the Upper Atmospheric Research Satellite (UARS) [Waters et al, 1993]. Due to a rotation manoeuvre of the satellite in mid-January, further development could not be studied until 15 February. The only ClO measurements over northern Europe during early February were performed by the SUMAS experiment.

In this paper we focus on four flights (Figure 1, Table 2). We first discuss two flights (I and II, see Table 2) in February, one with measurements of ClO and the other of HCl. The results of these flights are compared with two flights in March (III and IV, see Table 2). During February the flights were directed towards the regions of coldest temperatures (<198 K on the 475 K isentropic level), located clearly inside the vortex, while in flight III (March) the route was closer to the edge of the vortex which had moved far to the east. At the time of the last local flight, (IV), located inside the vortex, the final warming had

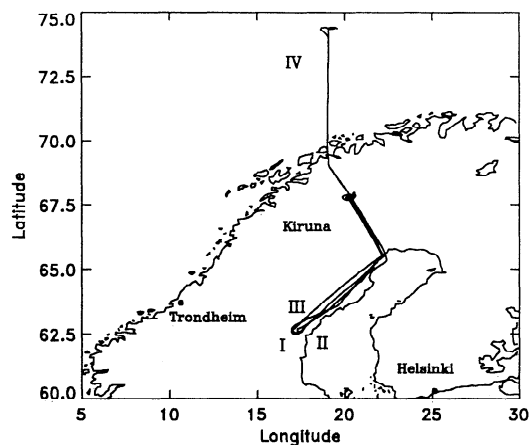


Fig. 1. Flight routes of the SUMAS field experiments discussed in the text.

TABLE 2: List of local flights used for the calculations in Figure 2 and Figure 4.

Flight No.	Date	start/landing (UTC)	Molecule
I	6 Feb., 1992	12:03 / 13:45	ClO
II	9 Feb., 1992	12:59 / 15:31	HCl, O ₃
III	10 Mar., 1992	13:26 / 15:49	HCl, O ₃
IV	12 Mar., 1992	11:55 / 14:26	ClO

started, leading to stratospheric temperatures 5-10 K higher than in February.

Data Analysis and Results

Emission line spectra were obtained by averaging individual spectra obtained for constant flight altitude and viewing direction. The spectra, with integration times of 10-20 minutes for HCl and ClO and less than 5 minutes for the strong ozone line at 647.84 GHz, are shown in Figure 2. The statistical error in an individual filterbank channel caused by the radiometric noise is a function of both bandwidth and integration time. The 3σ noise level for the different bandwidths are given in Figure 2. The error bars shown do not reflect possible linearly-sloped offset errors caused by multiple-beam interference within the window material that may be present in the experimental data. For comparison synthetic line spectra, based on model profiles as given in Figure 3, are shown (dashed lines). In order to compensate for differences in the background levels caused by water vapor and ozone, the measured curves have been shifted vertically by a few degrees. This offset value has been calculated using a least-square fit across the spectrum.

The total column amount of the individual species (O₃, HCl, ClO) is proportional to the spectral power obtained by integrating the emission feature over a given frequency interval, whereas the shape of the pressure broadened line is determined by the vertical VMR-profile. To illustrate the difference between the February and March flights the spectral power in an emission line has been integrated for a limited bandwidth (Figure 4). When computing the power integral the offset value, as determined from the spectral channels adjacent to the integration interval limits, are compensated for. As a measure of the total column amount the strong ozone line was integrated over the total usable bandwidth of 1040 MHz, while for the HCl molecule the inner 320 MHz interval was used covering the major fraction of the emission line (see synthetic spectra in Figure 2b,e). To distinguish between the contributions of high and low altitude ClO the spectral power integrals have been computed for two different bandwidths, 80 and 160 MHz, respectively.

Ozone. The ozone profile used in the model was taken from an ozone sounding at Kiruna on 10 March. Slight differences between the synthetic and the measured spectrum (Figure 2a) can be attributed to an inadequate knowledge of the ozone profile at altitudes above approximately 30 km where no sonde data are available. Comparing the power integrals (Figure 4) for the February and March flights it is seen that the ozone concentration was smaller for the February flight. This is in qualitative agreement with the total ozone data of the TOMS experiment, which measured 320 DU on 10 March

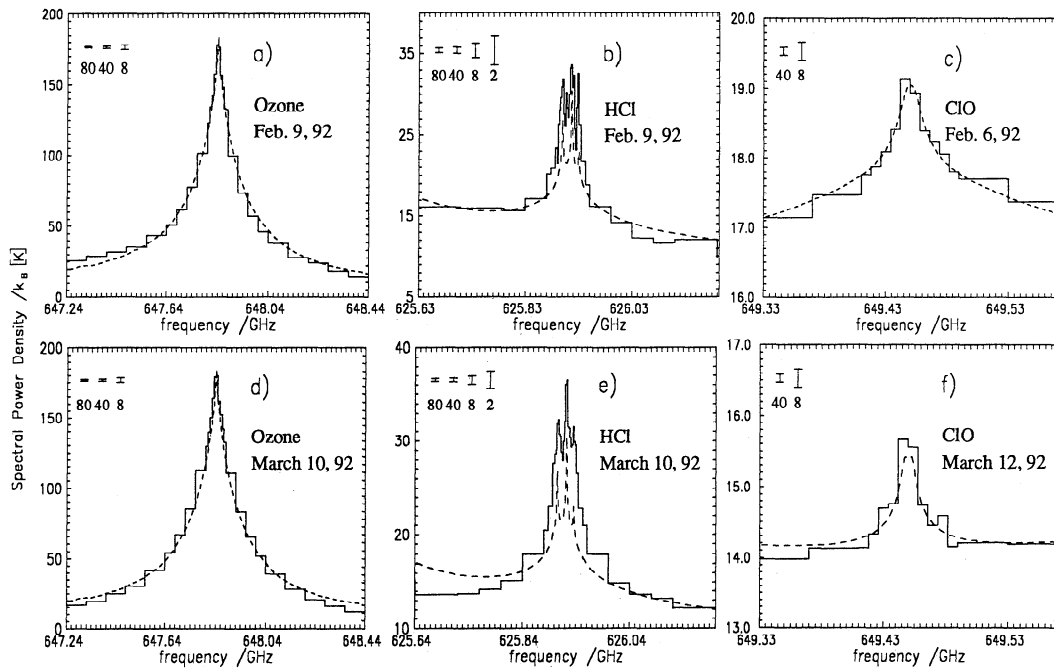


Fig. 2. O₃, H³⁵Cl and ³⁵ClO spectra measured in February (a, b,c) and in March (d,e,f). Dashed lines are the results of radiative transfer calculations with given model profiles (Figure 3). The error bars in the upper left corner of each diagram correspond to the 3σ radiometric noise level of an individual filterbank channel with the bandwidth [MHz] noted below.

compared to 260 DU on 10 February (information provided by the EASOE data center at NILU).

HCl. Figure 2b,e shows the theoretical spectrum computed using an HCl profile from [WMO, 1985] for the altitude range 20-50 km and from [Waters, 1989] for 50-80 km altitude. The triplet structure of the emission feature is clearly seen in the 2 MHz channels near the line center. Slight differences occur between the February and March data because the center frequency of the receiver was shifted by 4.8 MHz for the March flight in order to fully resolve the three peaks in the high-resolution part of the backend. The wings of the line, especially in March, are much stronger than expected from the model spectrum. The reason for this might be an overall increase of stratospheric HCl since 1985 [Stachnik, 1992]. From Figure 4 an increase of about 20-30 % in total of HCl for the March flight compared to the February data can be derived.

ClO. A vertical ClO profile for disturbed chemical conditions [deZafra *et al.*, 1989] shown in Figure 3 has been used to compute the theoretical spectrum in Figure 2c, whereas a profile for normal conditions [Ko and Sze, 1984] has been used for the spectrum in Figure 2f. The broader line shape in February indicates larger ClO concentrations at lower altitudes.

In order to study this effect in more detail we assumed a ClO profile with the same shape as shown in Figure 3 for disturbed chemistry with a lower layer ranging from flight altitude (11 km) to 28 km and an upper layer ranging from 28 to 50 km. Each of the power integrals calculated for 80 and 160 MHz bandwidth contains information on both the upper and the lower ClO-layer with a known relationship between the contributions of the two layers given by the weighting functions. As the lower layer contributes a larger fraction to the 160 MHz integral than to the 80 MHz value the change of both power integrals from February to March

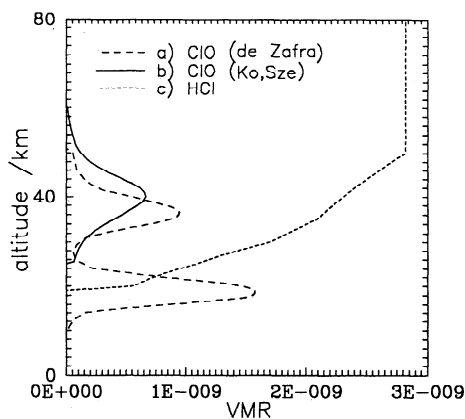


Fig. 3. Model vertical profiles of HCl and ClO.

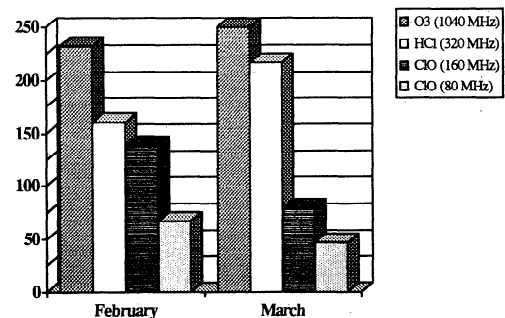


Fig. 4. Integrated spectral power for different bandwidths (see legend) of the spectra shown in Figure 2. The units of the vertical axis are 10⁻¹⁷ W for ClO, 10⁻¹⁶ W for HCl and 2·10⁻¹⁵ W for ozone.

can be used to extract quantitative information on variations in the lower and upper layers. Calculations based on the above assumptions indicated only minor changes in the upper layer concentration whereas the lower layer ClO had decreased by about 70-80 %. This effect can also be seen from Figure 4, indicating that the ratio between the 160 MHz and the 80 MHz values significantly changed from February to March.

Conclusions

Preliminary analysis of the data set collected during EASOE shows a condition of perturbed chemistry over northern Scandinavia in February with increased ClO amounts in the lower stratosphere and a reduced HCl column amount. Similar measurements in March indicate a recovery of the stratosphere with decreasing ClO accompanied by increasing HCl concentrations.

In the next step the data from the remaining flights will be processed, and profile retrievals will be performed for ClO and HCl for the altitude range 20 to 50 km.

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