

Chlorine Activation and Chemical Ozone Loss Deduced from HALOE and Balloon Measurements in the Arctic during the Winter of 1999-2000

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Abstract. We employ HALOE observations and balloon-borne measurements (on the large Observations of the Middle Stratosphere (OMS) and Triple balloons as well as on two small balloons) to investigate ozone loss in the stratospheric vortex in the 1999-2000 Arctic winter. Using HF and CH₄ as long-lived tracers, we identify chlorine activation and chemical ozone destruction in the polar vortex. Reference relations, representative of chemically undisturbed “early vortex” conditions, are derived from the OMS remote and in situ balloon measurements on 19 November and 3 December 1999, respectively. Deviations from this “early vortex” reference are interpreted as chemical ozone loss and heterogeneous chlorine activation. The observations show an extensive activation of chlorine; in late February 2000 the activation extends to altitudes of 600 K. Between 360 and 450 K chlorine was almost completely activated. At that time, about 70% of the HCl column between 380-550 K was converted to active chlorine. Furthermore, the measurements indicate severe chemical ozone loss, with a maximum loss of over 60% in the lower stratosphere (415-465 K) by mid-March 2000. Substantial ozone loss was still observable in vortex remnants in late April 2000 (80 ± 10 DU between 380-550 K). The average loss in column ozone between 380-550 K, inside the vortex core, in mid-March amounted to 84 ± 13 DU.

1. Introduction

During the past decade, evidence for substantial winter/spring ozone depletion in the Arctic lower stratosphere has been reported in numerous studies [e.g., *Kyrö et al.*, 1992; *Browell et al.*, 1993; *Waters et al.*, 1993; *Manney et al.*, 1994; *Donovan et al.*, 1995; *Goutail et al.*, 1999; *Andersen*, 1999]. A considerable number of large coordinated experiments have been conducted during the Arctic winter months since the late 1980s that addressed the issue of chemical ozone destruction in the Arctic [e.g., *Hofmann et al.*, 1989; *Turco et al.*, 1990; *Pommereau and Schmidt*, 1991; *Anderson and Toon*, 1993; *Pyle et al.*, 1994]. The most extensive measurement campaign so far in the polar region, however, was SOLVE-THESEO 2000 [*Newman et al.*, 2002], which was carried out during winter 1999-2000.

The Arctic stratosphere in winter 1999-2000 was unusually cold from mid-November 1999 to late March 2000. Nonetheless, the lower stratospheric vortex developed more slowly than usual and was weaker than average before late December [*Manney and Sabutis*, 2000]. As expected for cold vortex conditions, strongly elevated levels of active chlorine are reported for January to early March 2000 [e.g., *Santee et al.*, 2000; *Vömel et al.*, 2001; *Bremer et al.*, 2002; *Stimpfle*, 2002; *Vogel et al.*, 2002]. Moreover, a significant denitrification was observed throughout the Arctic vortex core [e.g., *Santee et al.*, 2000; *Fahey et al.*, 2001; *Popp et al.*, 2001]. As a consequence of chlorine activation and denitrification, strong chemical ozone loss was observed in the Arctic vortex in 1999-2000 by a variety of instruments [e.g., *Sinnhuber et al.*, 2000; *Santee et al.*, 2000; *Richard et al.*, 2001; *Robinson et al.*, 2002; *Rex et al.*, 2002; *Salawitch et al.*, 2002; *Newman et al.*, 2002]

Here, we focus on the analysis of chlorine activation and chemical ozone loss based on balloon measurements during SOLVE-THESEO 2000 in conjunction with satellite observations from the Halogen Occultation Experiment (HALOE). In early 2000, there was a good coverage of the high northern latitudes by HALOE; therefore a large number of profiles were obtained in the vortex in late February, mid-March, and late April 2000.

We employ concurrent measurements of chemically active compounds like HCl or ozone and long-lived tracers to deduce chlorine activation and chemical ozone loss inside the Arctic vortex. This methodology was originally applied by *Proffitt et al.* [1990, 1993] to observations of N_2O and O_3 by high altitude aircraft and was subsequently extended to measurements from satellite and balloon platforms [e.g., *Müller et al.*, 1996, 2001; *Salawitch et al.*, 2002, and references therein]. It is described in detail elsewhere [e.g., *Proffitt et al.*, 1993; *Müller et al.*, 1996, 2001; *Salawitch et al.*, 2002; *Richard et al.*, 2001, and references therein]. Briefly, the availability of measurements of long-lived tracers provides information on the magnitude of diabatic descent inside the polar vortex. Diabatic descent means that air observed at a given level at the time when chemical change is expected to have occurred will have originated at greater altitudes earlier in the season. Therefore, the change in the amount of ozone throughout the winter at a fixed altitude cannot be directly used to quantify chemical ozone loss. If, however, one can account for descent in an analysis of the temporal development of chemically active species, then a meaningful comparison of early and late vortex measurements is possible. In this way, a quantitative estimate of the chemical change of species like O_3 or HCl may be deduced.

We used several balloon flights during SOLVE-THESEO 2000 to derive HCl/tracer and ozone/tracer reference relations for early vortex conditions. These relations are combined with the HALOE vortex measurements to study chlorine activation and deactivation as well as chemical ozone loss in winter and early spring 1999-2000 until late April 2000.

The most suitable tracers among the species measured by HALOE are HF and CH₄. Their stratospheric lifetime is long enough so that they may be considered quasi-inert for the time period and latitudes in question here. HF is produced in the stratosphere following the breakdown of fluorine-containing source gases, in particular chlorofluorocarbons. Therefore the mixing ratio of HF increases with altitude in the stratosphere. The only known stratospheric sink of HF is transport to the troposphere [e.g., *Chipperfield et al.*, 1997]. It may therefore be considered chemically inert in the stratosphere. In contrast to HF, the source region of CH₄ is the troposphere. In the stratosphere CH₄ is mainly destroyed by reaction with OH, Cl, and O(¹D) so that its mixing ratio decreases with altitude. The stratospheric loss rate of CH₄ is below $\approx 3 \cdot 10^3$ molecules cm⁻³s⁻¹ [e.g., *Bergamaschi et al.*, 1996]. This implies a lifetime of more than 10 years at altitudes below the 20 hPa level throughout the stratosphere; at winter polar latitudes the CH₄ lifetime is considerably greater.

Questions have been raised about the validity of the application of tracer relations to deduce quantitative estimates of chemical change [see the discussion in *Michelsen et al.*, 1998; *Plumb et al.*, 2000; *Müller et al.*, 2001; *Salawitch et al.*, 2002; *Harris et al.*, 2002]. The comprehensive data set that was collected during SOLVE-THESEO 2000 provides a means of addressing such questions. Here, we

conclude that, for the meteorological conditions in the Arctic vortex in winter 1999-2000, a quantitative estimate of chemical change is possible. Neither mixing processes during the period of substantial ozone loss nor uncertainties in the vortex measurements over the course of the winter had a substantial impact on the deduced chemical change. We obtain a chemical loss in column ozone (for 380-550 K) inside the vortex core in mid-March 2000 of 84 Dobson units (DU) with an uncertainty of 13 DU.

2. Observations of ozone/tracer and HCl/tracer relations in Arctic winter 1999-2000

2.1. Measurements

Figure 1.

For this study, we employ measurements from a suite of instruments (Table 1). HALOE aboard the Upper Atmosphere Research Satellite (UARS) measures O_3 , H_2O , NO_2 , NO , HCl , HF , and CH_4 in solar occultation [*Russell et al.*, 1993]. Each day usually 15 sunset and 15 sunrise observations are obtained along two approximately constant latitude belts. Owing to the satellite orbit and the solar occultation observational geometry, the latitudes of sunrise and sunset observations vary with the season. In Fig. 1, the latitudinal coverage of HALOE in the time period in question, between November 1999 and April 2000, is shown. Here we analyze O_3 , HCl , HF , and CH_4 measurements from HALOE using data processing version 19; accuracies are shown in Table 2.

During SOLVE-THESEO 2000, Observations of the Middle Stratosphere (OMS) balloon-borne measurements were achieved from Esrange (67.5°N, 21.0°E)

near Kiruna, northern Sweden, of a variety of chemical species; here we focus on measurements of long-lived tracers (HF, CH₄, N₂O), ozone, and HCl. The OMS-remote payload usually consists of two instruments, namely the MkIV instrument [Toon *et al.*, 1999] and the Submillimeterwave Limb Sounder [SLS, Stachnick *et al.*, 1992]. The accuracy of MkIV measurements of HF, CH₄, O₃, and HCl are $\approx 5\%$. The SLS accuracy depends somewhat on the tangent altitude; values at 20 km are 11%, 12%, and 5% for N₂O, HCl, and O₃, respectively. From the OMS-in-situ measurements we use here the ozone measurements of the JPL dual cell ozone UV photometer [Proffitt and McLaughlin, 1983] and the tracer measurements of the Lightweight Airborne Chromatograph Experiment (LACE), an in situ gas chromatograph [Elkins *et al.*, 1996]. A conservative estimate of the accuracy of the JPL ozone UV photometer is 3-5%, the precision of the LACE CH₄ and N₂O measurements is 1%.

Long-lived tracers were also measured by DESCARTES (Détermination Et Séparation par Chromatographie lors de l'Analyse des Résultats des Traceurs Échantillonnés dans la Stratosphère), an instrument which collects samples in situ using an adsorbent material followed by post-flight gas chromatography and electron capture detection [Danis *et al.*, 2000]. Here we use DESCARTES CFC-11 measurements with an accuracy of $\approx 10\%$. Ozone was measured concurrently, either by ozone sondes or by the UV-vis spectrometer SAOZ [Système d'analyse par observation zénithale, Goutail *et al.*, 1999]. The accuracy of SAOZ ozone measurements varies from 1.6% at 30 km down to 3.5% at 11 km; a well-prepared ozone sonde has an accuracy of 5-10% [Harris *et al.*, 1998]. DESCARTES is normally launched on small balloons but was flown on 3 December 1999 as part of

the OMS-remote payload (Table 1).

Figure 2.

Furthermore, two flights of the Triple balloon payload were made from Esrange, near Kiruna on 27 January 2000 and on 1 March 2000 [Vogel *et al.*, 2002]. Here we employ the measurements of long-lived tracers obtained by the cryogenic whole air sampler on board Triple [Schmidt *et al.*, 1987] on 27 January 2000 together with ozone sonde measurements on board the HALOZ balloon [Vömel *et al.*, 2001] that was launched about one hour after Triple. The analytical precision of the gas-chromatography measurements of N₂O [Engel *et al.*, 1997] and CH₄ [Levin *et al.*, 1999] of the air samples collected in the Triple flight is 1% of the tropospheric value for N₂O and 3 ppb (0.2-0.6%) for CH₄. The accuracy of the NOAA/CMDL standard employed for both gases is 1%.

The vertical profiles of the tracers CH₄ and HF (plotted against potential temperature as the vertical coordinate) measured by MkIV on OMS-remote and by the OMS-in-situ instruments are compared in Fig. 2 with the Triple measurements, obtained about two months later. While the CH₄ profiles observed by OMS-remote and in situ are in agreement, the Triple measurements show the descent inside the vortex between early December and late January. Further, HALOE measurements in the late, but still intact vortex in mid-March (blue circles in Fig. 2) indicate continuing descent after the end of January.

In this study, we employ a combination of both in situ and remote sensing instruments (Table 1). The in situ instruments are the JPL dual cell ozone photometer and the tracer measurements of the LACE instrument on board the OMS-in-situ balloon, the cryosampler on board the Triple gondola, the DESCARTES instrument and the ozone sonde measurements. The balloon-borne

remote sensing instruments are the MkIV and the SLS instrument on board the OMS-remote balloon, and the SAOZ instrument. HALOE is a space-borne solar occultation instrument. Measurements from remote sensing instruments constitute spatial averages along the limb path of several hundred kilometers. In the case of HALOE, the averaging distance across the limb, when the weighting function is considered, is ≈ 300 km. The HALOE field of view is specified to be narrow enough to measure features ≤ 2 km in vertical extent. The reported mixing ratios for the MkIV and the SLS instrument represent horizontal averages along a line of sight of about 350 and 380 km respectively. The vertical resolution is 2 km for MkIV and 2-3 km for SLS.

Thus, if the location of the measurement of one of the remote sensing instruments is close to the vortex edge, outside vortex air may be included in such an average. On the other hand, in situ measurements might be influenced by small scale effects, like e.g., laminae of out of vortex air, that are not representative of the vortex as a whole. Furthermore, the measurements of the remote sensing instruments constitute vertical averages in the order of a few kilometers while a much higher vertical resolution is achieved by the in situ instruments.

2.2. Tracer relations in the “early vortex”

To derive reference relations of a tracer with the chemically active species ozone and HCl, we consider observations at high latitudes in late November and early December 1999. The reference relation should be derived for a situation when the vortex has formed and the air masses inside the “early vortex” are already isolated from the surrounding air. Additionally, however, the reference

relation must be derived for a time period before any noticeable chemical change, i.e. chlorine activation or chemical ozone loss, has occurred. Thus, the reference relation needs to be defined for a time in winter that is late enough, so that the vortex is strong, but at the same time early enough, so that no chemical change has yet occurred.

In studies based on HALOE measurements during earlier Arctic winters [Müller *et al.*, 1996, 1999, and references therein], HALOE measurements inside the early vortex between mid-November and early December were employed to deduce a reference relation. However, in early winter 1999-2000 there were only very few HALOE measurements at high latitudes. In November and December 1999 there were no observations poleward of 51°N, and 49°N respectively, and no observations for potential vorticity values (at 475 K) greater than 27 potential vorticity units based on UKMO analyses (PVU; $1 \text{ PVU} = 10^{-6} \text{ K m}^2 \text{ kg}^{-1} \text{ s}^{-1}$). (Potential vorticity values characteristic of the polar vortex exceeded 30 PVU at 475 K at that time). Therefore, there are no HALOE measurements in the early Arctic vortex in late 1999. Fortunately, during this period, two balloon flights were conducted inside the vortex: the OMS-in-situ flight on 19 November 1999 and the OMS-remote flight on 3 December 1999. Measurements from these two flights were used here to define the reference relation for chemically unperturbed conditions in the early Arctic vortex in 1999. Further, vortex observations of CFC-11 and ozone in December 1999 and January 2000 by the DESCARTES instrument and concurrent SAOZ or ozone sonde measurements on small balloons could be employed for comparison. Moreover, measurements of ozone and long-lived tracers are available from the Triple and the HALOZ flights on 27 January 2000 in the

established vortex (Table 1).

Figure 3.

Balloon-borne measurements of HF are only available from the MkVI instrument on the OMS-remote flight on 3 December 1999. Therefore, data from this flight are used here to deduce a HCl/HF reference relation (Fig. 3, top panel; Table 3, relation R1) and an O₃/HF reference relation (Fig. 3, bottom panel; Table 3, relation R5).

Figure 4.

Observations of the HCl/CH₄ relation from the MkIV on the OMS-remote flight are shown in Fig. 4 (top right panel). Because SLS on OMS-remote does not measure CH₄, employing N₂O as the long-lived tracer allows the comparison of the MkIV and SLS observations (Fig. 4, top left panel). Although there are some discrepancies, there is overall reasonable agreement between the MkIV and SLS observations. For N₂O mixing ratios less than ≈ 250 ppbv, the SLS and the MkIV observations agree within the measurement uncertainties. For N₂O mixing ratios greater than ≈ 250 ppbv, SLS show lower HCl values than MkIV; however, at these altitudes reported SLS accuracies are ≈ 20 ppbv.

SLS made measurements in two different directions during the flight; first, observing latitudes poleward of 68°N and second, observing latitudes equatorward of 68°N, that is in the same direction as MkIV. However, for the HCl/N₂O relation, neither the agreement between SLS and MkIV nor any remaining discrepancy depends on whether SLS observes latitudes north or south of 68°N. Empirical polynomial fits to the early vortex relation based on MkIV measurements of HCl/CH₄ (R3) and HCl/N₂O (R4) are listed in Table 3 and are shown in Fig. 4 (top panels).

Observations of the O₃/CH₄ relation from the OMS-remote and the OMS-

in-situ payload show close agreement, except for $0.6 \text{ ppm} < \text{CH}_4 < 1.3 \text{ ppm}$, where the OMS-in-situ measurements show lower O_3 mixing ratios (Fig. 4, bottom right panel); this discrepancy is further discussed below (see also Section 3.1.1). Measurements of the O_3/CH_4 relation inside the established vortex on 27 January 2000 by the Triple and HALOZ payloads [Vömel *et al.*, 2001; Vogel *et al.*, 2002] show greater ozone values than measured by OMS-in-situ, but are in accordance with the MkIV measurements (Fig. 4, bottom right panel).

Again, if N_2O is used as the long-lived tracer, SLS observations may also be considered (Fig. 4, bottom left panel) in addition to the MkIV and the OMS-in-situ measurements. The observations by SLS and MkIV for air masses south of 68°N (blue and red solid squares in Fig. 4, bottom left panel) agree well, whereas the SLS observations for air masses north of 68°N (blue solid circles in Fig. 4, bottom left panel) more closely resemble the OMS-in-situ measurements taken two weeks earlier. This suggests that the ozone measurements from the three different instruments are correct and that the discrepancies are due to ozone variability inside the early vortex in 1999. As in the case of the O_3/CH_4 relation, $\text{O}_3/\text{N}_2\text{O}$ measurements by the Triple/HALOZ balloons in the established vortex in late January are in accordance with the MkIV observations. Empirical polynomial fits to the early vortex relation of O_3/CH_4 based on MkIV and OMS-in-situ measurements (R7 and R8 respectively, in Table 3) and $\text{O}_3/\text{N}_2\text{O}$ again based on MkIV and OMS-in-situ measurements (R6 and R9 respectively, in Table 3) are shown in Fig. 4, bottom panels.

Figure 5.

In addition to measurements of the long-lived tracers HF, N_2O , and CH_4 , six vertical profile measurements of CFC-11 were made in the vortex in winter 1999-

2000 (Table 1). For each CFC-11 measurement, a concurrent ozone measurement is available so that those observations may be used to corroborate the validity of an early vortex reference relation. However, owing to the very low CFC-11 concentrations in the early vortex at altitudes above ≈ 22 km, an O_3 /CFC-11 relation can only provide information at lower altitudes. Nonetheless, the six measurements of the O_3 /CFC-11 vortex relation by four different instruments in the time period from 19 November 1999 to 28 January 2000 all are in agreement (Fig. 5) for mixing ratios of CFC-11 greater than ≈ 100 ppbv. This indicates that the ozone/tracer relation did not change significantly over this time period and altitude range. At greater altitudes (CFC-11 less than ≈ 100 ppbv) there is some indication of lower ozone mixing ratios for measurements later in winter. However, owing to the combined uncertainties of the different ozone and CFC-11 measurements, it is not possible to ascribe this observation unequivocally to chemical ozone loss in early winter. *Robinson et al.* [2002] further exploit the CFC-11 measurements discussed here to deduce chemical ozone loss.

Figure 6.

HALOE observations *outside* the vortex in mid-latitudes in November and December 1999 show an ozone/tracer relation that is distinctly different from the early vortex relation. This is shown in Fig. 6 for the O_3 /HF relation observed between 26 November and 31 December 1999; clearly larger ozone mixing ratios are observed for the same value of HF than the reference relation for the early vortex (relation R5 in Table 3).

2.3. Tracer relations in the Arctic vortex in February and March 2000

In winter 2000, HALOE sampled vortex air masses in late February (19–25. 2. 2000) and in mid-March (11–18. 3. 2000). We used criteria for defining the edge of the polar vortex and the line bounding of the vortex core (the poleward border of the vortex boundary region) [*Nash et al.*, 1996]. These criteria are based on potential vorticity gradients and the wind maximum along potential vorticity isolines. The location of the vortex edge determined in this way is in agreement with that deduced from high-resolution tracer measurements, although small-scale features are not captured due to the relatively coarse resolution of the meteorological analyses [*Greenblatt et al.*, 2002]. We determined the *Nash et al.* [1996] criteria on three isentropic levels: 475 K, 550 K and 650 K (except for 15–18. 3., when the 650 K level was not used). Then the location of the vertical profile measured by HALOE was advected using a trajectory calculation to the synoptic time of the PV analysis (see also Fig. 9 below). If the position of a HALOE measurement determined in this way was located poleward of the vortex boundary on all considered isentropic levels, it was considered to be within the vortex, if it was in addition located poleward of the line bounding the vortex core, it was considered to be inside the vortex core. In the following we will refer to the region between the vortex edge and the vortex core as the “outer vortex.”

Figure 7.

2.3.1. Chlorine activation: The HCl-tracer relation. The HALOE HCl measurements in the vortex core in February 2000 (Fig. 7) show extremely low HCl mixing ratios of below 0.1 ppbv for HF mixing ratios below 0.7 ppbv, i.e. for levels below ≈ 450 K, indicating complete activation of the HCl reservoir

below these altitudes. Considering the relation of the HALOE HCl and HF vortex measurements in February 2000 together with the reference relation (R1 in Table 3) from the MkIV measurements on 3 December 1999 (Fig. 7), it can be deduced that the layer of practically complete chlorine activation extended to altitudes where up to 1.5 ppbv of HCl is expected from the reference relation. Further, partial activation of HCl is observed for HF up to ≈ 1.3 – 1.4 ppbv, i.e. for levels up to ≈ 600 K. By mid-March (purple and red diamonds in Fig. 7), a small recovery of HCl is noticeable in the vortex core. Below HF ≈ 0.5 ppbv (≈ 420 K), however, HCl mixing ratios are still mostly below 0.2 ppbv, indicating that very little chlorine recovery took place at these lower altitudes. In the outer vortex similar patterns were observed as in the vortex core (purple and red crosses in Fig. 7). However, the HCl mixing ratios were somewhat larger, indicating a less complete activation and a faster recovery in this region.

Figure 8.

2.3.2. Chemical ozone loss: The ozone-tracer relation. The O_3/CH_4 and the O_3/HF relations for the vortex core and outer vortex air-masses sampled by HALOE in winter 2000 are compared in Fig. 8 (diamonds and plus signs, respectively) against reference relations for the early vortex deduced from the MkIV measurements on the OMS-remote flight and from the OMS-in-situ observations. For HF as the long-lived tracer (Fig. 8, bottom panel), the reference relation (R5, Table 3) from MkIV on OMS-remote is shown; for CH_4 as the long-lived tracer (Fig. 8, top panel), both the reference relation from MkIV on OMS-remote (R7) and from OMS-in-situ (R8, Table 3) are depicted. HALOE ozone/tracer measurements at the same locations as the HCl/HF measurements from Fig. 7 are shown here, i.e. the same criteria were applied for the selection of vortex core and

outer vortex observations for the measurements shown in Figs. 7 and 8. Clearly, all HALOE observations in March 2000 in the vortex core at altitudes below ≈ 500 K ($\text{CH}_4 = 0.5$ ppmv, $\text{HF} = 1.2$ ppbv) show lower ozone values than the reference relation for the early vortex, indicative of chemical ozone loss. Observations in late February in the vortex core show a stronger deviation from the reference relation at lower values of CH_4 and at larger values of HF , i.e., at greater altitudes, whereas at lower altitudes (larger values of CH_4 and lower values of HF) the February relations are closer to the reference relations.

The HALOE vortex core measurements in mid-March show extremely low ozone mixing ratios below 1 ppmv in the lower stratosphere ($\text{CH}_4 \approx 1.0\text{--}0.6$ ppmv; $\text{HF} \approx 0.6\text{--}1.0$ ppbv) and a substantial deviation from the reference relation, i.e. a strong chemical ozone loss down to low altitudes ($\text{CH}_4 \approx 1.5$ ppmv; $\text{HF} \approx 0.2$ ppbv).

Measurements in the outer vortex (plus signs in Fig. 8) show considerably more variability than the vortex core observations. For both February and March, some of the outer vortex profiles agree with the vortex core observations, while other profiles show substantially greater ozone values for a given tracer value. This finding could be either due to a weaker ozone loss in the outer vortex or due to mixing-in of outside vortex air that would lead to an increase in ozone for a given tracer value [Müller *et al.*, 2001; Tilmes *et al.*, 2002].

Figure 9.

2.3.3. Vortex remnants in late April 2000. The life cycle of the Arctic vortex in 2000 ended with the final warming in early April [Waugh and Rong, 2001; Newman *et al.*, 2002]. However, vortex remnants were still noticeable in potential vorticity analyses in late April (Fig. 9). Such vortex remnants were sampled by

Figure 10.

HALOE on 29 and 30 April 2000 at 64° – 66° N, 116° – 121° E (black dots in Fig. 9 indicate the location of the HALOE measurements). The HCl/HF relation showed values very similar to those of the early vortex relation from early December (Fig. 10, top panel, purple triangles) for HF mixing ratios less than ≈ 1 ppbv (potential temperature less than ≈ 475 K). In contrast, there were measurements of the O_3 /HF relation (Fig. 10, bottom panel, purple triangles) that very closely resembled the O_3 /HF relation measured by HALOE at the late stages of the intact Arctic vortex in mid-March. This observation is consistent with the view that the core of the vortex remnants in late April was not significantly affected by mixing and that the O_3 /HF relation in late April shows a “frozen-in” ozone loss signature. Such an interpretation is also in agreement with POAM III measurements of very low ozone in vortex remnants in late April 2000 [Randall *et al.*, 2002]. Moreover, the HCl/HF relation in late April (R2 in Table 3) indicates complete chemical recovery of the HCl levels at a time many weeks after the last occurrence of polar stratospheric clouds (PSC). Chemical recovery of ozone through photochemical ozone production is not possible as the ozone production rate is too low at the altitudes, latitudes and seasons in question.

The calculated loss in column ozone for the vortex remnants is 80 ± 10 DU (deduced for 380–550 K), and is thus not significantly different from the values calculated for the vortex before its break-up in mid-March (see below). This supports the view that the vortex remnant in late April 2000 remained largely intact and extended over a considerable altitude range throughout the lower stratosphere.

2.4. Chemical change in HCl and O₃ vertical profiles

2.4.1. Chlorine activation. Combining the early vortex relation R1 for HCl/HF from the MkIV measurements (Table 3) with the HALOE HF measurements in the vortex core in February and March yields a proxy for the unprocessed HCl mixing ratio. This is the HCl mixing ratio that would be expected if no chlorine activation through heterogeneous processing had occurred. This procedure is analogous to the derivation of a chemically undisturbed ozone proxy \hat{O}_3 from an early vortex reference and March/April measurements of long-lived tracers in the vortex for previous winters [e.g., *Müller et al.*, 1996, 1997, 2001]. However, for this winter, in the case of HCl, there is a possible alternative to the early vortex relation from MkIV. HALOE observations were made in small, but intact vortex remnants in late April (see above), many weeks after the last occurrence of PSC. If HCl chemically recovers and reaches the early vortex values, this late vortex relation (R2 in Table 3) could also be employed as a reference relation. However, owing to the decreasing lifetime of HCl at greater altitudes in early spring, we consider R1 to be the more reliable reference relation.

Figure 11.

The proxy HCl deduced from reference relation R1 (green diamonds in Fig. 11) may be compared with the actual HCl values measured concurrently with HF in the vortex core (red diamonds in Fig. 11). In late February 2000 (Fig. 11, top left panel), the layer of almost complete HCl activation is clearly noticeable between 360–450 K. The top of the activated layer is at ≈ 600 K. This value is consistent with the top of the activated layer deduced from balloon-borne ClO measurements on 27 January and 1 March 2000 [*Vogel et al.*, 2002]. In mid-March (Fig. 11, top

right panel), the layer below ≈ 450 K is still strongly activated with HCl values below 0.5 ppbv and a deficit in HCl exceeding 1 ppbv extending down to ≈ 400 K. Above 440 K, a partial recovery of the HCl levels has occurred. Later in March (Fig. 11, bottom left panel), also some recovery of the HCl levels at altitudes below ≈ 440 K is noticeable. In late April (Fig. 11, bottom right panel), the deactivation is complete in the lower stratosphere, i.e., the HCl values have recovered to their early vortex levels.

Integrating the vertical profile of HCl loss, one obtains an estimate of the deficit in column HCl. The column loss was calculated for the altitude range 380–550 K for the early vortex reference relation R1 (Table 4). The greatest loss was calculated for mid-February 2000; it exceeds $2 \cdot 10^{15}$ molec/cm² and amounts to $\approx 70\%$ of the unperturbed HCl column between 380–550 K. Some recovery was noticeable by mid-March 2000 with a HCl deficit of $\approx 50\%$ of the unperturbed HCl column. Very similar conclusions would be obtained if the late vortex relation (R2) were employed. The strongest variability of the calculated HCl loss for individual HCl profiles measured by HALOE was found for the entire vortex in mid-February ($\sigma = 0.6 \cdot 10^{15}$ molec/cm²). The variability was considerably less ($\sigma \approx 0.3 \cdot 10^{15}$ molec/cm²) both in the vortex core in mid-February and in the entire vortex in mid-March.

Figure 12.

Figure 13.

2.4.2. Ozone loss. Similar to earlier studies [e.g., Müller *et al.*, 1996, 1997, 2001], we combine the early vortex reference of an ozone/tracer relationship with measurements of long-lived tracers inside the vortex core later in winter to deduce a proxy for the chemically unperturbed ozone mixing ratio \hat{O}_3 . Such an ozone mixing ratio would be expected at the time of the tracer

measurement in late winter if no chemical ozone loss had occurred. Here, we employ both CH_4 and HF as long-lived tracers. Further, both the observations of the OMS-remote balloon (on 3. 12. 1999) and the OMS-in-situ balloon (on 19. 11. 1999) are used as reference relations for the early vortex.

In Fig. 12 the proxy ozone profiles $\hat{\text{O}}_3$ deduced from relation R5 (Table 3) using HF as a long-lived tracer (green symbols) are compared to the actually measured ozone vertical profile (red symbols). Also shown (black symbols) is the chemical ozone loss: the difference between proxy ozone and measured ozone.

By late February 2000, substantial ozone destruction was already noticeable as a separation between the proxy ozone and the ozone profiles measured inside the vortex core (Fig. 12, top left panel). The maximum local ozone loss in late February was about 1.3 ppmv (Fig. 12, top left panel, black symbols) and occurred at ≈ 450 K. The strongest local ozone loss was deduced from the HALOE measurements in mid-March; the local accumulated ozone loss peaked at 430–450 K and amounted to ≈ 2.2 ppmv (Fig. 12, top right panel). An ozone deficit is noticeable throughout the lower stratosphere between 380–550 K. A few days later in March (Fig. 12, bottom left panel), the measurements showed very similar conditions, although one profile showing less ozone loss was observed. Measurements in the vortex remnants in late April (Fig. 12, bottom right panel) show very similar loss profiles to those of the the mid-March observations.

For CH_4 as the long-lived tracer, both relations R7 (3 December) and R8 (19 November) were employed as the reference relation for the early vortex (Table 3). Relation R7, like R5, was derived from the MkIV measurements on 3 December 1999. In Fig. 13 the ozone loss profiles deduced from reference relations R5, R7,

and R8 are compared for the period 11–14 March. The resulting vertical profiles of ozone loss inside the vortex core using CH_4 (relations R7 and R8) are very similar to the profiles obtained using HF (relation R5) as the long-lived tracer. However, the ozone loss deduced using relation R8 is less than that deduced from R7 in this altitude regime (compare diamonds with triangles in Fig. 13). This is the case because between $\approx 420\text{--}460$ K, lower ozone mixing ratios were measured on 19 November 1999 by OMS-in-situ than on 3 December 1999 by MkIV. The differences in the deduced ozone losses that are caused by considering both OMS flights on 19 November and on 3 December 1999 and by the use of the tracers HF and CH_4 are discussed in detail in Sections 3.1.1 and 3.1.3 below.

The deduced vertical profiles of ozone loss (Fig. 12, black symbols, and Fig. 13) may be vertically integrated to obtain a measure of the chemical loss in column ozone [e.g., *Müller et al.*, 1996]. In Table 5 column ozone losses for all three reference relations (R5, R7, and R8, see Table 3) for late February (19–25. 2. 2000) and mid-March (11–18. 3. 2000) are listed. While substantial ozone losses were already evident in late February, these losses had approximately doubled by mid-March.

Figure 14.

In mid-March 2000 there was good coverage of the vortex by HALOE measurements; 18 profiles were obtained inside the vortex, of which 8 were inside the vortex core. Figure 14 shows the probability distribution of the column loss (for 380–550 K) in the vortex deduced from the reference relations R5, R7, and R8 for this period. The distribution deduced for the vortex core from all three relations shows a rather narrow range of ozone losses of 30–50 DU. If the studied vertical range is reduced to 400–500 K (not shown) a similar spread of column ozone

loss is obtained. Also noticeable if the entire vortex is considered (dotted lines in Fig. 14) is a tight range of relatively large ozone losses and a tail towards somewhat smaller losses. A similar range of ozone losses was observed in the Arctic winters 1991-1992 to 1994-1995 [Müller *et al.*, 1996]; however, for winter 1996-1997 a much greater range was found [Tilmes *et al.*, 2002]. Further, in 1996-1997, a substantial difference in ozone loss between the vortex core and the outer vortex was observed that was not apparent in measurements during late winter 2000 (Fig. 14).

3. Discussion

3.1. Discussion of uncertainties in the deduced ozone loss and chlorine activation

The lifetime of ozone in the high-latitude winter stratosphere is long enough for compact relations of ozone with tracers to be expected in the polar vortex in the absence of halogen-catalyzed ozone destruction [Proffitt *et al.*, 1992; Müller *et al.*, 2001]. However, uncertainties are introduced if the reference relation employed is not truly representative of the conditions in the vortex prior to chemical loss or if the ozone tracer relation is non-chemically altered by transport. Moreover, HALOE measures two long-lived tracers independently, namely HF and CH₄. This provides an opportunity of assessing possible uncertainties of the deduced amount of ozone loss.

3.1.1. Uncertainties in the early vortex reference relation. The balloon flights on 19 November 1999, 3 December 1999, and 27 January 2000 were all conducted in the core of the vortex. Nonetheless, there is an apparent discrepancy between the ozone mixing ratios measured on 19 November 1999 and 3

December 1999 that most likely represents true variability inside the vortex during that time period (see Section 2.2). The difference in column ozone observed on these two flights is considerable (20 DU for 380-550 K and 15 DU for 400-500 K, see Table 5). This difference contributes to the uncertainty of the deduced ozone loss as discussed in detail by *Salawitch et al.* [2002], who analyzed the ozone/N₂O relation over the course of the winter 1999-2000.

However, the vortex mean of the POAM III ozone measurements [*Hoppel et al.*, 2002] within ± 3 days of 19 November 1999 resembles relatively closely the ozone vertical profile measured by MkIV on 3 December 1999 [Figure 4 in *Salawitch et al.*, 2002]. Therefore, the MkIV measurements seem to be more representative of the average conditions in the early winter polar vortex. Indeed, the Triple and HALOZ ozone sonde measurements of both the O₃/N₂O and the O₃/CH₄ relation later in the winter, on 27 January 2000, are in accordance with the MkIV measurements on 3 December 1999 (Fig. 4). Thus we consider the reference relations derived from the 3 December 1999 measurements as the most appropriate ones for studies of winter 1999-2000. The difference to the 19 November 1999 measurement is taken into account as a conservative estimate of the uncertainty.

The chemical change of HCl due to heterogeneous chemistry occurs much earlier in the winter than ozone loss, namely directly after the first occurrence of PSC. Therefore, the HCl/tracer reference relation must be derived from measurements prior to the first occurrence of PSC. There is somewhat less information available on HCl/tracer relations than on ozone/tracer relations. However, in contrast to ozone, the HCl/tracer relation does not differ substantially between the inside and outside of the vortex and the relation is linear over a large

tracer range (Figs. 3 and 4). Therefore, the HCl/tracer relation is less sensitive than the ozone/tracer relation to mixing processes, both to mixing within the vortex and across the vortex edge. We employed the MkIV measurements on 3 December 1999 to derive a HCl/HF reference (R1 in Table 3) that was used to deduce chemical change in HCl (see Section 2.4.1).

3.1.2. The impact of mixing on tracer-tracer relationships in the vortex in 1999-2000. Continuous mixing over the course of the winter of extra-vortex air into a polar vortex characterized by progressing diabatic descent (see Fig. 2) has been put forward [*Plumb et al.*, 2000] as a possible process that might change ozone/tracer relations in the vortex without chemical ozone loss. *Plumb et al.* [2000] suggested that such mixing processes should lead to an overestimate of deduced column ozone loss. In contrast, *Müller et al.* [2001], *Rex et al.* [2002], and *Salawitch et al.* [2002] argue that mixing of mid-latitude air into the vortex should lead to an *underestimate* of deduced column ozone loss. These different conclusions are reached because the ozone/tracer relation outside the vortex is characterized by greater ozone mixing ratios for the same values of the tracer, a statement valid for the vortex between about November to April [*Michelsen et al.*, 1998; *Müller et al.*, 1999; *Tilmes et al.*, 2002, see also Fig. 6]; a fact not taken into account in the conceptual model of *Plumb et al.* [2000]. Nonetheless, mixing across the vortex edge, if it occurs in a significant magnitude, would have a quantitative impact on deduced column ozone loss.

For the Arctic winter 1999-2000, a large number of tracer measurements with good coverage of the vortex are available that can be used to estimate the extent of mixing of mid-latitude air into the vortex. *Ray et al.* [2002] use in situ

measurements of six different tracers from the LACE instrument and from the Airborne Chromatograph for Atmospheric Trace Species (ACATS) IV to examine mixing in the polar vortex in 1999-2000. They report that until early March 2000 mixing of mid-latitude air into the vortex is insignificant.

Similarly, based on an analysis of CFC-11 and N₂O measurements, *Salawitch et al.* [2002] report that the inner vortex was essentially isolated from intrusions of mid-latitude air for the time of chemical loss of ozone. Further, *Richard et al.* [2001] analyze ER-2 measurements of CFC-11, N₂O, and CO₂ up to altitudes of ≈ 450 K and conclude that throughout the mid to late winter the lower stratospheric inner vortex was relatively well isolated from mid-latitude intrusions. Moreover, *Konopka et al.* [2002] use model calculations in conjunction with ACATS measurements of CH₄ and HALON 1211 to show that the vortex in the altitude range 400-475 K was well isolated between mid-February and mid-March 2000 without significant mass exchange across the vortex edge. Therefore, similar as *Salawitch et al.* [2002], we conclude here that in winter 1999-2000 the uncertainty introduced by possible mixing processes across the vortex edge on the deduced column ozone loss due to chemistry can be neglected.

Even if no mixing across the vortex edge occurs however, intra-vortex mixing of air parcels subject to differential descent inside the vortex could potentially have an impact on the ozone/tracer relation in the absence of chemistry. *Salawitch et al.* [2002] have investigated this question in detail. They conclude that, owing to the approximately constant ozone values observed in early winter 1999 above ≈ 500 K (that lead to a “flat” reference relation at greater altitudes), intra-vortex mixing during the time of rapid chemical loss of ozone was unlikely to have led to

appreciable changes in the ozone/tracer relation. Moreover, radiative calculations for the period of rapid ozone loss show fairly low vertical displacements in the vortex [< 25 K, *Konopka et al.*, 2002], a result which implies that differential descent must have been considerably less. If differential descent occurs over only a small vertical range, mixing occurs over only a small range in tracer-tracer space. Such mixing processes will have a negligible effect on tracer-tracer relations.

3.1.3. HF versus CH₄ as the long-lived tracer in the analysis of chemical ozone loss. An assessment of the impact on the deduced chemical ozone loss of employing HF or CH₄ as the long-lived tracer is only possible using the MkIV measurements on 3 December 1999 as the reference since HF measurements in the early vortex are available only from MkIV. For the altitude range of ≈ 430 -550 K, comparable vertical profiles of ozone loss were obtained using HF (early vortex reference R5) and CH₄ (early vortex reference R7) as the long-lived tracer (Fig. 13). At lower altitudes, some ozone loss profiles deduced using the tracer CH₄ agree with those using HF, while other profiles deduced using CH₄ indicate greater losses than those using HF (Fig. 13). This discrepancy increases towards lower altitudes. It is caused by a variability of HALOE CH₄ observations inside the vortex in March at lower altitudes that is not apparent in the concurrent HF measurements (Fig. 2). Uncertainties in the late vortex tracer measurements at lower altitudes have a particularly strong impact on the ozone loss calculations because there ozone varies strongly with the tracer value in the early vortex relations.

Because the HALOE CH₄ measurements show an enhanced variability at low altitudes due to signal saturation problems, we consider these greater ozone

losses deduced from CH_4 for some profiles to be problematic. The ozone losses at lower altitudes deduced from other CH_4 profiles which are in accordance with those deduced from HF seem to be more reliable. Differences in the ozone loss vertical profiles cause differences in the calculated column ozone loss. Because of the increasing pressure towards lower altitudes, the contribution to column ozone loss of a given difference in local ozone loss (expressed in mixing ratios) increases with decreasing altitude.

The greatest column ozone losses for the altitude range 380–550 K are deduced using CH_4/O_3 measured by MkIV (i.e., relation R7) as the reference relation. However, owing to the enhanced variability of HALOE CH_4 at lower altitudes caused by CH_4 saturation problems (see above) and owing to the impact of such uncertainties on calculations of column ozone loss, we consider the mean column losses deduced using HF as the long-lived tracer (i.e. relation R5 as the reference) to be more reliable. These mean column ozone loss values (for 380–550 K) are about 15% lower than those deduced using CH_4 (R7).

3.2. Overview of the deduced chemical ozone loss and comparison with other studies

As discussed in Section 3.1.1, we consider the MkIV measurements on 3 December 1999 to be the most appropriate reference. Further, in Section 3.1.3 we discussed why HF is considered to be the most suitable long-lived tracer to be employed under the circumstances in question here. Therefore, we use the ozone loss deduced from reference relation R5 (Table 3) as the basis for the reported chemical ozone losses.

The uncertainty of the reported losses was estimated employing two sources. Firstly, from the uncertainty of the employed reference relation (see Section 2.2 and Table 5) and, secondly, from the spread of the column ozone loss values deduced from the individual HALOE observations in the late winter vortex (Table 5). This spread is considered as a measure of the uncertainty introduced by the late winter HALOE measurements. As discussed above (Section 3.1.2), and in accordance with the conclusions of *Salawitch et al.* [2002], we consider the uncertainty introduced by the possible effects of mixing processes on the deduced chemical column ozone loss to be negligible for winter 1999-2000. Again, following *Salawitch et al.* [2002], we assume the two sources of errors to be independent so that the combined uncertainty should be expressed as a “root sum of squares”.

Thus, we report here a cumulative column ozone loss for the altitude range 380-550 K for the vortex core by mid-March 2000 of 84 ± 13 DU. For the smaller altitude range 400-500 K we find a vortex core loss of 65 ± 10 DU. Substantially less ozone loss is deduced for the entire Arctic vortex by mid-February 2000: 32 ± 20 DU for the altitude range 380-550 K and 24 ± 18 DU for the altitude range 400-500 K. Considerably more cumulative ozone loss with much less spread is deduced for the vortex core by mid-February; 40 ± 11 DU and 31 ± 11 DU for the altitude range 380-550 K and 400-500 K, respectively.

For the vortex remnants in late April we obtain an average column ozone loss for the altitude range 380-550 K of 80 DU with a standard deviation of 5 DU. Again we consider the latter number as a measure of the uncertainty introduced by the late vortex measurements and combine it with the uncertainty introduced by the reference relation (9 DU) as a root sum of squares. Thus, we report here $80 \pm$

10 DU for the ozone column loss in the late April vortex remnants.

If the OMS-in-situ measurements on 19 November 1999 were used to deduce a reference relation (relation R8) instead of the MkIV measurements on OMS-remote on 3 December 1999 (relation R5), considerably lower, ≈ 20 DU (for 380-550 K), column ozone losses would be deduced. For a conservative estimate of the uncertainties, this number should be taken into account. However, in spite of all the uncertainties discussed above, the values of ozone loss deduced from the three possible reference relations (R5, R7, and R8) all agree within the combined error estimates under all conditions (Table 5).

A large number of estimates of chemical ozone loss based on a variety of techniques are available for winter 1999-2000 [*Newman et al.*, 2002, and references therein]. However, if different ozone loss estimates are compared in detail, it is essential to ensure that only numbers are compared that are determined for exactly the same conditions [*Harris et al.*, 2002].

The loss of column ozone between early January and mid-March determined by the Match technique amounts to 71 ± 12 DU [*Rex et al.*, 2002, Fig. 6], in good agreement with the column ozone loss reported here for mid-March 2000. Further, the finding of the Match study that the local ozone loss in the vortex on the 450 K level in mid-March 2000 amounted to 2.0 ± 0.3 ppmv [*Rex et al.*, 2002, Fig. 6] is in agreement with the values deduced here (see Fig. 13 and Fig. 12). Our results are likewise in agreement with an analysis of chemical ozone loss by *Richard et al.* [2001], who used tracer and ozone measurements between early January and mid-March 2000 from the ER-2 to deduce chemical ozone loss. They report a chemical ozone loss of 1.8 ± 0.3 ppmv of ozone at 450 K, in accordance with the

results determined here based on independent balloon and satellite measurements (see Fig. 13). A somewhat lower chemical ozone loss, of about 1.5 ± 0.3 ppmv is deduced by *Hoppel et al.* [2002] for mid-March 2000 on the 450 K level based on POAM III satellite measurements; however, this value is still in agreement with our results within the combined uncertainties. Further, *Klein et al.* [2002] conclude that the ozone loss reported here is in accordance with the ozone loss they estimate from ground-based microwave observations. *Salawitch et al.* [2002] focus on the investigation of the OMS balloon measurements in winter 1999-2000. They deduce a column ozone loss of 61 ± 14 DU by 5 March 2000, the day of the second OMS-in-situ flight inside the vortex. Column ozone was reduced at a substantial rate in early March 2000; from the Match analysis one expects loss rates of approximately two Dobson units per day [*Rex et al.*, 2002] so that an extrapolation of the result for 5 March to mid-March would lead to $\approx 81 \pm 14$ DU as the more appropriate value for comparison with our results. This value is indeed in excellent agreement with the column ozone loss deduced here (84 ± 13 DU) for mid-March 2000.

The altitude distribution of chemical ozone loss in the Arctic vortex in late winter 2000 was deduced from several independent data sets [e.g., *Hoppel et al.*, 2002; *Rex et al.*, 2002; *Schoeberl et al.*, 2002]; here we compare data for 15 March 2000. *Hoppel et al.* [2002] find the maximum O_3 loss at ≈ 470 or 480 K depending on the passive O_3 employed (that is effectively depending on the heating rate calculation used). *Schoeberl et al.* [2002] report ≈ 465 and 475 K as the altitude of maximum O_3 loss depending on whether POAM or sonde measurements are used as the O_3 data set. The altitude of maximum O_3 loss on 15 March 2000

obtained with the Match technique is 460 K [*Rex et al.*, 2002; *Hoppel et al.*, 2002]. In all these studies a greater altitude of maximum O₃ loss is obtained than found here (≈ 440 K, see Fig. 12). Possibly, this could be due to differences in the magnitude of vertical transport entering the O₃ loss calculations. Here, we take into account vertical transport implicitly by considering O₃/tracer relations whereas in other studies [*Hoppel et al.*, 2002; *Rex et al.*, 2002; *Schoeberl et al.*, 2002] model calculations of the vertical descent enter the O₃ loss calculations in various different ways. However, without further study it is unclear whether these discrepancies are not solely caused by the relatively coarse vertical resolution of occultation satellite instruments (≈ 40 K) and the vertical averages employed in the analysis of O₃ sonde measurements.

In a model simulation of the ozone loss in the Arctic vortex between 10 February and 15 March 2000 at the 450 K level, *Grooß et al.* [2002] find an ozone destruction of 1.6 ppm in the core of the vortex. An ozone loss rate of ≈ 25 ppbv/day is simulated in this model for mid-February 2000 [Fig. 4 in *Grooß et al.*, 2002]. This implies a simulated ozone loss of ≈ 1.35 ppmv between late February and mid-March 2000 at the 450 K level that may be compared with the ozone loss deduced here. For 450 K, we deduced a chemical ozone destruction of 1 ppmv for late February (Fig. 12, top panel) and of 2.2 ppmv for mid-March (Fig. 12, middle panel) leading to a loss between late February and mid-March 2000 of about 1.2 ppmv. Therefore, we conclude that the chemical ozone loss deduced here is in accordance with the model calculations by *Grooß et al.* [2002].

4. Conclusions

We combined measurements in the Arctic vortex from several balloon-borne instruments between late November 1999 and late January 2000 with satellite measurements from HALOE in the vortex in February, March, and April 2000 to deduce chlorine activation and chemical ozone loss. Based on the available tracer measurements we conclude that for the vortex core in 1999-2000 the impact of mixing processes, both across the vortex edge and within the vortex, had a negligible effect on tracer-tracer relations during the period of strong chemical change (January-March).

HALOE HCl measurements in the vortex in late February 2000 show an extensive activation of chlorine. The activation extended to altitudes of 600 K and was practically complete in the vortex core below about 450 K. In late February 2000 about 70% of the HCl column between 380-550 K was converted to active chlorine. A partial recovery of HCl was observed by mid-March; the recovery was complete in vortex remnants observed in late April.

Errors in the deduced ozone losses caused by uncertainties in the early vortex reference relation are estimated to be $\lesssim 10$ DU (Table 5). Approximately 20 DU less column ozone loss (for 380-550 K) would be deduced if the measurements on 19 November 1999 had been employed for the early vortex reference. We have argued above that the later measurements on 3 December 1999 constitute a more suitable data set to deduce an early vortex reference; however, the possible overestimate by 20 DU should be included for a conservative estimate of the error. The set of HALOE measurements in the late vortex in mid-March provide information on the

spread of ozone loss inside the vortex core; the spread amounts to ≈ 10 DU.

Based on the balloon-borne and the HALOE measurements, we report here a column ozone loss for the vortex core in mid-March 2000 of 84 ± 13 DU for the altitude range 380-550 K and 65 ± 10 DU for 400-500 K. In the outer vortex ozone loss is clearly noticeable, but considerably more variable. The deduced average of loss in column ozone (380-550 K) over the entire vortex in mid-March 2000 is 45 ± 25 DU. Further, substantially less ozone loss is deduced for the entire Arctic vortex in mid-February 2000: 32 ± 20 DU and 24 ± 18 DU for the 380-550 K and 400-500 K altitude ranges, respectively. At that time the vortex core shows considerably more ozone loss with less variability; 40 ± 11 DU and 31 ± 10 DU for the altitude range 380-550 K and 400-500 K, respectively. Vortex remnants were identified in HALOE observations in late April 2000. While the HCl data indicate a complete recovery of the chlorine reservoirs, ozone values are still substantially reduced, $\approx 80 \pm 10$ DU for 380-550 K. These observations imply that by late April the vortex remnants remained largely intact with little mixing-in of (ozone-rich) mid-latitude air.

The local chemical loss deduced here for ≈ 450 K is in agreement with other studies based on ER-2, Match ozone sonde, and POAM III satellite measurements [Richard *et al.*, 2001; Rex *et al.*, 2002; Hoppel *et al.*, 2002]. Further, the loss in column ozone reported here for the vortex core is in agreement with estimates based on several other techniques [Klein *et al.*, 2002; Rex *et al.*, 2002; Salawitch *et al.*, 2002].

Finally, in spite of all the uncertainties discussed above, the measurements presented here provide clear evidence that during the Arctic winter and spring

1999-2000 a strong chlorine activation occurred in the polar vortex, which was practically complete in the altitude range $\approx 360\text{-}450$ K. This activation of chlorine led to a substantial chemical destruction of ozone in the vortex core, noticeable as a reduction in column ozone of approximately 25%.

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Table 1.

Table 2.
Table 3.

Table 4.

Table 5.

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Figure Captions

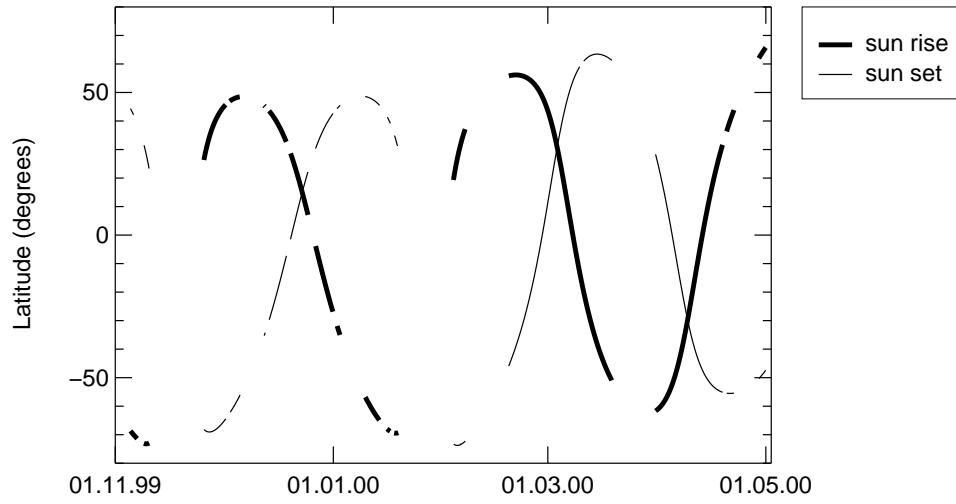


Figure 1. Latitude coverage of HALOE measurements from 1 November 1999 to 30 April 2000. Thin lines indicate sunset, thick lines sunrise measurements.

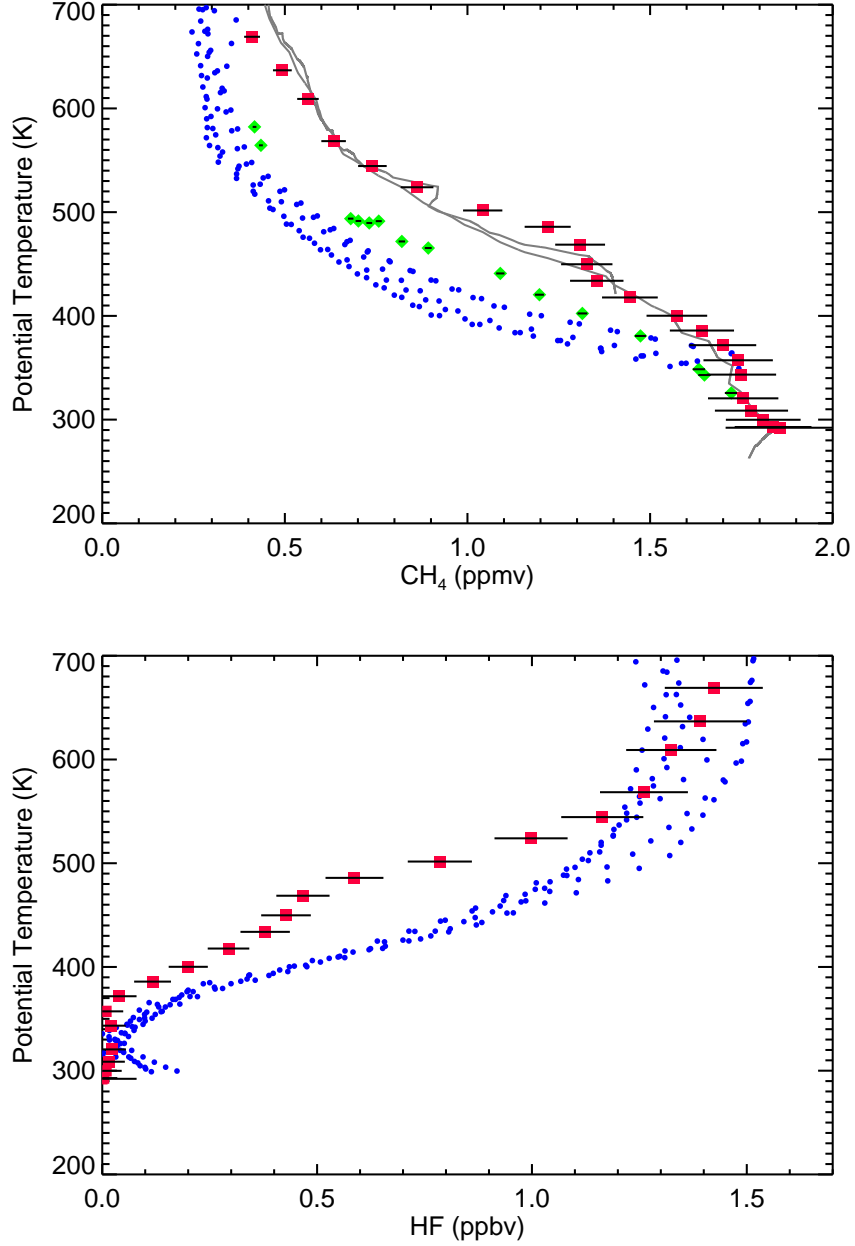


Figure 2. Vertical profiles of CH_4 (top panel) and HF (bottom panel) mixing ratios in winter 1999-2000. Shown are MkIV measurements on OMS-remote on 3 December 1999 (red squares), LACE measurements on OMS-in-situ on 19 November 1999 (gray lines, top panel), and Triple measurements on 27 January 2000 (green diamonds, top panel). The accuracy of MkIV and Triple tracer measurements is shown as a black horizontal bar. There are two gray lines in the top panel as the profiles measured by LACE on ascent and descent are somewhat different. HALOE measurements inside the core of the late vortex between 11–14 March 2000 (blue circles) are shown for comparison. (See also Table 1 for an overview of the instruments).

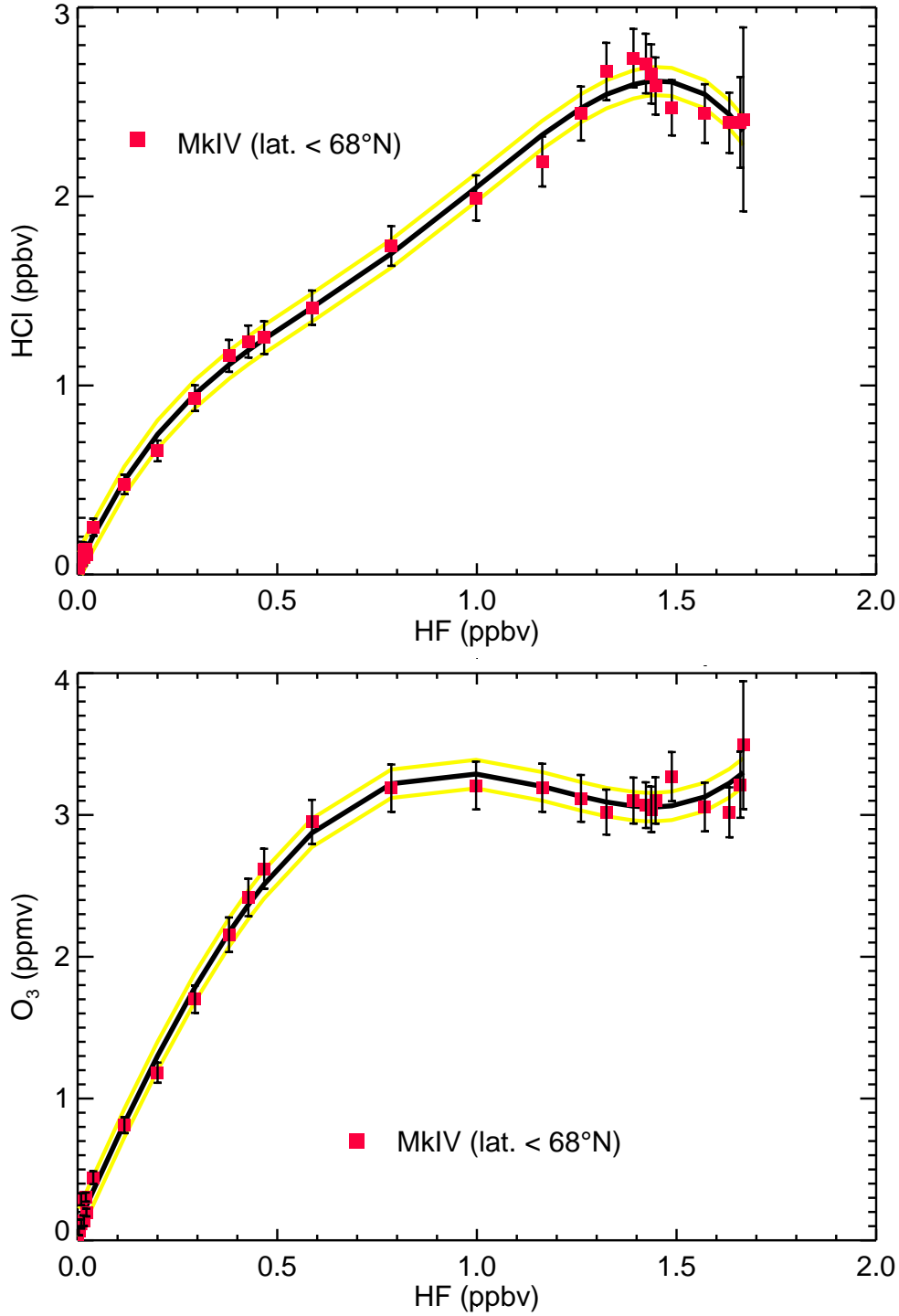


Figure 3. Measurements of the MkIV instrument on the OMS-remote flight (red solid squares with reported measurement accuracy) of 3 December 1999. Top panel shows HCl versus HF observations, bottom panel O₃ against HF. Further, empirical polynomial fits to the measurements of the MkIV instrument are shown (solid black lines) together with their one sigma uncertainty (solid yellow lines). Both empirical polynomial relations are listed in Table 3.

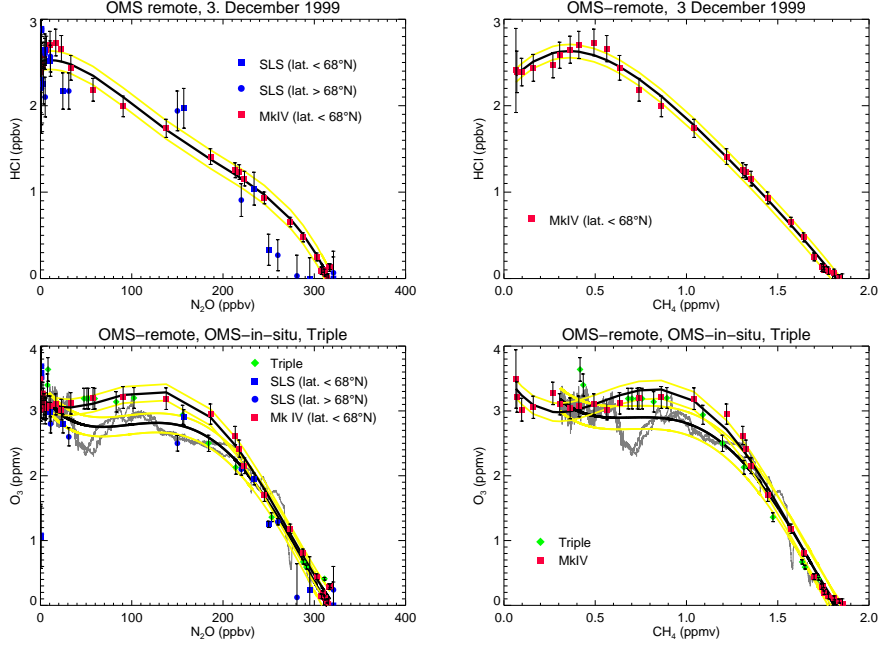


Figure 4. Measurements of the OMS-in-situ flight on 19 November 1999 (gray lines, ascent and descent) and from the OMS-remote flight on 3 December 1999; red and blue symbols show MkIV and SLS measurements, respectively, with reported measurement accuracy. Further, measurements are shown from the Triple and HALOZ flights on 27 January 2000 (green symbols). For the ozone sonde measurements an accuracy of 5% is shown. Top panels show HCl/tracer relations, bottom panels O₃/tracer relations. Left panels show relations for N₂O as the tracer, right panels show relations for CH₄ as the tracer. Measurements of the MkIV instrument on OMS-remote are shown in all four panels (red squares). Top left panel additionally shows SLS data from the OMS-remote flight on 3 December 1999, both for latitudes equatorward of 68°N (blue squares) and for latitudes poleward of 68°N (blue circles). OMS-in-situ data (gray lines) and Triple/HALOZ data (green symbols) are additionally shown in both bottom panels. Empirical polynomial fits to the MkIV observations are shown as a solid black line in all four panels, the solid yellow lines indicate the one sigma uncertainty of the fit. In the bottom panels, in addition, empirical polynomial fits to the OMS-in-situ data are shown (black lines) together with their one sigma uncertainty (yellow lines). All the empirical polynomial relations are listed in Table 3. (See also Table 1 for an overview of the instruments).

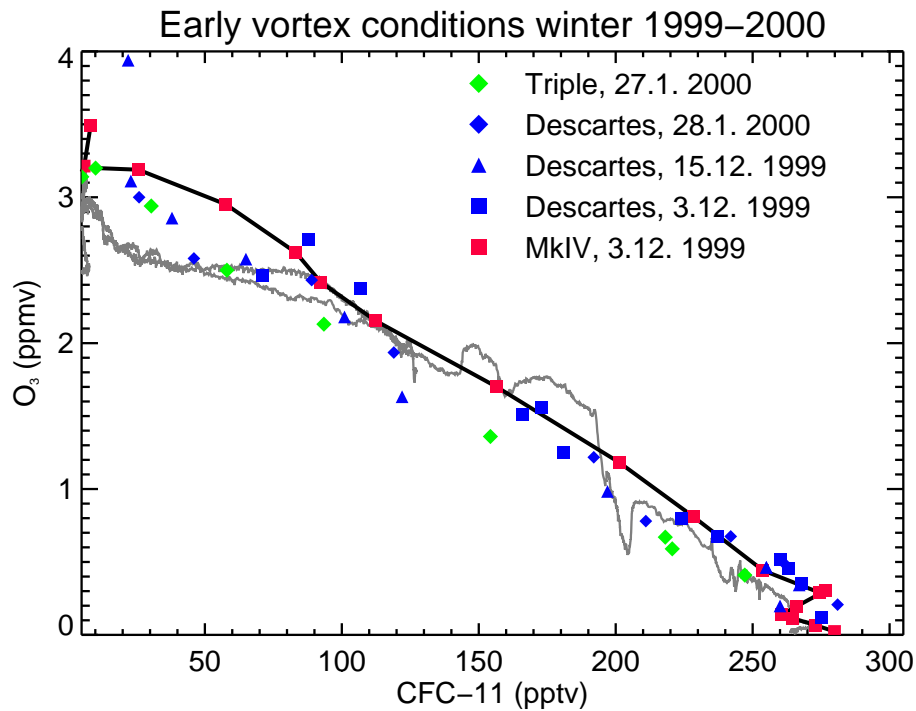


Figure 5. The relationship of CFC-11 and O_3 for the period from 19 November 1999 to 28 January 2000. Green symbols show measurements from the Triple and HALOZ flights on 27 January 2000, blue symbols the Descartes flights on 3 and 15 December 1999 and on 28 January 2000, red symbols indicate the MkIV measurements on OMS-remote on 3 December 1999 and the gray line the OMS-in-situ observations on 19 November 1999. (See also Table 1 for an overview of the various instruments).

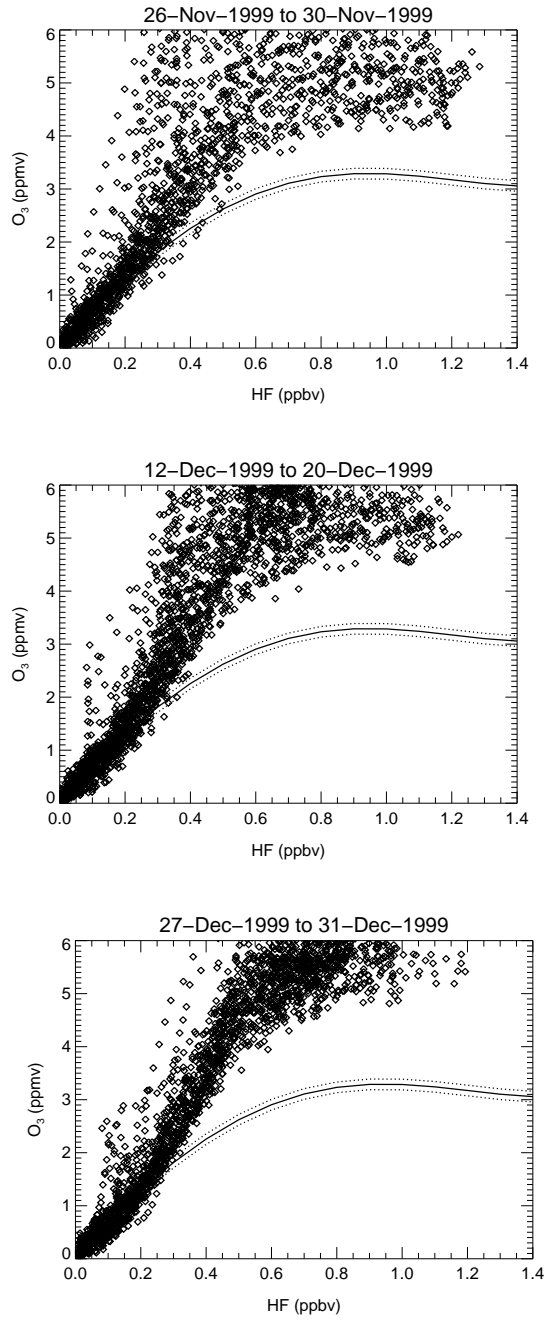


Figure 6. The relationship of HF and O₃ for the period 26 November to 31 December 1999 for HALOE measurements outside the vortex (diamonds). Also shown is the early vortex relation (solid line, see relation R5 in Table 3).

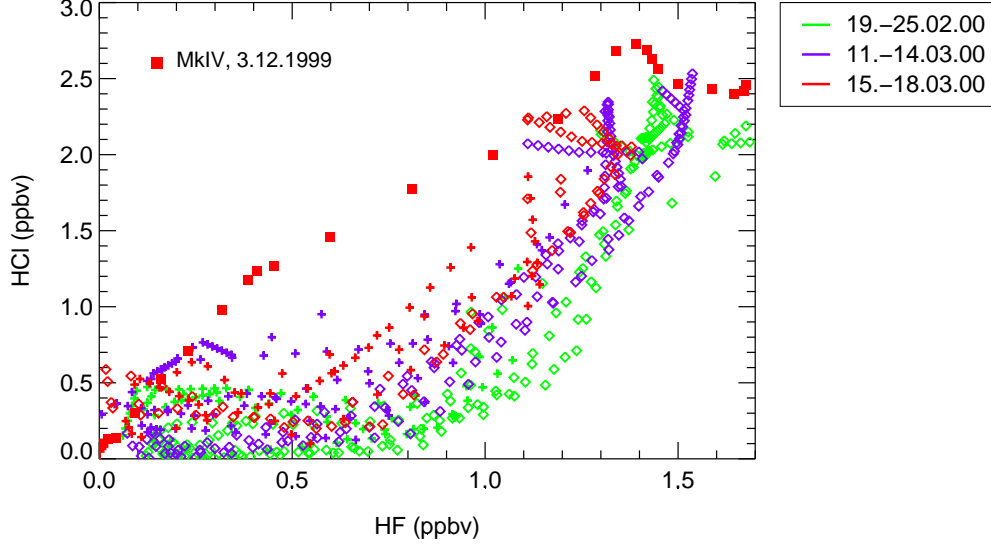


Figure 7. The relation between HF volume mixing ratios and those of HCl inside the Arctic vortex in the winter of 1999-2000. Also shown are the observations of the MkIV instrument on 3 December 1999 in the early vortex (red squares). HALOE measurements inside the vortex were obtained during 19–25 February 2000 (green symbols), 11–14 March 2000 (purple symbols), and 15–18 March 2000 (red symbols). Measurements are considered to be inside the vortex if they are taken poleward of the vortex edge and inside the vortex core if taken poleward of the line bounding the vortex core, both being defined by the *Nash et al.* [1996] criterion (see text). Vortex core measurements are shown as diamonds, outer vortex measurements as plus signs. The vertical profiles (against potential temperature) of HF and HCl employed in this figure are shown in Figs. 2 and 11, respectively.

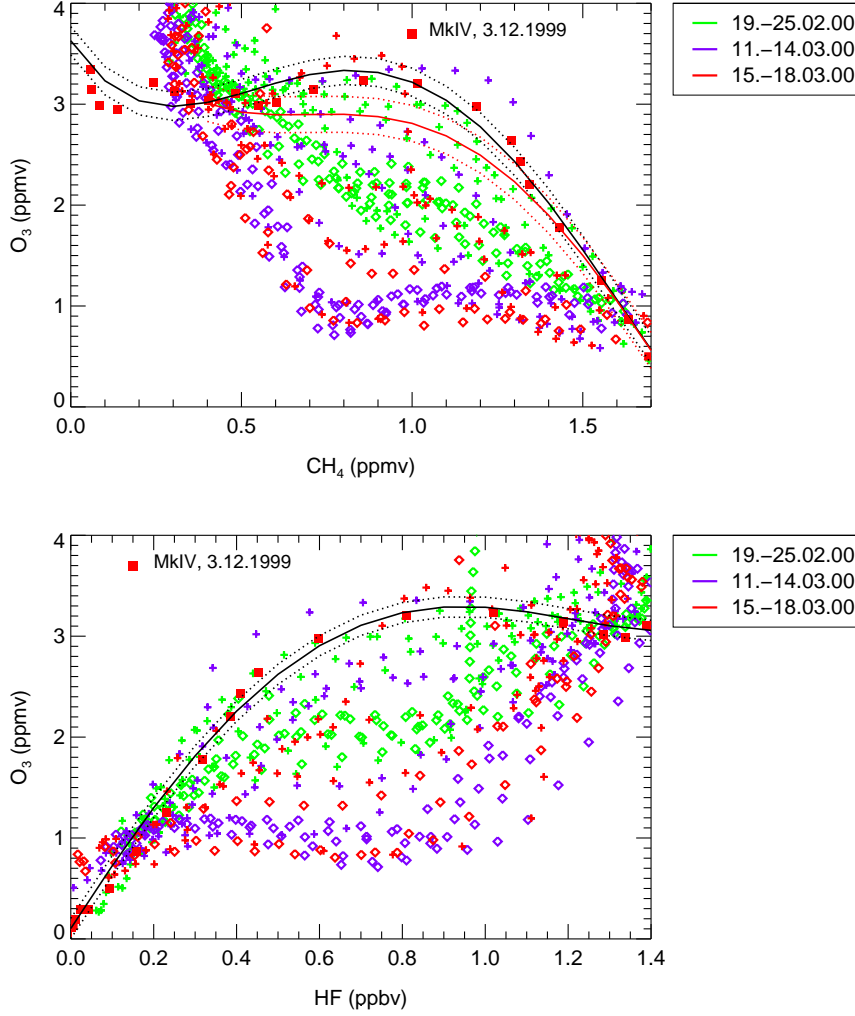


Figure 8. The relation between O_3 volume mixing ratios and those of CH_4 (top panel) and HF (bottom panel) inside the Arctic vortex in the winter of 1999-2000. Also shown are the observations of the MkIV instrument on the OMS-remote flight on 3 December 1999 in the early vortex (red squares in both panels). HALOE measurements inside the vortex (see text) were obtained during 19–25 February 2000 (green diamonds), 11–14 March 2000 (purple diamonds), and 15–18 March 2000 (red diamonds). HALOE measurements in the outer vortex are shown as plus signs, vortex core measurements as diamonds. The empirical polynomial fits to the MkIV observations are shown as a solid black line in both panels, the dotted black lines indicate the one sigma uncertainty of the fit. In the bottom panel, in addition, the empirical polynomial fit to the OMS-in-situ data is shown (red line) together with the one sigma uncertainty (dotted red line).

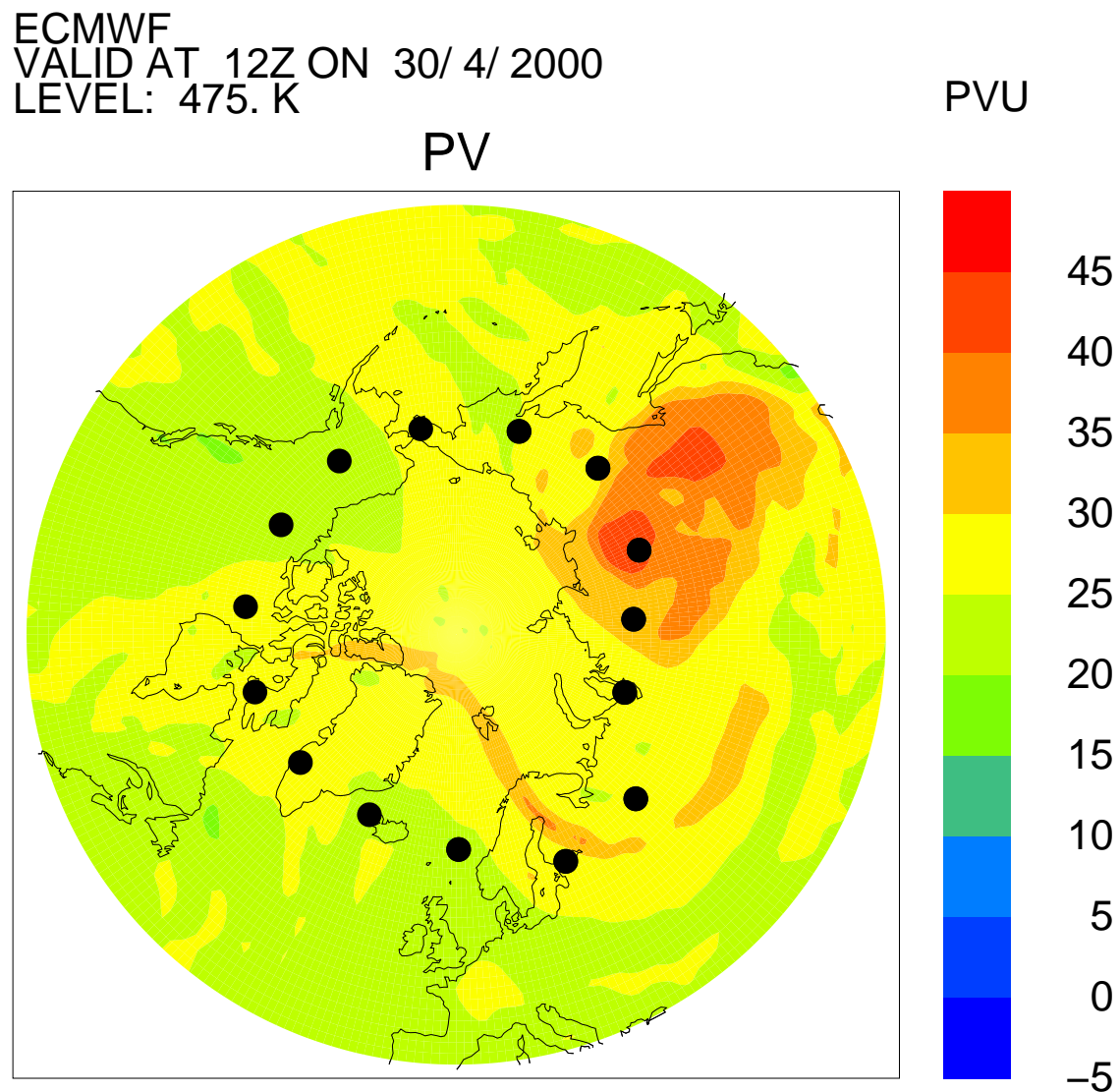


Figure 9. The northern hemisphere distribution of potential vorticity (in PVU) on the 475 K isentropic level from analyses of the ECMWF for 30 April 2000 at 12 UTC. Also shown (black dots) are the locations of the HALOE measurements on that day transformed to 12 UTC by a trajectory calculation.

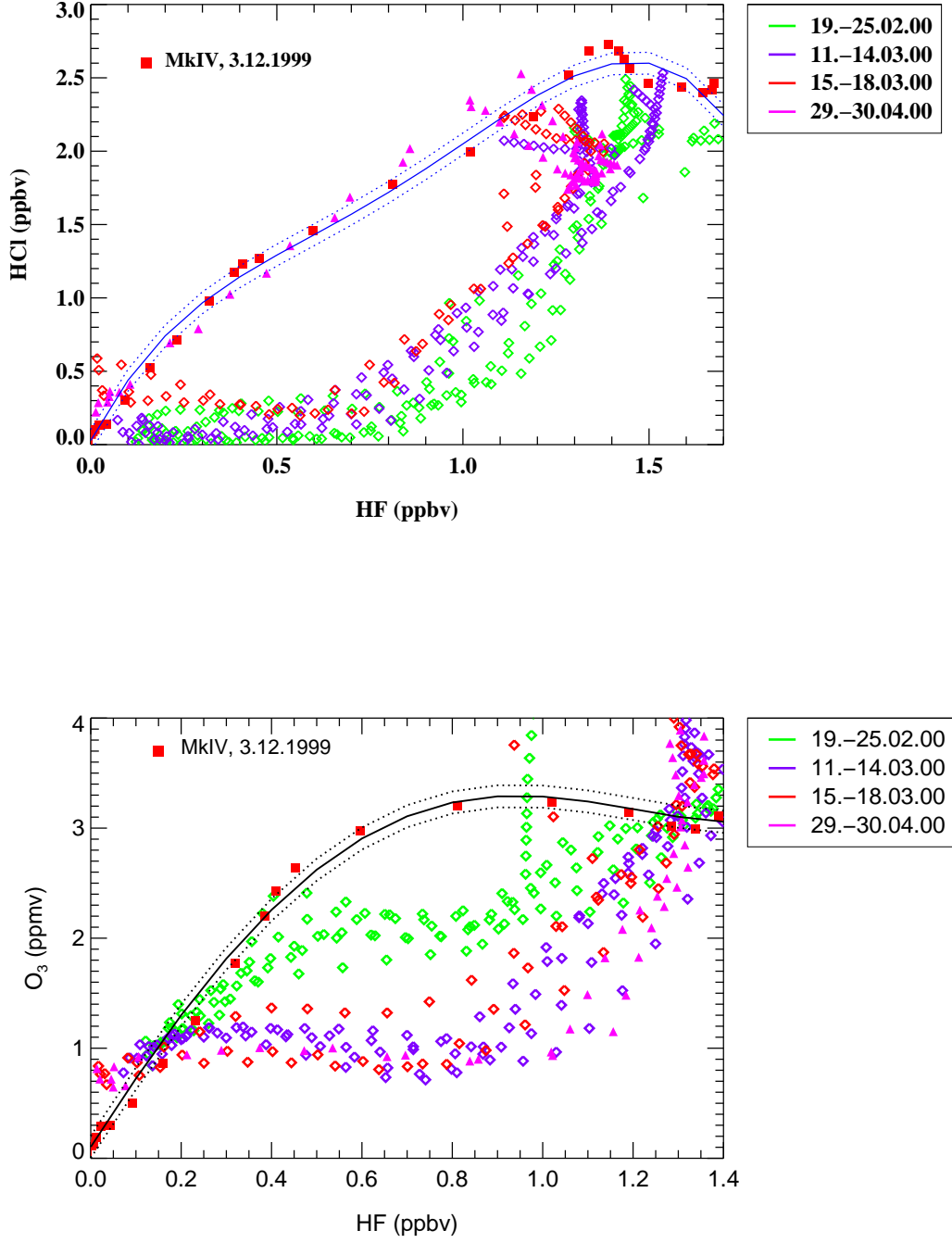


Figure 10. As Figures 7 and 8, but showing in addition the HALOE measurements inside vortex remnants on 29 and 30 April 2000 (purple triangles). Top panel shows the HCl/HF relation, bottom panel shows the O₃/HF relation. The solid lines show the reference relations R1 (top panel) and R5 (bottom panel), the dotted line the one sigma uncertainties (see Table3).

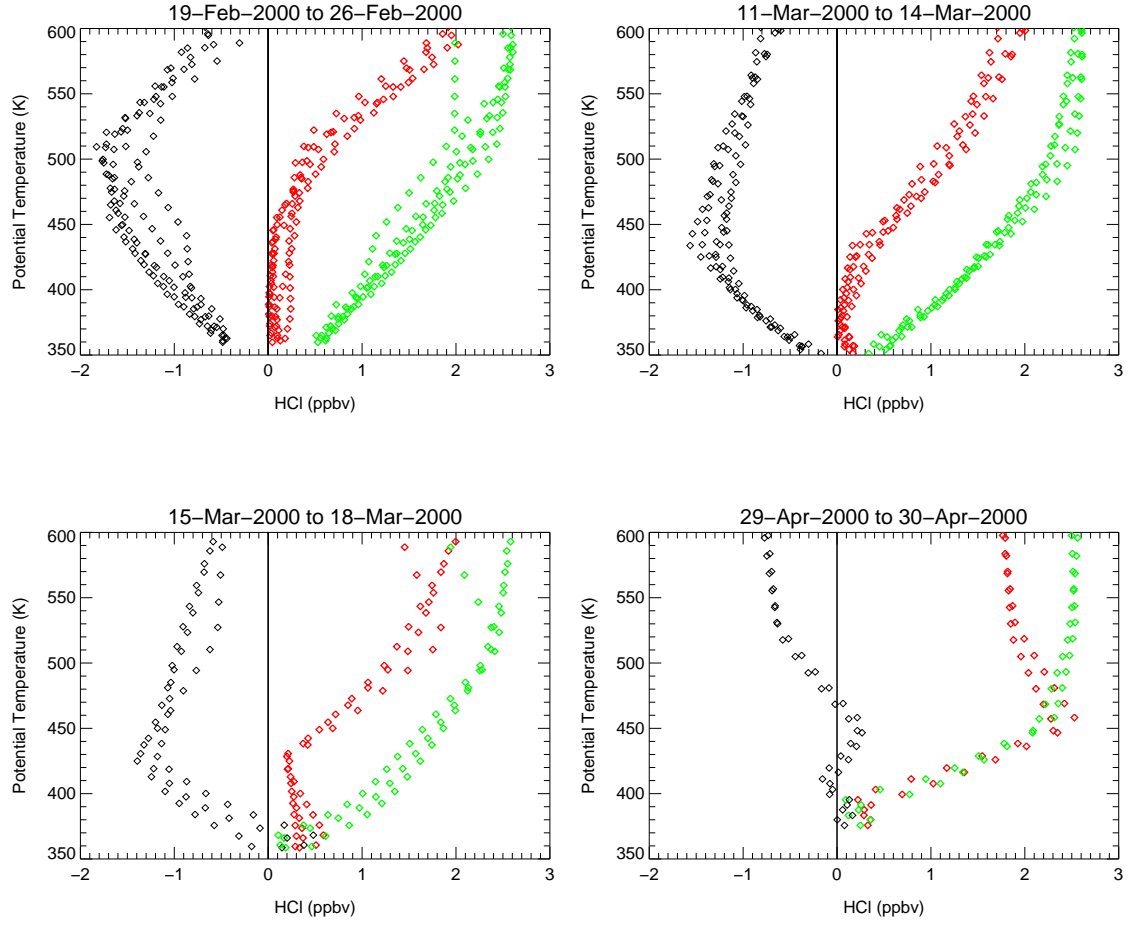


Figure 11. HALOE HCl measurements inside the Arctic vortex core in the winter of 2000. Shown are vertical profiles (against potential temperature) of the measured HCl mixing ratios (red diamonds), HCl mixing ratios expected in the absence of chemical change (green diamonds), and the difference between expected and observed HCl (black diamonds). The HCl expected in the absence of chemical change was deduced from the early vortex relation R1 (see text). Top left panel shows observations for 19–26 February 2000, top right panel for 11–14 March 2000, and bottom left panel for 15–18 March 2000 and bottom right for 29–30 April 2000.

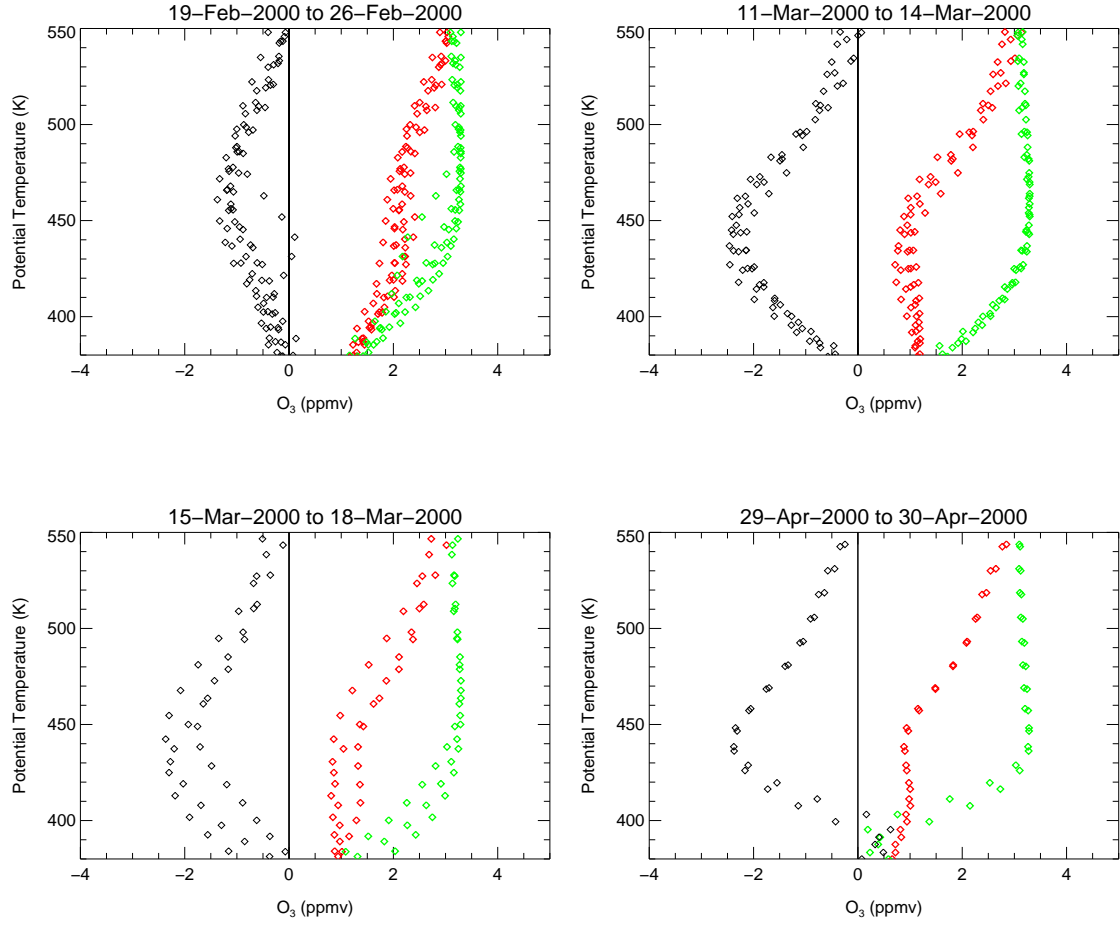


Figure 12. HALOE O_3 measurements inside the Arctic vortex in the winter of 2000. Shown are vertical profiles (plotted against potential temperature) of the measured O_3 mixing ratios (red diamonds), $\hat{\text{O}}_3$, the ozone mixing ratios expected in the absence of chemical change (green diamonds), and the difference between expected and observed O_3 (black diamonds). $\hat{\text{O}}_3$ was deduced using HF as the long-lived tracer and the early vortex relation R5 (see text). Top left panel shows observations for 19–26 February 2000, top right panel for 11–14 March 2000, and bottom left panel for 15–18 March 2000 and bottom right for 29–30 April 2000.

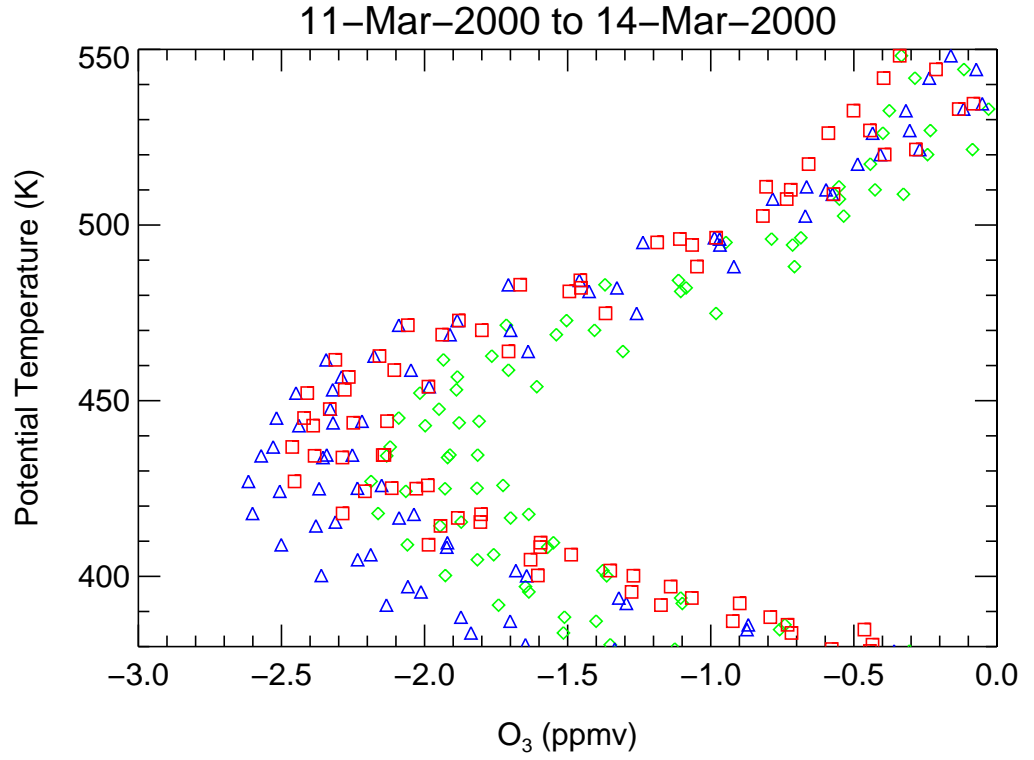


Figure 13. Vertical profile of chemical ozone loss in the vortex (calculated as the difference between proxy ozone \hat{O}_3 and measured ozone as in Fig. 12) for the period 11–14 March 2000. Shown are loss profiles using HF from MkIV (relation R5, red squares), CH₄ from MkIV (relation R7, blue triangles) and CH₄ from LACE on OMS-in-situ (relation R8, green diamonds) as the reference relation.

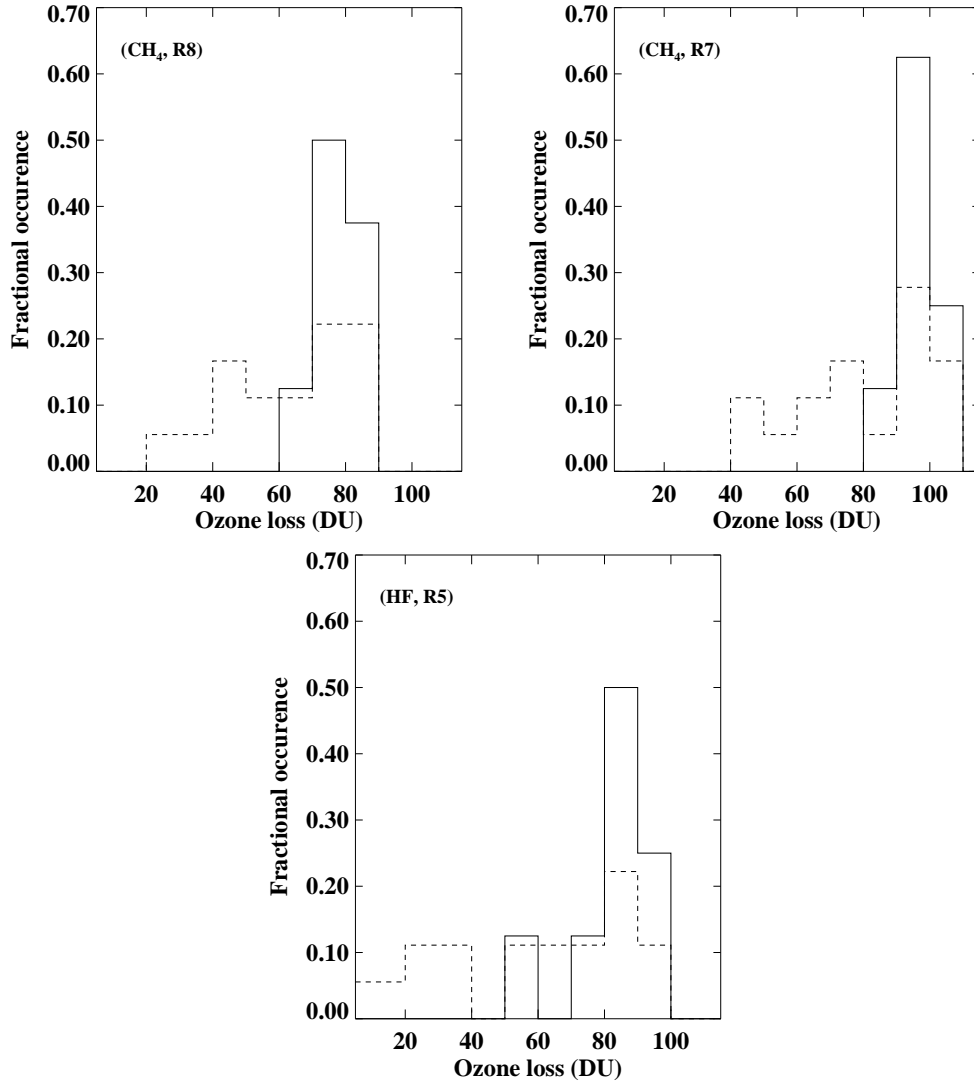


Figure 14. Frequency distribution of column ozone loss inside the Arctic vortex (in Dobson units, DU) for the period 15–18 March 2000 and the altitude range 380–550 K. Column ozone loss is deduced from HALOE measurements of O₃, CH₄, and HF using both the MkIV measurements on 3 December 1999 (R5, R7) and the OMS-in-situ measurements on 19 November 1999 (R8) to deduce initial relations (Table 3). Results are shown for CH₄, OMS-in-situ (top left panel), CH₄, MkIV on OMS-remote (top right panel), and for HF, MkIV (bottom panel). Vortex measurements are shown as dashed lines, vortex core measurements as solid lines.

Tables

Table 1. Overview of the Measurements

Platform	Date	Instrument	Species	Type
OMS-in-situ	19. 11. 1999	LACE	N ₂ O, CH ₄ , CFC-11	in situ
		UV-Photom.	O ₃	in situ
OMS-remote	3. 12. 1999	SLS	N ₂ O, O ₃ , HCl	remote
		MkIV	N ₂ O, O ₃ , HCl, CH ₄ , CFC-11, HF	remote
		Descartes	CFC-11	in situ
		O ₃ -Sonde	O ₃	in situ
Small Ball.	15. 12. 1999	Descartes	CFC-11	in situ
		O ₃ -Sonde	O ₃	in situ
Triple	27. 1. 2000	Cryosamp.	N ₂ O, CH ₄ , CFC-11	in situ
HALOZ	27. 1. 2000	O ₃ -Sonde	O ₃	in situ
Small Ball.	28. 1. 2000	Descartes	CFC-11	in situ
		SAOZ	O ₃	remote
UARS	Feb.-Apr. 2000	HALOE	O ₃ , HCl, CH ₄ , HF	remote

Table 2. Accuracy of HALOE V19 data

Pressure [hPa]	1	5	10	50	100
O ₃ [%]	8	9	12	18	30
CH ₄ [%]	6	9	11	15	19
HCl [%]	15	12	14	21	24
HF [%]	15	14	15	21	27

Table 3. Reference Tracer Relations

	$[y]$	$[x]$	Val. Range of $[x]$	a_0	a_1	a_2	a_3	a_4	sigma	Ref.
R1	HCl	HF	0.003–1.6 ppbv	0.0285	4.7649	−7.2330	6.5354	−2.0462	7.43340e-02	MkIV
R2	HCl	HF	0.05–1.4 ppbv	0.228	1.57	1.99	−1.67	–	0.125	HALOE
R3	HCl	CH ₄	0.06–1.8 ppmv	2.1876	2.75	−5.01	2.37	−4.46 · 10 ^{−1}	7.43 · 10 ^{−2}	MkIV
R4	HCl	N ₂ O	0.04–317 ppbv	2.51	2.44 · 10 ^{−3}	−1.2457e-04	6.1325e-07	−1.022 · 10 ^{−9}	1.07 · 10 ^{−1}	MkIV
R5	O ₃	HF	0.05–1.6 ppbv	0.103	6.389	−1.4331	−3.3052	1.5327	1.00445e-01	MkIV
R6	O ₃	N ₂ O	20–310 ppbv	3.1924	−1.01 · 10 ^{−2}	2.5805e-04	−1.1731e-06	1.4454e-09	1.25964e-01	MkIV
R7	O ₃	CH ₄	0.1–1.7 ppbv	3.6285	−5.1534	1.2939e+01	−1.0688e+01	2.4924e+00	1.39369e-01	MkIV
R8	O ₃	CH ₄	0.3–1.8 ppmv	4.8222	−9.1303	1.5215e+01	−1.0151e+01	2.0545e+00	1.78198e-01	OMS-is
R9	O ₃	N ₂ O	10–315 ppbv	3.3004	−2.06 · 10 ^{−2}	2.5805e-04	−1.1731e-06	1.4454e-09	1.47787e-01	OMS-is

Reference relations were derived for early vortex measurements with the exception of R2, which was derived from late April measurements. Polynomial functions of the form: $[y] = \sum_{i=0}^n a_i \cdot [x]^i$ with $n \leq 4$ are reported. The empirical relations are valid for mixing ratios of HCl in ppbv, of HF in ppbv, of CH₄ in ppmv, of N₂O in ppbv, and of O₃ in ppmv.

Table 4. Loss in column HCl in 10^{15} molec/cm².

vortex	MkIV (R1)		HALOE (R2)	
	entire	core	entire	core
19.–25. Feb.	2.3 ± 0.1	2.6 ± 0.1	1.9 ± 0.2	2.2 ± 0.2
11.–18. Mar.	1.7 ± 0.1	1.8 ± 0.1	1.3 ± 0.2	1.5 ± 0.2

Loss in column HCl (in 10^{15} molec/cm²) for the altitude range 380–550

K is deduced both by employing the reference relation from MkIV (R1 in Table 3) and from the relation deduced for the HALOE measurements in vortex remnants in late April 2000 (R2 in Table 3). Further, both values for the entire vortex and the vortex core are listed. The location of the vortex and the vortex core was selected according to the *Nash et al.* [1996]-criterion. The reported uncertainty (not to be confused with the variability inside the vortex discussed in the text) is deduced from the uncertainty in the reference relation.

Table 5. Chemical loss in total ozone in Dobson units (DU)

		HF (MkIV, R5)	CH4 (MkIV, R7)	CH4 (is, R8)
<i>380–550 K</i>				
Feb.	vortex	31.9 ± 18.9	51.6 ± 20.9	31.8 ± 17.7
	core	40.3 ± 8.9	61.7 ± 5.8	40.4 ± 5.5
	maximum	49.0	73.6	50.4
Mar.	vortex	59.5 ± 29.7	75.8 ± 30.7	57.9 ± 29.3
	core	84.4 ± 10.9	96.1 ± 6.6	78.8 ± 6.8
	maximum	93.6	103.0	85.4
	error	6	8	10
<i>400–500 K</i>				
Feb.	vortex	24.2 ± 17.6	36.7 ± 14.3	25.5 ± 6.2
	core	31.0 ± 9.8	43.6 ± 3.4	27.5 ± 2.8
	maximum	40.7	49.6	31.2
Mar.	vortex	44.9 ± 24.5	53.6 ± 22.8	40.8 ± 21.1
	core	65.1 ± 9.1	69.8 ± 9.3	60.7 ± 6.3
	maximum	76.7	81.8	66.8
	error	4	5	7

Listed is the average of column ozone loss for HALOE measurements over the vortex core and the entire vortex (selected on the basis of the *Nash et al.* [1996]-criterion as in Table 4) as well as the maximum ozone loss over the time period considered. Averages were calculated for late February (19–25. 2. 2000) and for mid-March (11–18. 3. 2000). Also shown in the table is the (one sigma) variability of the averaged ozone losses. The uncertainty in ozone loss due to the uncertainty in the reference relation (“error”, applicable for February and March) is also listed. Ozone loss estimates based on three reference relations (R5, R7, and R8, see Table 3) are shown.