

HALOE observations of the vertical structure of chemical ozone depletion in the Arctic vortex during winter and early spring 1996–1997

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Abstract. We discuss observations by the Halogen Occultation Experiment on the Upper Atmosphere Research Satellite in the lower stratosphere in the Arctic vortex during winter and spring 1996–1997. Using HF as a chemically conserved tracer, we identify chemical ozone depletion and chlorine activation, despite variations caused by dynamical processes. For the Arctic vortex region, significant chemical ozone loss (up to two thirds around 475 K potential temperature) due to extensive activation of the inorganic chlorine reservoir is deduced, as observed similarly for previous winters. Chemical reductions in column ozone of up to 70–80 Dobson units (DU) in the lower stratosphere are calculated. Both chlorine activation and ozone loss inside the vortex, however, are more variable than observed in previous years.

Introduction

Since several years, chemical ozone loss in the Arctic vortex has been inferred from ozonesonde, aircraft, and satellite measurements [e.g., Hofmann *et al.*, 1989; Proffitt *et al.*, 1990, 1993; Browell *et al.*, 1993]. Recent observations [Larsen *et al.*, 1994; Manney *et al.*, 1994, 1996a, b; Donovan *et al.*, 1996; Müller *et al.*, 1996, 1997] indicate particularly strong ozone loss in the Arctic vortex for early 1993, 1995 and 1996. Theoretical work had already indicated the likelihood of ozone destruction in the Arctic vortex due to halogen catalysis; in particular for late winter 1989 and 1992, large ozone losses were calculated [e.g., McKenna *et al.*, 1990; Salawitch *et al.*, 1990; Brune *et al.*, 1991; Müller *et al.*, 1994; Lefèvre *et al.*, 1994].

However, dynamical processes cause considerable transient ozone variations in the Arctic, making it more difficult than for the Antarctic, to quantify chemical ozone depletion [Manney *et al.*, 1994; Müller *et al.*, 1996]. To consider the relationship between an effectively inert trace substance and chemically more active compounds (like e.g., O₃ or HCl) has been established as a method to discriminate chemical change from large variations due to dynamical processes [see e.g., Proffitt *et al.*, 1993; Müller *et al.*, 1996, and references therein]. An unchanging, compact relationship between ozone and an inert tracer (such as N₂O, CH₄ or HF) is predicted for the air mass inside the polar vortex, if no chemical ozone loss would occur [Phumb and Ko, 1992]. This

behavior is actually observed in measurements of the relationship of the inert compounds HF and CH₄ in the Arctic vortex in 1996–1997 throughout the lower stratosphere (potential temperature $\Theta \approx 350$ –600 K). Any deviation from the O₃/HF relation in the vortex is therefore an indication of chemical ozone change.

Here, we analyze the vertical structure of measurements of O₃ and HCl within the Arctic vortex obtained by the Halogen Occultation Experiment (HALOE) [Russell *et al.*, 1993] on the Upper Atmosphere Research Satellite (UARS) in the 1996–1997 winter and early spring seasons, at a time when anomalously low ozone columns were observed [Newman *et al.*, 1997]. For consistency with a companion study [Pierce *et al.*, 1997], which discusses the horizontal distribution of HALOE observations of O₃, HCl, NO_x and H₂O for the northern hemisphere during March 1997, we use here HF as an inert tracer, as an alternative to CH₄, which was used in our recent studies [Müller *et al.*, 1996, 1997]. The observations indicate both a substantial reduction in HCl, implying the conversion of HCl to more reactive chlorine species, and a significant chemical ozone loss in the lower stratosphere of the Arctic vortex during the winter of 1996–1997.

Observations in the Arctic Vortex

Regular HALOE measurements in the Arctic vortex are not available because of the UARS orbit; nevertheless, vortex observations were obtained in late November 1996 and in March/early April 1997. The vortex is characterized by enhanced potential vorticity (PV) and substantially higher HF mixing ratios – the latter being caused by diabatic descent – compared to mid-latitude air. The HF vertical profiles indicate that the vortex air has descended between early November and late March from 630 K to 480 K, i.e., by about 7 km, in agreement with estimates for earlier winters [Abrams *et al.*, 1996].

We use the HF/O₃ and the HF/HCl relation inside the vortex in November 1996 (black symbols in Fig. 1) as a reference for chemically unperturbed conditions. For previous years, the HALOE “early vortex” relation agrees well with corresponding relations observed from aircraft and balloon in the winter 1991–1992 [Proffitt *et al.*, 1993; Müller *et al.*, 1996] and shows a certain year to year variability. The change of the relations between November 1996 and March/April 1997 (Fig. 1) indicates extensive chlorine activation and significant ozone loss in the Arctic stratospheric vortex, similar to HALOE observations in earlier winters [Müller *et al.*, 1996, 1997]. However, the observed chlorine activation and ozone depletion in early 1997 is less uniform than in previous years (Fig. 1) – in accordance with observations by the Microwave Limb Sounder (MLS) [Manney *et al.*, 1997; Santee *et al.*, 1997]. Although throughout March, ozone profiles are

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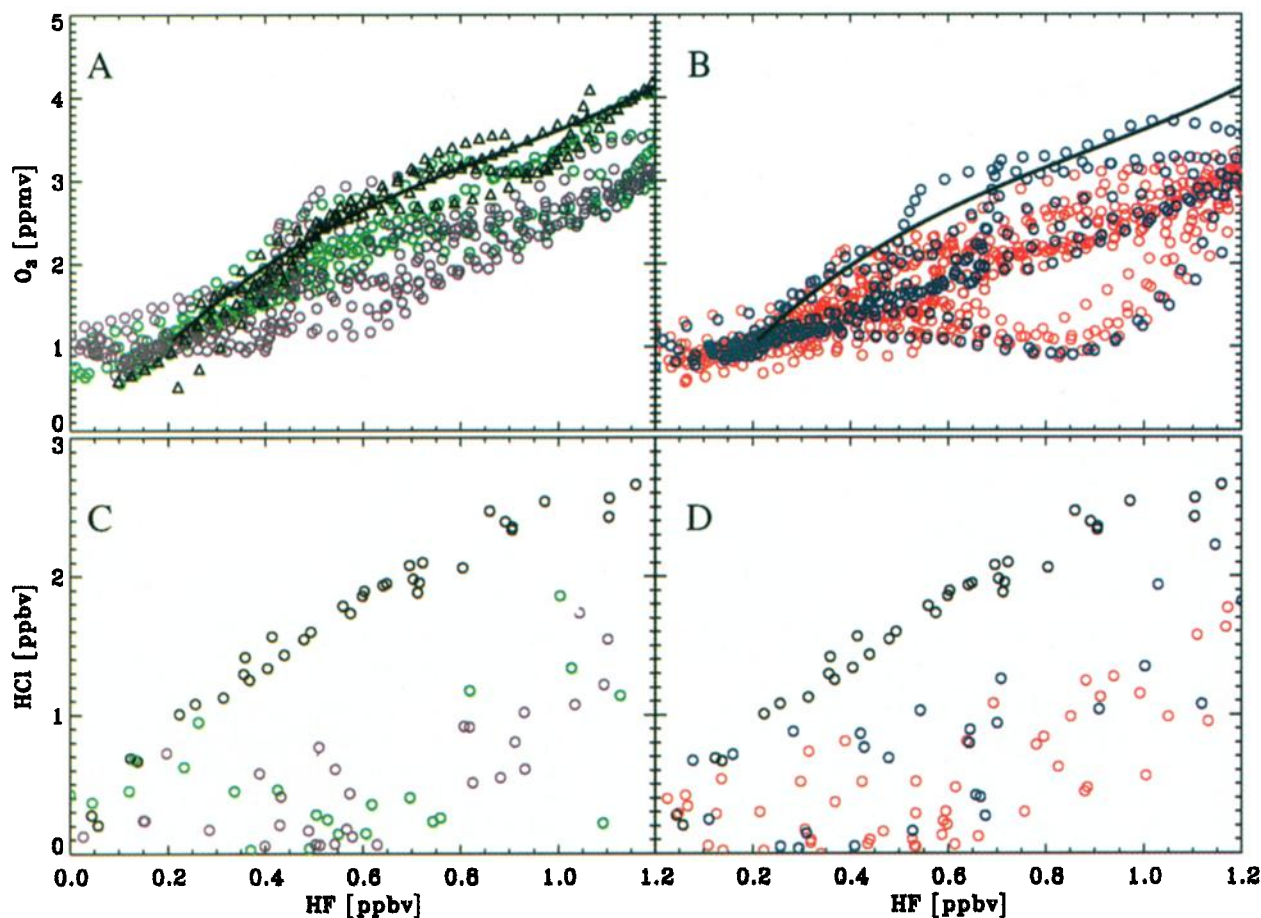


Figure 1. The relation between HF volume mixing ratios and those of O_3 (panels A, B) and HCl (panels C, D) in the northern hemisphere stratosphere for the winter of 1996-1997. Black symbols in panels A, C and D indicate November measurements (15.-17.), the black line in panels A and B shows the relation (Eq. 1) derived from the November observations. Colors indicate time periods; green, March 10-13, purple March 23-25, red March 26-28 and blue March 29-April 1. Note that in contrast to Fig. 2 of *Pierce et al.* [1997], the data encompass the pressure range from 10 to 150 hPa, but exclude data points outside the vortex. HALOE observations were selected so that $PV > 40$ PVU at 475 K, $PV > 90$ PVU at 550 K, and $PV > 200$ PVU at 675 K at the location of the measurement. HALOE V18 data are used exclusively.

observed by HALOE that show considerable ozone loss there are still measurements which show no significant deviation from the initial November HF/ O_3 relation.

TOMS observed the lowest Arctic total ozone in early 1997 on March 26 [Newman *et al.*, 1997]; HALOE measured extremely low O_3 mixing ratios in the lower stratosphere at this time (see Fig. 1 and *Pierce et al.* [1997]). Thus, the vortex O_3 /HF relation on March 26, 1997 is compared with vortex observations on the same day and the three days with the largest ozone loss in late March 1996 (Fig. 2), a winter for which record Arctic ozone loss was observed [Donovan *et al.*, 1996; Manney *et al.*, 1996b; Müller *et al.*, 1997]. While the lowest observed O_3 mixing ratios are similar, very low ozone is more consistently observed in 1996 than in 1997. Furthermore, the HF/ O_3 relation in the incipient vortex in November (Fig. 2) indicates that chemical ozone loss started from higher ozone levels on constant HF isopleths in 1995-1996 than in 1996-1997. However, as HF isopleths are not located on identical Θ -surfaces in different years, this does not imply that O_3 mixing ratios on specific Θ -surfaces are higher in 1996-1997 than in the previous year.

The temporal development of O_3 and HCl in March and

April 1996 and 1997 in an airmass of constant HF mixing ratio of 0.8 ppbv (i.e., \approx at $\Theta = 480$ K, 19.5 km, 50 hPa in late March 1997) is shown in Fig. 3. There, it is again evident that the ozone mixing ratios prevailing inside the vortex in 1997 are somewhat larger and more variable than in the previous year. Thus, – consistent with lidar measurements [Donovan *et al.*, 1997] – the HALOE ozone observations indicate that there was a larger overall chemical ozone loss in 1995-1996 than in 1996-1997.

The HCl mixing ratios in the late vortex in both 1996 and 1997 show a continuous increase with time, indicative of chlorine deactivation. In 1996, the HCl increase began in early March, whereas in 1997 it started in late March, i.e., about when the minimum vortex temperatures rose above the PSC existence threshold (≈ 195 K) in the respective winters [Coy *et al.*, 1997]. Like for ozone; also the HCl measurements indicate more variability inside the vortex in 1997.

Ozone Column Loss

To estimate the ozone mixing ratios which are expected in the absence of chemical removal of ozone, we take the

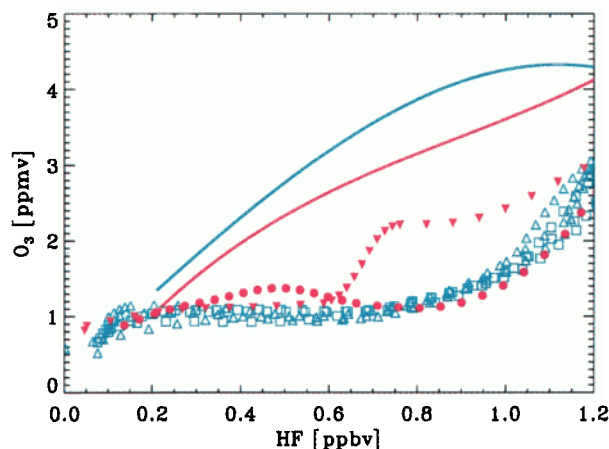


Figure 2. As Fig. 1, but for the HF/O₃ relation on March 26 in the years 1996 (cyan triangles) and 1997 (magenta symbols). Also shown is the HF/O₃ relation for the three days (29.-31. 3.) with the largest ozone loss in the last two weeks of March in 1996 (cyan squares). The solid magenta line shows the “early vortex” relation from Eq. (1), the cyan line the corresponding relation for 1995-1996.

O₃/HF relationship in the early vortex in 1996 as a reference for chemically unperturbed conditions. An empirical relationship

$$O_3 = 2.31 \cdot (HF)^3 - 6.21 \cdot (HF)^2 + 7.82 \cdot (HF) - 0.31 \quad (1)$$

(for O₃ in ppmv and HF in ppbv; valid for 0.2 ppbv < HF < 1.2 ppbv) is derived from HALOE observations in the vortex in November 1996 (black line in Fig. 1A, B). Combining HF profiles measured in March and April 1997 with this “early vortex” O₃/HF relationship (Eq. (1)), we obtain a proxy for the ozone mixing ratio $\hat{O}_3 = f(HF)$ that would be expected in the vortex in early spring if chemical processes were absent [Müller *et al.*, 1996]. Using potential temperature Θ as the vertical coordinate, Fig. 4 shows a comparison between the unperturbed, proxy ozone profiles \hat{O}_3 (green symbols) and the ozone profiles that were actually measured in March/April (red symbols). In many profiles, a strong deficit of ozone is evident throughout the lower stratosphere for March 1997, similar to the five previous winters [Müller *et al.*, 1996, 1997]. The maximum implied local ozone losses of about 2/3 of the proxy ozone mixing ratio are observed for late March around $\Theta = 475$ K, ≈ 19 km, (Fig. 4, bottom panel). However, there are also several observations for which little ozone loss is apparent.

Discussion and Conclusion

The accumulated O₃ reduction between November 1996 and March/April 1997 was integrated over the altitude range 350–550 K (12–21 km, 150–25 hPa) for each HALOE profile in the vortex in March/April to obtain an estimate of the depletion in column ozone. The calculated ozone column loss again reflects the observed variability inside the vortex, with many observations showing chemical ozone loss of up to 50 DU and several profiles indicating larger losses between 60–70 DU. The larger ozone losses tend to occur at measurement locations with larger values of potential vorticity, i.e., further

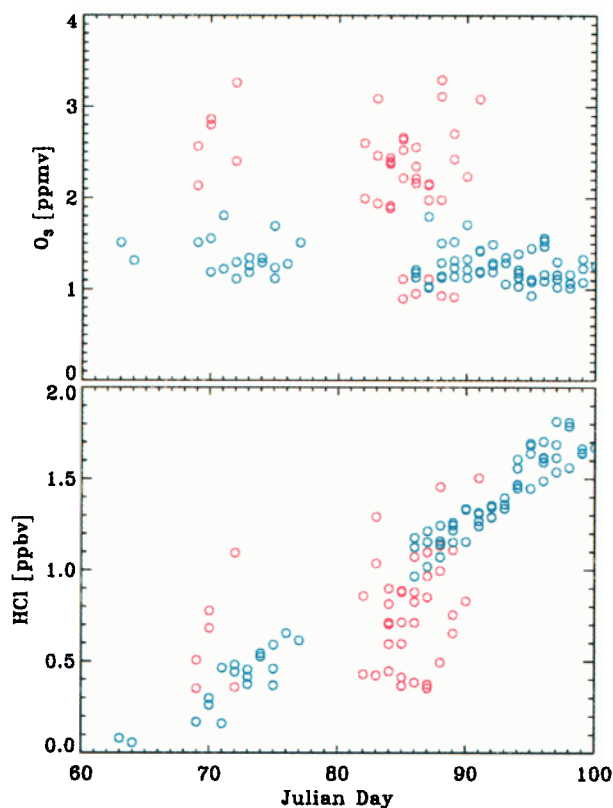


Figure 3. The temporal development of O₃ (top panel) and HCl (bottom panel) at HF = 0.8 ppbv (i.e., \approx at 480 K, 19.5 km, 50 hPa in late March 1997) in the Arctic vortex in the years 1996 (cyan symbols) and 1997 (magenta symbols).

towards the vortex interior, consistent with the findings of Manney *et al.* [1997] and Pierce *et al.* [1997]. These losses are significantly smaller than those derived for March/April 1996 [Müller *et al.*, 1997], consistent with the observation of both higher initial ozone mixing ratios (on a constant tracer isopleth) and lower ozone in the vortex in March/April in 1996 than in 1997 (Fig. 2).

Discussion and Conclusion

As for the five previous Arctic winters, extensive chlorine activation and large ozone losses are indicated by the HALOE observations for 1996-1997. However, the winter of 1996-1997 stands out as one with a unique meteorology, with the vortex being exceptionally weak in early winter, but lasting extremely long (into late April) and showing record low temperatures in early spring [Coy *et al.*, 1997; Santee *et al.*, 1997]. Nonetheless, on the whole, temperatures below the ice frost point ($T \approx 190$ K) were observed much more rarely in 1996-1997 than in the previous winter [Coy *et al.*, 1997]. If one conjectures that such low temperatures are necessary for denitrification of vortex air by the sedimentation of ice particles (the latter being observed in January 1996 [Vömel *et al.*, 1997]), this implies less favorable conditions for O₃ loss in early 1997 than in early 1996. Indeed, vortex averaged ClO is lower and the portion of the the lower stratospheric vortex showing enhanced ClO is smaller in 1996-1997 than in 1995-1996 [Santee *et al.*, 1997]. This might, at least partially,

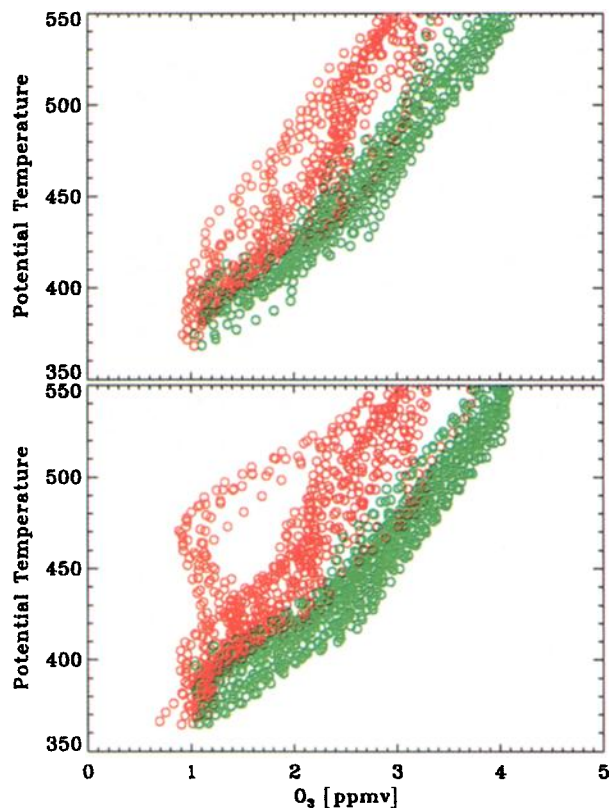


Figure 4. Vertical profiles of ozone mixing ratio (red symbols) measured by HALOE inside the polar vortex in March and April 1997. Also shown is the proxy for the ozone O_3 expected in the absence of chemical processing (green symbols), which is derived from the simultaneous HF measurements (see text). Data for March 10-25 (top panel) and March 26 - April 1, 1997 (bottom panel) are shown.

explain why less O_3 loss is derived here for 1996-1997 than for 1995-1996.

Both chlorine activation and chemical ozone loss in 1997 are substantially more variable throughout the Arctic vortex than observed in previous years. While significant, of the order of up to 50-70 DU, the chemical ozone loss in the Arctic in 1996-1997 did not reach the very large values of 130-160 DU observed in the previous winter [Donovan et al., 1996; Manney et al., 1996b; Müller et al., 1997].

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