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Very early chlorine activation and ozone loss in the Arctic winter 2002–2003

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[1] Chlorine activation and chemical ozone destruction is investigated in the Arctic winter 2002–03 using the tracer-tracer correlation technique. Consistent with very low temperatures in the early vortex, strong chlorine activation at 520 K potential temperature was observed already in mid-December 2002 by the MkIV balloon and at 400–500 K in early January 2003 from HALOE satellite measurements. Large column ozone loss was derived inside the outer vortex in January (23 ± 9 DU) and substantially greater losses in February (51 ± 9 DU) inside the vortex core in 380–550 K. Calculated ozone loss is similar in February in the two completely separated parts of the vortex. Little influence of mixing in of mid-latitude is noticeable after the reunification of the vortex. Further, some ozone loss at lower altitudes likely occurred during March and April consistent with polar stratospheric clouds detected by MIPAS-ENVISAT towards the end of March. *INDEX TERMS:* 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0341 Atmospheric Composition and Structure: Middle atmosphere—constituent transport and chemistry (3334); 0394 Atmospheric Composition and Structure: Instruments and techniques. **Citation:** Tilmes, S., R. Müller, J.-U. Grooß, M. Höpfner, G. C. Toon, and J. M. Russell III, Very early chlorine activation and ozone loss in the Arctic winter 2002–2003, *Geophys. Res. Lett.*, *30*(23), 2201, doi:10.1029/2003GL018079, 2003.

1. Introduction

[2] Ozone depletion inside the Arctic vortex differs substantially from winter to winter [*Manney et al.*, 2003; *Tilmes*, 2003], due to the strong temperature variation. Here, the winter 2002–03 is analyzed using the tracer-tracer correlation (TRAC) technique [e.g., *Proffitt et al.*, 1993; *Müller et al.*, 2002; *Tilmes et al.*, 2003] applied to HALOE satellite measurements [*Russell et al.*, 1993]. Additionally, measurements of various trace gases (e.g., HCl, O_3, CH_4 and HF) were made by the MkIV instrument [*Toon et al.*, 1999] in December 2002 inside the Arctic vortex.

[3] The TRAC technique considers the relation between gases (here HCl and O_3) that may be changed chemically during the course of the Arctic winter and long-lived tracers (here HF) that are known to be chemically inert in the Arctic stratosphere [*Tilmes et al.*, 2003]. Using the TRAC technique, chlorine activation can be identified from changes in the HCl-tracer relation during winter and spring [*Müller et al.*, 1996, 2002]. Further, changes from an O_3-tracer reference relation can be identified as chemical ozone loss. In addition to HALOE and MkIV measurements, we employ observations of high clouds from the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) on ENVISAT [*Fischer and Oelhaf*, 1996]. These data are useful for investigating the development of PSC (polar stratospheric cloud) occurrence over the course of the winter.

2. Development of Temperature and PSC Occurrence Within the Polar Vortex in Winter 2002–03

[4] The Arctic polar vortex formed in November 2002. It showed a symmetric shape and was rather strong during the entire December 2002 and in early January 2003. During the second part of January 2003 the vortex was perturbed and the vortex core was shifted off the pole. During January 13–15 the vortex core was located partly over central Europe (Figure 4, electr. suppl.). During January 19–21 the vortex split and a part of the vortex core was located over North America (Figure 5, electr. suppl., top panels). At the beginning of February the polar vortex became more symmetric again. Afterwards, around February 20, 2003, it split again into two separate parts, one part being situated over North America and one over northern Europe. On February 22, 2003, the vortex re-unified again (Figure 5, electr. suppl., bottom panels) and remained symmetric to the pole during the end of February. In March and the beginning of April the vortex center moved partly towards lower latitudes, but did not split anymore. In mid-April the final warming occurred.

[5] The temperatures in the Arctic polar stratosphere were extremely low in December 2002. At that time, the area of possible PSC existence, A_{PSC}, calculated from the UKMO analysis, is the largest for the entire lifetime of the Arctic vortex 2002–03 (Figure 1); the maximum of the PSC area was located at altitudes between 450 and 600 K. Indeed the first PSCs in winter 2002–03 were detected by MIPAS-ENVISAT on December 1 with top altitudes of ≈24 km (Figure 6, electr. suppl.). PSCs continued to exist until December 29 at altitudes of ≈18 km. In early January, a smaller A_{PSC} was derived for the altitude range of 400–500 K (≈15–19 km). MIPAS measurements show PSC occurrences between January 5–13, mainly in the region of Iceland, Scandinavia and the British Isles. After mid-January, A_{PSC}

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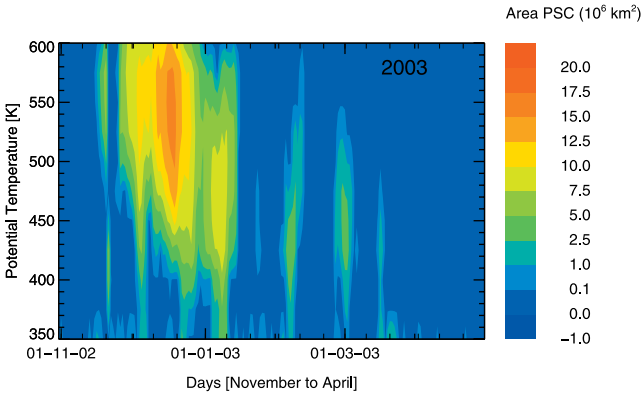

Figure 1. Altitude dependent A_{PSC} over the entire polar vortex for winter 2002–03 from November until April. A_{PSC} was determined from the meteorological analysis of the UKMO and from the PSC threshold temperature calculated for HNO_3 mixing ratio of 10 ppbv and H_2O mixing ratio of 5 ppmv.

is mostly negligible. A small A_{PSC} was found at the beginning of February (Figure 1) and a very small PSC area (a limb-scan) on February 10, 2003, measured by MIPAS at altitudes of 21 km. Although temperatures are low enough for PSC existence around March 1 (Figure 1), no PSCs were detected by MIPAS. The last PSCs for this winter were measured by MIPAS on March 21–23 at ≈15 km over Scandinavia. This is consistent with the last occurrence of A_{PSC} at ≈360–370 K (≈14 km) at that time (Figure 1, Figure 6, electr. suppl.).

3. Chlorine Activation and Ozone Depletion in the Arctic Vortex

[6] In the winter 2002–03, HALOE observations at latitudes north of 50°N are available for January, February and April. The available profiles were assigned to different vortex regions: the vortex core and the outer vortex (the area between vortex core and vortex edge) [*Nash et al.*, 1996; *Tilmes et al.*, 2003]. During January 19–26, 2003, HALOE measurements are available inside the outer vortex. On February 20–25, 2003, the HALOE instrument took measurements in both parts of the separated polar vortex (Figure 5, electr. suppl., bottom panels). No HALOE measurement are available in March 2002 inside the vortex. Later, in mid-April, vortex profiles were measured up to the break up of the vortex.

[7] The MkIV measurements on 16 December 2002 show very low HCl mixing ratios down to ≈0.1 ppbv at ≈520 K (≈1.4 ppbv HF) (Figure 2, top panel, red solid squares). These low HCl mixing ratios clearly indicate that strong chlorine activation has occurred by that time inside the vortex core. For January 2003 HALOE measurements show very low HCl mixing ratios (down to 0.1 ppbv for HF between 0.6–1.1 ppbv (Figure 2, top panel, cyan symbols). Although these profiles are located inside the outer vortex, a strong HCl reduction and, therefore, a strong chlorine activation inside the entire vortex can be assumed in 400–500 K already in January. This is consistent with the large A_{PSC} in December 2002 and the beginning of January 2003. Strong chlorine activation indeed was observed inside the entire vortex by the HALOX instrument on the Geophysica during four flights between 15 and 30 January 2003 [M. v. Hobe and F. Stroh pers. comm.]. An increase of the HCl mixing ratios and, thus, a beginning of chlorine deactivation is noticeable during February 2003. In April, a complete deactivation of chlorine was found (Figure 2, top panel.)

[8] No HALOE measurements are available inside the early vortex 2002. The observations of the MkIV instrument on December 16, 2002, however, are located inside the vortex core, so that a reliable early winter reference function can be derived (Figure 2, red solid squares, bottom panel). Using HF as a long-lived tracer (mixing ratios in ppbv) and O_3 (mixing ratios in ppmv) this early winter reference function (valid for 0.05 ppbv < HF < 1.5 ppbv) is:

$$O_3 = 1.09 \cdot (HF)^3 - 4.36 \cdot (HF)^2 + 6.25 \cdot (HF) + 6.56 \cdot 10^{-3}$$

with an uncertainty of σ = 0.125 ppmv. Early winter reference functions differ from year to year [*Tilmes*, 2003].

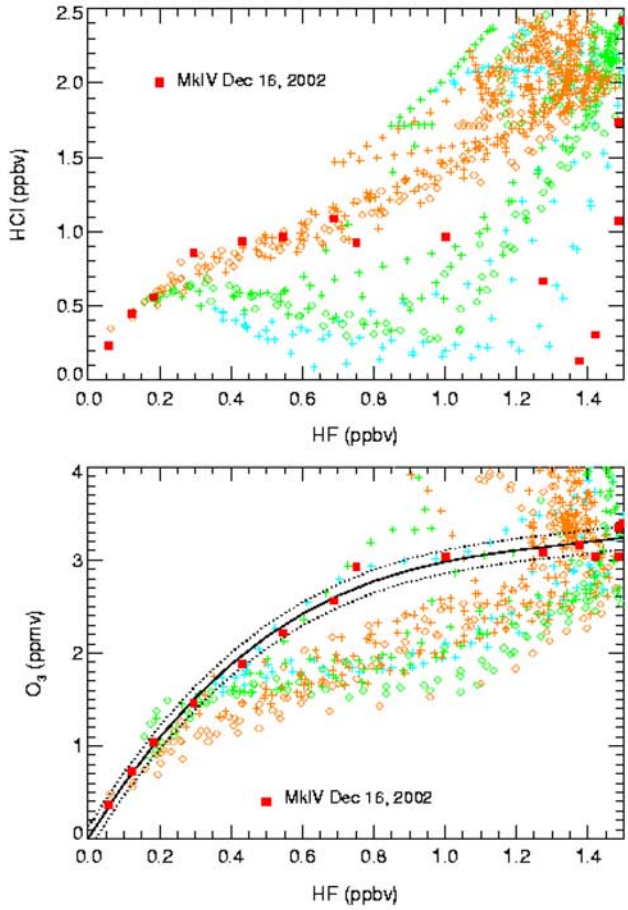

Figure 2. HCl/HF correlations (top panel) and O_3/HF correlations (bottom panel) from HALOE measurements inside the vortex core (diamonds) and the outer vortex (plus signs). Black solid line (bottom panel): early winter reference function derived from MkIV measurements on December 16, 2002, with the uncertainty, black dotted lines. Time intervals of observed profiles: 19–26 January, 2003 (cyan), 15–25 February 2003 (green), 11–19 April, 2003 (orange).

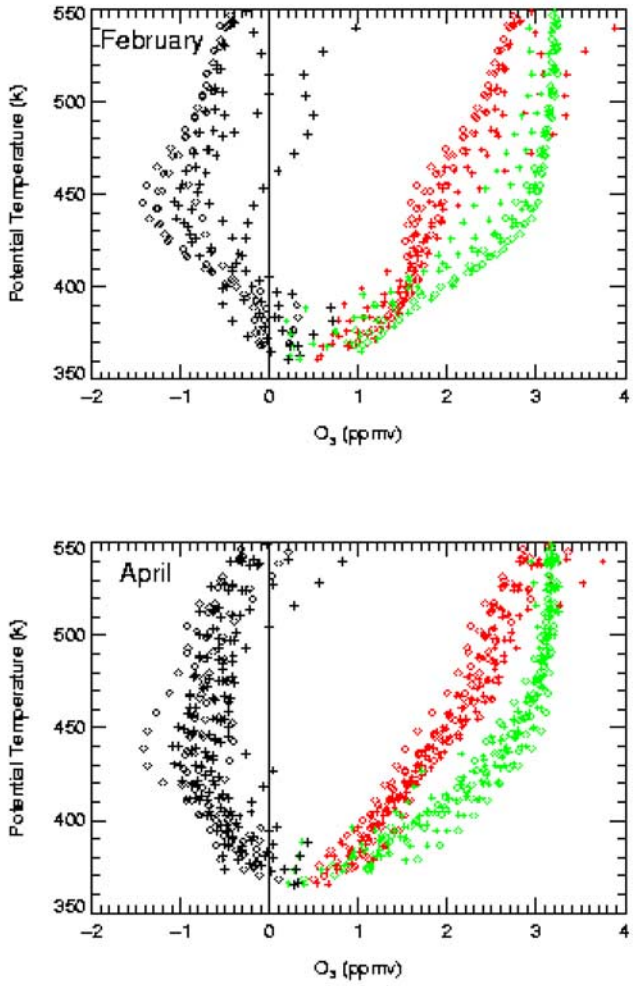

Figure 3. Vertical profiles of measured O_3 mixing ratios by HALOE, red, O_3 mixing ratios expected in absence of chemical change ($\hat{O}_3$), green, and calculated O_3 loss profiles, black, for February (top panel) and April (bottom panel) in winter 2002–03. O_3 was deduced using HF as the long-lived tracer. Profiles are located inside the vortex core (diamonds) and inside the outer vortex (plus signs).

The reference function for the year 2002 is similar to that derived with the TRAC technique in recent years (1999–2000 and 2001–02). However, due to prior chlorine activation some ozone loss may have already occurred by mid-December at the time for which the reference function is determined. This loss, that is limited owing to the lack of sunlight, can not be included in the calculations below.

[9] Deviations from the O_3-tracer reference relation (Figure 2, bottom panel) are stronger during the second half of February for profiles inside the vortex core compared to measurements in January and February inside the outer vortex. Deviations from the reference relation in January and February are rather similar inside the outer vortex. Local ozone loss values of ≈1.0 ppmv were reached at that time (Figure 3, left panel, black plus signs).

[10] Profiles of local ozone loss (Figure 3, top panel, black symbols) are rather homogeneous during February for the separated vortex cores. The maximum of 1.5 ppmv local ozone loss occurred in February at ≈440 K. This indicates a homogeneous ozone destruction in the two vortex cores in spite of their separation during this winter in January and February. Indeed, very similar ozone mixing ratios of less than 2.2 ppmv at 475 K were measured on 20 and 22 February over North America and Russia in the two vortex cores (Figure 5, electr. suppl., bottom panels).

[11] However, a few profiles inside the entire vortex in January and February scatter above the O_3/HF reference function in altitudes below 400 K (Figure 2, bottom panel, Figure 3, top panel) and show smaller ozone loss at higher altitudes. These profiles were measured during February 23–25, when the separated vortex parts were re-unifying again. Thus, these profiles are very likely influenced by mid-latitude air which was mixed into the vortex during the reunification process. Nevertheless, deviations from the early winter reference function are generally quite homogeneous inside the vortex core in February.

[12] In April (Figure 2, bottom panel, orange symbols) one profile shows the strongest deviation from the reference function measured in this winter. Smaller losses are found inside the entire vortex in 400–550 K compared to February (Figure 3). On the other hand, stronger deviations from the reference function are obvious at lower altitudes (380–400 K) in April. This in an indication of ozone loss still occurring sometime during March and April, and not an effect of mixing of air from outside the vortex, because isentropic mixing would lead to an increase of the ozone-tracer relation, also at altitudes below 400 K, and not a decrease as observed here [*Müller et al.*, 2001; *Tilmes et al.*, 2003].

[13] The derived column ozone loss in Dobson Units (DU) with the TRAC technique is summarized in Table 1 loss for the altitude range 380–550 K and 400–500 K. In winter 2003 already in January 23 ± 9 DU ozone loss were reached for 380–550 K and 21 ± 5 DU for 400–500 K inside the outer vortex. Thus, the main fraction of ozone loss occurred between 400–500 K. Between January and February, ozone loss inside the outer vortex for 380–550 K and 400–500 K did not change significantly.

[14] The mean ozone loss inside the vortex core for February 15–25 is 51 ± 9 DU in 380–550 K and 43 ± 6 DU in 400–550. Here, the standard deviation (σ) is less than for the outer vortex. This is in agreement with the notion of a homogeneous distribution of ozone loss inside the vortex core, as described above.

[15] Between February and April, the mean ozone loss inside the vortex core in 400–500 K decreases (by 6 DU) and increases inside the outer vortex (by 8 DU) in the same

Table 1. O_3 loss in Du calculated from HALOE measurements in the winter 2002–2003 using HF as the long-lived tracer[a]

Date	Vortex Core (σ)	Outer Vortex (σ)	Max
380–550 K			
19.–26.01.		23 ± 9 (14)	33 ± 8
15.–25.02.	51 ± 9 (6)	26 ± 9 (12)	57 ± 10
11.–19.04.	49 ± 10 (11)	40 ± 10 (12)	61 ± 10
400–500 K			
19.–26.01.		21 ± 5 (13)	29 ± 6
15.–25.02.	43 ± 6 (7)	24 ± 6 (11)	47 ± 6
11.–19.04.	37 ± 6 (10)	32 ± 6 (9)	52 ± 6

[a]The uncertainty is derived from the uncertainty of the reference function; standard deviation: σ. Max: the maximum O_3 loss of all observed profiles.

altitude range. This results in smaller differences between column ozone loss inside the vortex core and the outer vortex and indicates a well mixed entire vortex in April. The mean column ozone loss of the entire vortex (core and outer vortex) remains nearly constant (from 34 DU in February to 35 DU in April in 400–500 K).

[16] In 380–550 K the decrease of ozone loss inside the vortex core is much smaller (2 DU) and the increase of column ozone inside the outer vortex is stronger (14 DU) between February and April compared to 400–500 K. The mean column ozone loss of the entire vortex increases from 39 DU to 45 DU in this altitude range. This indicates that further ozone loss occurred, mainly below 400 K.

4. Discussion and Conclusion

[17] Due to the very low temperatures during December 2002, a large A_{PSC} was deduced. Already at that time, very strong chlorine activation was detected by the MkIV instrument at ≈520 K. In January, strong chlorine activation occurred at altitudes between 400–500 K as measured by HALOE. The occurrence of chlorine activation in this altitude range corresponds to the altitude range of high probability of PSCs existence derived from UKMO analysis and MIPAS-ENVISAT observations. Afterwards, a temperature increase around mid-January, resulted in only little potential for PSCs during the following month (Figure 1). Some chlorine deactivation was deduced from the HALOE measurements in the vortex in February. In April, chlorine was completely deactivated.

[18] The maximum column ozone loss amounts to 33 ± 8 DU in January inside the outer vortex and 57 ± 10 DU in February inside the vortex core. In April, still one vortex profile exists with very large ozone loss (61 ± 10 DU). Thus, some further ozone loss likely occurred sometime between February and April consistent with the likely existence of localized PSCs until the end of March mainly at altitudes below 400 K. Local ozone loss is 1.0 ppmv in January and February inside the outer vortex. The maximum local ozone loss is 1.5 ppmv at ≈440 K between mid-December and February/April. The calculated ozone loss is very large in January inside the Arctic vortex and it was not observed to this extent before, using the TRAC technique [*Tilmes*, 2003]. Large early winter column ozone losses were also reported for the winters 1993–94 and 1994–95 by *Goutail et al.* [1999]. If large local ozone losses were deduced for January, they were found to be significantly smaller than in the winter 2002–03, for example 0.5 ppmv in 1994–95 derived from MLS and Match [*Harris et al.*, 2002; *Manney et al.*, 2003; *Rex et al.*, 1999].

[19] Although the vortex core split in two separate parts in January and February, a very similar amount of chlorine activation and ozone loss was found in the two parts. Some influence of mixing from mid-latitude air was detected mainly inside the outer vortex at a time when the vortex was re-unified again in February 23–25, 2003.

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References

Fischer, H., and H. Oelhaf, Remote sensing of vertical profiles of atmospheric trace constituents with MIPAS limb-emission spectrometers, *Appl. Opt.*, *35*, 2787–2796, 1996.

Goutail, F., et al., Total ozone depletion in the Arctic during the winters of 1993–94 and 1994–95, *J. Atmos. Chem.*, *32*, 35–59, 1999.

Harris, N., M. Rex, F. Goutail, B. Knudsen, G. Manney, R. Müller, and P. von der Gathen, Comparison of empirically derived ozone loss rates in the Arctic vortex, *J. Geophys. Res.*, *107*(D20), doi:10.1029/2001JD000482, 2002.

Manney, G., L. Froidevaux, M. Santee, N. Livesey, J. Sabutis, and J. Waters, Variability of ozone loss during Arctic winter (1991 to 2000) estimated from UARS Microwave Limb Sounder measurements, *J. Geophys. Res.*, *108*, doi:10.1029/2002JD002634, 2003.

Müller, R., P. J. Crutzen, J.-U. Grooß, C. Brühl, J. M. Russel III, and A. F. Tuck, Chlorine activation and ozone depletion in the Arctic vortex: Observations by the Halogen Occultation Experiment on the Upper Atmosphere Research Satellite, *J. Geophys. Res.*, *101*, 12,531–12,554, 1996.

Müller, R., U. Schmidt, A. Engel, D. McKenna, and M. Proffitt, The O_3/N_2O relationship from balloon-borne observations as a measure of Arctic ozone loss in 1991–1992, *Q. J. R. Meteorol. Soc.*, *127*, 1389–1412, 2001.

Müller, R., et al., Chlorine activation and chemical ozone loss deduced from HALOE and balloon measurements in the Arctic during the winter of 1999–2000, *J. Geophys. Res.*, *107*, 8302, doi:10.1029/2001JD001423, 2002.

Nash, E. R., P. A. Newman, J. E. Rosenfield, and M. R. Schoeberl, An objective determination of the polar vortex using Ertel's potential vorticity, *J. Geophys. Res.*, *101*, 9471–9478, 1996.

Proffitt, M. H., K. Aikin, J. J. Margitan, M. Loewenstein, J. R. Podolske, A. Weaver, K. R. Chan, H. Fast, and J. W. Elkins, Ozone loss inside the northern polar vortex during the 1991–1992 winter, *Science*, *261*, 1150–1154, 1993.

Rex, M., et al., Chemical ozone loss in the Arctic winter 1994/95 as determined by the Match technique, *J. Atmos. Chem.*, *32*, 1–34, 1999.

Russell, J. M., L. L. Gordley, J. H. Park, S. R. Drayson, A. F. Tuck, J. E. Harries, R. J. Cicerone, P. J. Crutzen, and J. E. Frederick, The Halogen Occultation Experiment, *J. Geophys. Res.*, *98*, 10,777–10,797, 1993.

Tilmes, S., Chemical ozone loss in the Arctic polar stratosphere derived from satellite observations, Dissertation, Uni Frankfurt, 2003.

Tilmes, S., R. Müller, J.-U. Grooß, D. McKenna, J. M. Russell, and Y. Sasano, Calculation of chemical ozone loss in the Arctic winter 1996–1997 using ozone-tracer correlations: Comparison of ILAS and HALOE results, *J. Geophys. Res.*, *108*, 4045, doi:10.1029/2002JD002213, 2003.

Toon, G. C., et al., Comparison of MkIV balloon and ER-2 aircraft measurements of atmospheric trace gases, *J. Geophys. Res.*, *104*, 26,779–26,790, 1999.

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