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Chemical ozone depletion during Arctic winter 1997/98 derived from ground based millimeter-wave observations

J. Langer, B. Barry, U. Klein, B.-M. Sinnhuber, I. Wohltmann, K. F. Künzi

Institute of Environmental Physics, University of Bremen, Bremen, Germany

Abstract. We present ground based millimeter-wave measurements of Arctic stratospheric ozone at Ny-Ålesund, Spitsbergen (79N, 12E), for winter 1997/98. Vortex averaged chemical ozone depletion rates around the 475 K isentropic level were derived from our observations using measured ozone trends for 20 day periods and calculations of diabatic descent inside the vortex. Back trajectory calculations for air-parcels crossing Ny-Ålesund show that measurements at Ny-Ålesund were representative for vortex air-masses. Significant chemical ozone depletion was observed during one period at the end of February 1998 with loss rates of 32 ppb/day around the 475 K isentropic level. During this period the loss rate was higher than in February 1997. Due to the early breakup of the polar vortex, the chemical ozone depletion stopped in March and the accumulated loss is found to be 0.64 ±0.2 ppm in 1997/98.

Introduction

Observations in the 1990s of ozone in the Arctic winter stratosphere show significant ozone decline which has been found to be of chemical origin [e.g., *Rex et al.*, 1997; *Müller et al.*, 1997; *Sinnhuber et al.*, 1998]. Chemical precursors of fast ozone depletion develop during periods with low temperatures allowing the activation of chlorine from its reservoir species. Liberation of chlorine occurs on surfaces of particles in PSCs and on surfaces of cold sulfate aerosols (coated by HCl) or liquid ternary solutions below a threshold temperature of approx. 195 K [e.g., *Kawa et al.*, 1997]. The vortex area with temperatures below 195 K was found to be related to ozone depletion rates [*Rex et al.*, 1997; *Sinnhuber et al.*, 1998].

Both, winter 1995/96 and spring 1997, were characterized by record low stratospheric temperatures with ozone depletion rates comparable to Antarctic winter situations [*Rex et al.*, 1997]. Although the chemical processes leading to ozone depletion are believed to be the same in both hemispheres, the accumulated ozone loss in the Arctic is lower. This is due to the fact, that temperatures inside the Arctic polar vortex are higher than inside its Antarctic pendent [*Santee et al.*, 1995]. Also periods with air well isolated inside the Arctic vortex are usually shorter than in the Antarctic. Several approaches were used to separate dynamically induced ozone variations from chemical depletion [e.g., *Rex et al.*, 1997; *Sinnhuber et al.*, 1998]. *Sinnhuber et al.* [1998] presented a technique to estimate loss rates from millimeter-wave ozone time series at Ny-Ålesund, Spitsbergen (79N, 12E), for spring 1997. In this paper we use the same technique to investigate the ozone loss in winter 1997/98.

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Ozone data and meteorological data

Ground based millimeter-wave measurements of ozone were performed at one of the Arctic primary stations of the Network for the Detection of Stratospheric Change (NDSC) at Ny-Ålesund, Spitsbergen. Profiles were obtained from the Radiometer for Atmospheric Measurements (RAM) belonging to the standard instrumentation of the NDSC station. From the shape of the pressure broadened 142 GHz ozone line we retrieve volume mixing ratio (VMR) profiles using the optimal estimation method [e.g., *Rodgers*, 1976]. Pressure and temperature profiles used in the retrievals were taken from the National Center for Environmental Prediction (NCEP) meteorological analysis. We use a dynamical integration scheme averaging spectra over 10 minutes to one day to achieve high profile quality independent of weather conditions. The retrieved ozone profiles extend from 12 to 55 km on a 1 km vertical grid and the vertical resolution is approx. 8 km. For a description of the RAM see *Langer et al.* [1996].

Information on potential vorticity (PV) was derived from meteorological data of the European Centre for Medium Range Weather Forecasts (ECMWF). We identified the vortex edge according to *Nash et al.* [1996] as the region with the strongest PV gradient with respect to equivalent latitude. The vortex was well established from mid-November 1997, but remained weak until the beginning of January 1998 compared to February/March 1998. From reverse domain filling (RDF) calculations [*Sinnhuber et al.*, 1996] we found that the vortex center was built up of coherently moving air-masses. A minor warming occurred in the beginning of January leading to significant intrusions of, and mixing with outer-vortex air as RDF calculations revealed. Thereafter a stronger vortex reformed with the inner-vortex again well isolated from mid-latitude air for the period January 23 to the beginning of March. During this period the strength of the vortex defined by the maximum PV gradient at the 475 K isentropic level (approx. 20 km altitude) was unusually high compared to the 80s and early 90s [*Manney et al.*, 1994], but similar to last years vortex. However, the area covered by the inner polar vortex was only half as big as last years Arctic vortex. Minimum hemispheric temperatures in January 1998 were comparable to January 1997, but in February/March 1998, temperatures were considerably higher than in 1997.

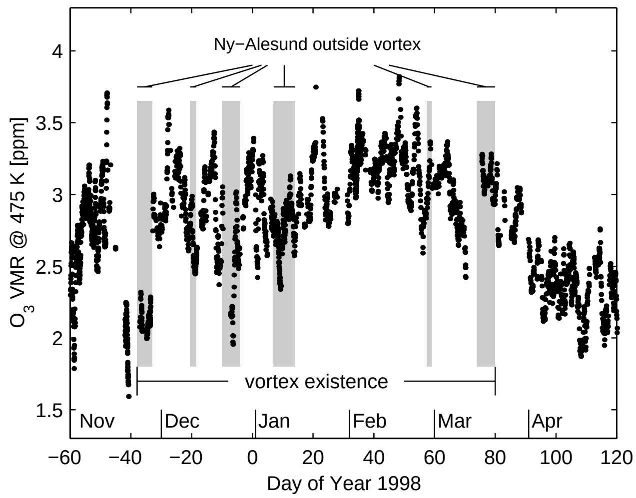

Figure 1. Ozone volume mixing ratio on the 475 K isentropic level for winter/spring 1997/98 (dots) measured by the ground based millimeter-wave radiometer at Ny-Ålesund. The bar indicates the vortex existence period. Gray areas indicate situations when Ny-Ålesund was located outside the vortex.

Ozone evolution and data analysis

RAM ozone measurements were available continuously throughout the winter 1997/98. The ozone profiles were vertically interpolated to the 475 K isentropic level representing averaged ozone content around this level according to the RAM vertical resolution. The potential temperature was derived from NCEP temperature data, which were also used in the retrievals. Figure 1 shows the evolution of ozone for winter/spring 1997/98. Periods when Ny-Ålesund was outside the vortex are marked by gray boxes.

When the vortex formed, the ozone content at the 475 K isentropic level was around 2.8 ppm and stayed at this value to mid-January. Values slightly increased to about 3.2 ppm until mid-February and then dropped down to about 2.8 ppm by mid-March. Afterwards, the vortex vanished and the ozone content was about 2.5 ppm. Significantly lower ozone content (around 2.1 ppm) was observed during two short intervals at the end of November and the end of December 1997. PV-maps revealed that these two events are related to a displacement of the vortex away from Ny-Ålesund and the advection of mid-latitude air (from far outside the vortex with low PV and low equivalent latitude) into the polar region.

We obtained vortex-averaged ozone change rates by fitting a linear trend on the data for 20 day periods [*Sinnhuber et al.*, 1998]. During the 20 day fitting period air circles around the vortex usually two to four times. We thus average over spatial inhomogeneties inside the vortex seen on hemispheric ozone maps [e.g., *Manney et al.*, 1997] and get vortex-averaged information.

To make sure that measurements at Ny-Ålesund were representative for the vortex during the 20 days fitting period, we performed back-trajectory calculations of air parcels ending at Ny-Ålesund for every hour. We analyzed the location of each parcel with respect to the location of the vortex in order to determine suitable periods for our analysis. Therefor we used PV maps derived from 10 day reverse domain filling calculations [*Sinnhuber et al.*, 1996] giving more insight into the detailed structure of the vortex and also providing the opportunity to identify intrusions. Air-masses considered in our trend analysis must fulfill two criteria: Firstly, air-parcels must have been inside the vortex for the last ten days prior to the measurement at Ny-Ålesund. This criterion is equivalent to the conservation of PV along the path of the air-masses. Secondly, the air-masses crossing Ny-Ålesund consecutively must originate from locations which were close to each other ten days before. This means that situations were rejected when a strong horizontal wind shear was present along the path of the air-masses. Table 1 summarizes all available 20 day periods for trend analysis fulfilling the criteria above.

Chemical ozone depletion

We derived chemical ozone loss rates from the fitted trends by correcting measured trends for the expected ozone changes due to diabatic vertical transport of air-masses. Diabatic vertical transport is produced by radiative cooling or solar heating. This transport through the 475 K isentropic level induces ozone content changes due to the gradient of ozone VMR with respect to potential temperature.

Vortex averaged radiative heating/cooling rate calculations on the 475 K isentropic level were performed for days when Ny-Ålesund was inside the vortex. The calculation scheme used is described in *Sinnhuber et al.* [1998] and references therein. Long-wave cooling for December 1997 to March 1998 varies from $d\theta/dt = 0.6$ K/day to $d\theta/dt = 1.3$ K/day (where θ is potential temperature) for low and high vortex mean temperatures, respectively. Short-wave solar heating with rates around 0.1 K/day is relatively unimportant due to the absence of sun-light inside the vortex during the periods considered.

We have calculated the diabatically induced ozone change rates on the 475 K isentropic level from our observed vertical ozone gradients and the calculated subsidences. Chemical ozone depletion rates are estimated as difference between the expected ozone increase due to diabatic subsidence and the observed ozone trends. Figure 2 shows the expected ozone increase (solid line), the fitted trends (filled circles with 1 sigma errorbars) and the resulting chemical ozone loss (open diamonds, gray boxes indicate the averaging period and the error of the trend).

We estimated ozone loss rates per sunshine hour from the daily loss rates by calculating the area-weighted mean stratospheric sunshine exposure time inside the vortex (Figure 3, open diamonds, gray boxes indicate the averaging period and error of the trend). Dark gray areas in Figure 3 indicate the area inside the vortex below 195 K as derived from ECMWF temperature analyses.

Table 1. Periods available for trend analysis with Ny-Ålesund inside an undisturbed vortex (Exceptions: Ny-Ålesund outside the vortex for a short time).

	Period 1	Period 2	Period 3
Date	97/11/28 - 97/12/18	98/01/25 - 98/02/14	98/02/14 - 98/03/06
Day #	-33 to -13	25 to 45	45 to 65
Exceptions	-18.5 to -20.5		57.5 to 59

Discussion

Chemical ozone depletion rates were derived for three periods in winter 1997/98 (Figure 2). During the first period from November 28 to December 18, 1997, the observed ozone trend was smaller than the expected change from diabatic descent. However, the derived chemical ozone depletion rate is not statistically significant. Because of the short sunlight exposure during that period this is to be expected due to the small accumulated ozone loss. A prolongation of the analysis period to reduce the error in the trend is not possible since the inner vortex was disturbed before and after the analysis period. The disturbance was especially severe in mid-January when major intrusions of outer vortex air occurred. Chemical ozone changes can not be separated from the effect of mixing in this case, since the amount of air mixed into the vortex during such events is hard to quantify in general [*Sobel et al.*, 1997].

By end of January 1998, after the reformation of a strong vortex, trend-analyses were performed again for two consecutive periods. For the first period from January 25 to February 14, 1998 no significant depletion was found.

For the period from February 14 until March 6, 1998 the observed ozone trend was negative while an ozone increase was to be expected from diabatic subsidence. From this we conclude that strong chemical ozone depletion occurred which compensated for the expected increase and led to a net ozone reduction. The calculated ozone depletion rate is high (32 ± 10 ppb/day or 4 ± 1.25 ppb/sunlit-hour). After March 6, the vortex was disturbed and vanished 15 days later. The accumulated ozone loss in winter 1997/98 was estimated to be 0.64± 0.2 ppm on the 475 K isentropic level for periods when the vortex was well established.

Compared to the previous winter, we have observed higher ozone depletion rates at the end of February 1998 than in February 1997. In February 1997 rates were about 22 ppb/day or 2.8 ppb/sunlit-hour [*Sinnhuber et al.*, 1998]. However, estimations on the accumulated ozone loss in 1996/97 were considerably higher with 1.6 ppm since the vortex was persistent to the beginning of May and depletion occurred over a longer period than in 1997/98.

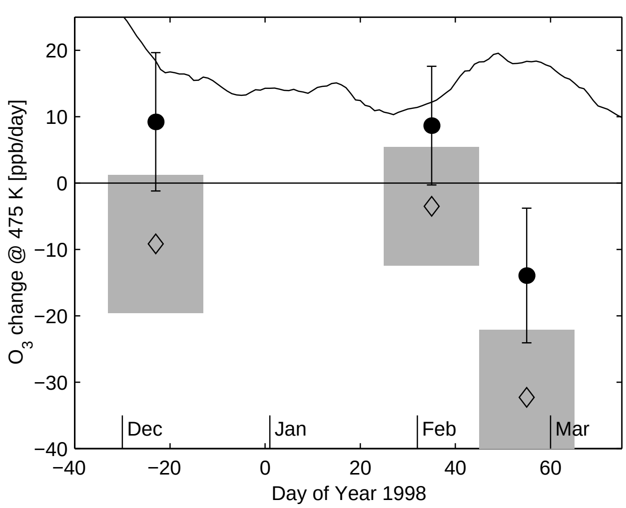

Figure 2. Observed ozone trend at the 475 K isentropic level derived from ground based millimeter-wave measurements at Ny-Ålesund (filled circles, errorbars due to the statistical uncertainty of the trend analysis). The solid line shows the expected ozone change due to diabatic vertical movement. Estimated chemical ozone depletion is indicated by diamonds, gray boxes correspond to the averaging period and errorbars of the trend analysis.

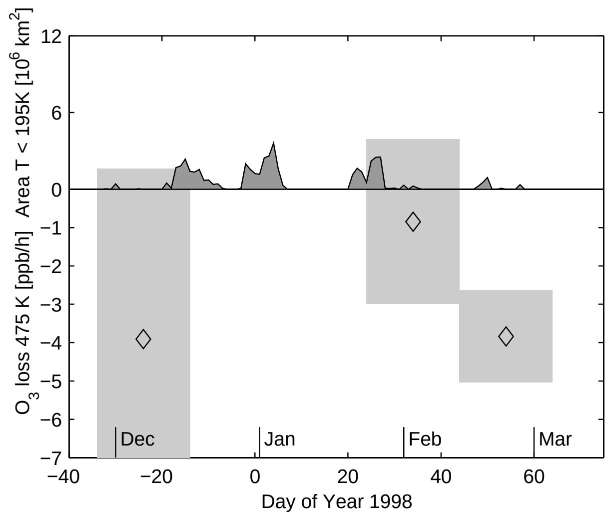

Figure 3. Estimated chemical ozone depletion rate on the 475 K isentropic level (open diamonds) per sunlit hour. Gray boxes indicate the averaging period and the errors from observed ozone trends. Also included is the vortex area with temperatures below 195 K according to the ECMWF analysis.

Depletion rates in February 1998 indicate that a strong chlorine activation must have been present. This is supported by observations of chlorine monoxide measured with the RAM at Ny-Ålesund. Preliminary retrievals show an enhanced chlorine monoxide content in the lower stratosphere around the middle of February 1998. Activated chlorine is expected to be found for air-masses, that experienced temperatures below approx. 195 K and a correlation between the area of temperatures below 195 K and ozone depletion rates was found by *Sinnhuber et al.* [1998] for the winter 1997/98 and by *Rex at al.* [1997] for winter 1995/96. But in contrast to previous winters when strong ozone depletion coincided with large areas below 195 K, temperatures below 195 K were predicted only on small areas in winter 1997/98 and no correlation between loss rates and the area of low temperature was found. Evidence for chlorine activation for a situation when synoptic temperatures were higher than 195 K is given by *Sinnhuber et al.* [1998] and *Raffalski et al.* [1998]. Ozone depletion and enhanced chlorine levels were observed in April 1997 more than two weeks after the last PSCs (temperatures below 195 K) were predicted.

The influence of mesoscale temperature reductions induced by mountain waves on chlorine activation and ozone loss is presently discussed [*Carslaw et al.*, 1998]. Temperature reductions of as much as 15 K are to be expected, leading to the formation of PSCs in regions where synoptic scale temperature data were predicted to be above 195 K. However, the degree of chlorine activation and the resulting ozone depletion in these mesoscale phenomena is uncertain yet.

Conclusion

Millimeter-wave ozone measurements revealed that in the winter 1997/98 again substantial chemical ozone loss around the 475 K isentropic level occurred. The vortex was less stable than in the previous year and temperatures dropped only for short periods below temperature where chlorine activation has to be expected. However, the ozone depletion rate of 32 ppb/day at the end of February is even higher than last years depletion rates indicating a strong chlorine activation. No dependency of the depletion rate on the area with temperatures below 195 K was found in 1998. Due to the early breakdown of the vortex in 97/98, chemical ozone depletion stopped early and the accumulated loss was only 0.64 ± 0.2 ppm in 97/98.

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J. Langer, B. Barry, U. Klein, B.-M. Sinnhuber, I. Wohltmann, K. Künzi, Institute of Environmental Physics, University of Bremen, PO Box 33 04 40, D-28334 Bremen, Germany. (e-mail: Ulf.Klein@uni-bremen.de)

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