STRATOSPHERIC CHLORINE ACTIVATION IN THE ARCTIC WINTERS 1995/96 TO 2001/02 DERIVED FROM GOME OCIO MEASUREMENTS

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ABSTRACT

In this article, we present satellite observations of OCIO from the years 1995 to 2002. The focus is on observations of OCIO in the Arctic wintertime stratosphere, which are compared to results of the SLIMCAT model and to observations in the Antarctic. In particular, we investigated the beginning and ending of the chlorine activation in the Arctic stratosphere. The Slant Column Densities of OCIO increase significantly, when the temperature falls below the threshold for formation of Polar Stratospheric Clouds. The time for decrease of the OCIO-SCDs in the deactivation phase (early spring) varies strongly and is related to the degree of denitrification. In the Arctic, chlorine activation can be further increased when there is strong activity of stratospheric mountain waves.

INTRODUCTION

In the polar winter, when temperatures fall below a certain threshold, Polar Stratospheric Clouds (PSCs) can form. By heterogenous reactions on these particles, the chlorine reservoirs are converted to ozone destroying species (active chlorine, ClO_x) (Solomon, 1999), mainly by reaction (1). This activation of chlorine initiates catalytic ozone destruction cycles, which are responsible for the depletion of ozone in the polar spring (McElroy, 1986; Molina, 1987). By reaction of ClO with BrO, chlorine dioxide (OCIO) is formed (reaction (2)).

Since this is the only important reaction leading to the formation of OCIO in the stratosphere, OCIO can serve as an indicator for stratospheric chlorine activation. While the main processes that lead to the depletion of ozone are well understood, there are still open questions like the duration of chlorine activation, its dependence on the abundance of nitrogen oxides or the influence of stratospheric mountain waves. Satellite-measurements have the advantage that they observe the whole globe with the same instrument on a long time scale. GOME observations of OCIO can therefore be useful to investigate these open questions.

METHOD OF MEASUREMENT

Global Ozone Monitoring Experiment (GOME)

The GOME instrument aboard the European Research Satellite ERS-2 consists of a set of four spectrometers covering the spectral range from 240 to 790 nm (Burrows et al., 1999). It measures the intensities from the direct sunlight and from the light scattered back from the earth and its atmosphere to the satellite. Developed mainly for the monitoring of ozone, GOME is able to detect a range of atmospheric absorbers, among them NO_2 , BrO, SO_2 , HCHO and OCIO.

Differential Optical Absorption Spectroscopy (DOAS)

For the retrieval of the column densities of the atmospheric absorbers, the method of DOAS is used (Platt, 1994). This algorithm simultaneously fits the slant column densities of several absorbers to the ratio of the earthshine spectrum and a Fraunhofer reference measured by GOME. For the OCIO fit we use the wavelength range between 363 and 391 nm. Details of the OCIO-analysis are described in Wagner et al. (2001). Similar OCIO measurements by GOME have been reported by Wittrock et al. (1999).

RESULTS

OCIO in the Activation Phase

Due to a higher probability for formation of PSCs, chlorine activation increases with falling temperatures. We investigated the relation between the minimum temperature at the $T_{\text{pot}} = 475$ K level (approx. 19 km) and the slant column densities (SCDs) of OCIO and found a strong anticorrelation (see Figure 1). This anticorrelation is seen in the temporal evolution of the OCIO SCDs in all Arctic winters observed with GOME (Wagner et al., 2001; Wagner et al., 2002; Wilms-Grabe et al., 2002). Significant activation of chlorine is seen only for temperatures below the PSC-threshold.

Comparison to SLIMCAT

We compared the maximum SCDs of OCIO measured by GOME with the maximum concentration of ClO_x calculated by SLIMCAT (Chipperfield, 1999) for the winter 1999/2000. Although GOME measures slant column densities of OCIO and SLIMCAT calculates the concentrations of $\text{ClO}_x (= \text{ClO} + 2 \text{Cl}_2\text{O}_2)$, we found a qualitative agreement of the observed with the modelled values (see Figure 2). Also, the corresponding maps show activation of chlorine in the same intensity and same spatial extension for almost all days of that winter (Kühl et al., 2002). These findings support the usefulness of OCIO as an indicator for ClO, at least for a SZA below 92° .

Fig. 1. Maximum SCDs of OCIO at a solar zenith angle of 90° , plotted as a function of the minimum temperature at the 475 K level (ECMWF data). It can be seen that the SCDs of OCIO show an increase as soon as the minimum temperature falls below 195 K, which is the threshold for PSC-type 1a (NAT)-formation at the 475 K level.

Fig. 2. Maximum SCDs of OCIO measured by GOME at a solar zenith angle of 90° (white dots) compared to the maximum concentration of ClO_x at the 475 K level calculated by SLIMCAT (black triangles) for the arctic winter 1999/2000. Due to the polar night, GOME can not observe chlorine activation close to the pole in the early winter.

OCIO in the Arctic winters 1995/96 to 2001/02

The formation of PSCs is related to the temperatures in the stratosphere, which show a large annual variability in the Arctic. Therefore, the intensity of chlorine activation in the Arctic winters varies strongly (see Figure 3). Strong activation is found for the cold winters 1995/96, 1996/97, 1999/2000 and 2000/01. Only sporadic activation is seen in the warmer winters 1997/98, 1998/99 and 2001/02. The different degrees of chlorine activation correspond with the observed depletion of ozone in these winters (Rex et al., 2002).

Fig. 3. Maximum OCIO SCDs at a solar zenith angle (SZA) of 90° in the arctic winters 1995/96 to 2001/02 as observed by GOME. Also shown is the minimum temperature at the $T_{\text{pot}} = 475$ K level (grey dashed line). The dotted line indicates the threshold for formation of PSCs type 1 (NAT) at the 475 K level. The highest chlorine activation is found in 1999/2000, while in 1996/97 OCIO SCDs are increased until mid of march, which is the time, where the ozone-depletion cycles are most effective due to long daily duration of sunlight. From late January until early February 2001, no GOME data are available.

Comparison to Antarctic

Meteorological conditions in the Antarctic stratosphere are very different from those in the Arctic. The polar vortex is stronger and temperatures are lower, leading to a higher probability of PSC-formation, especially PSC type 2 (Ice). Accordingly, the SCDs of OCIO above the Antarctic are higher and show a much lower variability than in the Arctic (see Figure 4). Also, chlorine activation is extended over a larger area (see Figure 5) and lasts longer into the spring, when the sunlight returns, both factors leading to a larger ozone loss than in the Arctic.

Fig. 4. Maximum SCDs of OCIO at a solar zenith angle of 90° for the Arctic winters 1995/96 to 2001/02 (see legend) compared to minimum and maximum values of the Antarctic winters 1996 to 2001 (red envelope). For comparison, the Antarctic values are shifted by 6 months. The SCDs of OCIO in the Antarctic are around 30% higher than those in the Arctic; chlorine activation in the Antarctic has a longer duration and shows less annual variability.

Fig. 5 Maps of the OCIO SCDs above the Arctic and Antarctic, each at a time where the spatial extension of chlorine activation is at its maximum. Colour scale: see Figure 6.

Activation by Stratospheric Mountain Waves

It has been shown by Carslaw et al. (1998) that adiabatic cooling due to mountain induced gravity waves can lead to formation of PSCs and therefore an increase in depletion of ozone in the Arctic Stratosphere.

On January 21, 1997, temperatures on the synoptic scale were above the threshold for PSC type 2 (Ice) formation. In contrast, calculations of the mesoscale model MM5 for January 21st show that temperatures over Northern Scandinavia were below the frostpoint, and the formation of PSC-type 2 has been reported by LIDAR-measurements at Kiruna and Sodankylä (Dörnbrack et al., 1999).

GOME measurements of that day show a significant increase of OCIO SCDs in this region (see Figure 6). Similar increases of OCIO SCDs related to strong activity of mountain waves, especially above northern Scandinavia, were found for January 1996, 1998 and 2000.

Fig. 6. Maps of the SCDs of OCIO from the 20th to the 22nd of January, 1997. On the 21st of January, a sudden increase is seen over northern Scandinavia, the same region where strong activity of mountain waves has been reported for the same day (Dörnbrack et al., 1999). The strong westerly wind, which caused these mountain-waves, is seen in the plume with lower activation (red colour-scale) east of the center of activation. One day later, the activated air-masses have been transported to the east (red area above northern Russia).

OCIO in the Deactivation Phase

To determine the time for deactivation of chlorine in the arctic winters, the SCDs of OCIO in the late winter/early spring were examined. For that study, we investigated how long it took until the OCIO SCDs decrease to values below the detection limit (approx. $5 \cdot 10^{13}$ molec/cm², see Wagner et al., 2001) after the temperatures have risen above the threshold for PSC-formation. As a common tool to determine a lifetime, an exponential decay was fitted to the data. The thus determined deactivation time was found to be 16 days for the year 2000 (see Figure 7), 14 days for 1996, 8 days for 1997 and 9 days for 2001. These findings correspond to the different degrees of denitrification in these years (Santee et al., 2000; Davies et al., 2002). The deactivation of chlorine mainly happens by the reaction of chlorine monoxide with nitrogen dioxide:

Hence, if the vortex is poor in NO₂ due to the removal of the nitrogen reservoirs by denitrification, the deactivation will take longer as in years where NO₂ is more abundant, because the nitrogen reservoirs have been depleted only slightly. For the Antarctic, where strong denitrification takes place each winter, a deactivation time of 18-24 days was found for the years 1996-2000.

Fig. 7. SCDs of OCIO in the deactivation phase of several arctic winters (black squares) and an exponential fit to the data (black curve): $N(t) = N_0 \exp(-t/\tau)$. This fit allows us to derive the time τ needed until the OCIO SCDs drop to values below the detection limit. Also shown is the minimum temperature at the 475 K level (grey dashed line). No further significant increase in the OCIO SCDs is seen, when this temperature rises and stays above 195 K.

CONCLUSIONS

GOME observations of OCIO give a good overview of the chlorine activation in the Arctic stratosphere and are suitable to investigate topics of stratospheric chlorine chemistry such as the following findings:

The Slant Column Densities of OCIO are anticorrelated to the minimum temperature at the 475 K level and show a strong increase when $T_{\min}$ falls below 195 K. For the winter 1999/2000, the maximum SCDs of OCIO at a solar zenith angle of 90° measured by GOME show a good agreement with the maximum concentration of ClO_x at the 475 K level calculated by SLIMCAT. Stratospheric mountain waves can lead to a significant increase of OCIO SCDs measured by GOME. These observations reaffirm the importance of such waves for stratospheric chlorine

activation above the Arctic. The time for deactivation of stratospheric chlorine in arctic winters, derived from the lifetime of OCIO, depends on the degree of denitrification: for winters where a strong denitrification was observed, we find a deactivation time of 14-16 days. Accordingly, chlorine deactivation takes place faster (8-9 days) in winters with weak denitrification.

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