FIRST RESULTS ON THE DOAS - RETRIEVAL OF OClO FROM SCIAMACHY NADIR MEASUREMENTS

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ABSTRACT

The Scanning Imaging Absorption Spectrometer for Atmospheric Chartography was launched successfully onboard ENVISAT on March 1, 2002. It observes solar radiation transmitted, backscattered from the atmosphere and reflected from the ground in nadir, limb and occultation viewing modes. Chlorinedioxide (OClO), an important indicator for stratospheric chlorine activation, can be measured in the UV spectral range by Differential Optical Absorption Spectroscopy (DOAS).

First results of the DOAS retrieval of OClO slant column densities (SCDs) from the SCIAMACHY measurements are presented. The influence of several parameters like the wavelength range chosen as fitting window or the reference spectra included in the fit on the quality of the retrieval is examined. It is found that a proper correction of polarisation features in the spectra is essential for a good DOAS analysis of OClO.

The OClO SCDs derived from SCIAMACHY are compared to measurements of the Global Ozone Monitoring Experiment (GOME) which has successfully measured OClO since 1995. SCIAMACHY flies in the same orbit, but measures approx. 30 minutes earlier than GOME. As OClO shows a strong diurnal variation, this leads to differences in the observed column densities, which may be useful to investigate the photochemistry of OClO and related compounds. Also, the spatial resolution of SCIAMACHY is higher (30*60 km^2 compared to 40*320 km^2 for GOME), which will allow a more detailed study of small scale effects like e.g. chlorine activation in mountain waves.

1. STRATOSPHERIC CHLORINE ACTIVATION

In the polar winter, stratospheric temperatures can fall below the threshold for formation of polar stratospheric clouds (PSCs). On PSC particles, heterogeneous reactions take place, which convert the ozone-inert chlorine reservoirs (mainly $ClONO_2$ and HCl) into ozone destroying species (active chlorine, mainly Cl, ClO and ClOOCl, see e.g. [1]). This activation of chlorine initiates catalytic ozone destruction cycles like the ClO-ClOOCl and the ClO-BrO cycle [2,3]. OClO (chlorine dioxide) is almost exclusively formed by reaction of ClO with BrO [4]. The amount of OClO in an air mass therefore gives a good indication of the level of chlorine activation, especially for solar zenith angles below 90 degrees [5,6,7]. Since OClO shows strong differential absorption features in the UV spectral range, it can be detected by means of Differential Optical Absorption Spectroscopy (DOAS) [8,9,10]. GOME observations of OClO have been applied for the long-term monitoring of chlorine activation [10,11,12] and for case studies [13,14,15].

2. SCIAMACHY

The Scanning Imaging Absorption Spectrometer for Atmospheric Chartography [16] is a UV/VIS/NIR grating spectrometer aboard the European Environmental satellite ENVISAT. It measures the intensities of the direct sunlight and of the light scattered back from the earth and its atmosphere in moderate spectral resolution over a wide wavelength range, see Table 1.

Ch.	Spectral range [nm]	Spectral resolution [nm]	Species detectable by DOAS
1	240 - 314	0.24	O_3, ClO, NO
2	309 - 405	0.26	HCHO, SO_2, BrO, **OClO**, O_4, NO_2
3	394 - 620	0.44	O_3, O_4, NO_2, H_2O
4	604 - 805	0.48	O_2, O_4, NO_3, H_2O
5	785 - 1050	0.54	H_2O
6	1000 - 1750	1.48	H_2O, CO_2, CH_4
7	1940 - 2040	0.22	H_2O, CO_2
8	2265 - 2380	0.26	H_2O, CO, CH_4, N_2O

Table 1: Spectral channels of SCIAMACHY with wavelength range, spectral resolution, and the atmospheric trace gases that can be retrieved by DOAS.

Compared to its precursor GOME [17], SCIAMACHY has a better spatial resolution (groundpixel size of 30x30 to 30x240 km^2 compared to 40x320km^2 for GOME). In addition to the nadir measurements, it performs also limb radiance and solar and lunar occultation measurements. Also, the spectral range is enlarged, thereby enabling for the retrieval of greenhouse gases like CO_2, CH_4, and CO.
While ENVISAT flys in a sun synchronous near polar orbit, descending from north to south on the sunlit side, SCIAMACHY scans the surface in the perpendicular west east direction. During each scan, the spectra of 4 to 32 ground-pixels are recorded, depending on the variable spatial resolution. With up to 15 orbits per day, and due to the alternating limb and nadir measurements, global coverage is achieved in six days.

3. DOAS

For the retrieval of the OClO column densities from the SCIAMACHY nadir spectra, the method of Differential Optical Absorption Spectroscopy (DOAS) is used [9, 10].
This algorithm minimizes the difference between the logarithmized Fraunhofer reference and a polynomial representing scattering processes on one side and the logarithm of the measured earth shine spectra and the sum of the absorptions due to trace gases on the other side by a least square fit. As result, the slant column densities of several trace gases absorbing in the respective wavelength range can be retrieved.
For the OClO DOAS analysis of SCIAMACHY spectra we use the wavelength range from 363 to 391 nm, the same as for GOME (see Fig. 1). Included reference spectra are: OClO, NO_2, O_3, O_4, Ring, and the Eta and Zeta Spectrum (from keydata) for correction of polarisation features, see Table 2.

Spectrum	Remark
OClO	213 K, Krominga et al., 2003 [18]
O_3	223 K, Bogumil et al., 2003 [19]
O_4	298 K Greenblatt et al., 1990 [20]
NO_2	220 K, Vandaele et al., 1997 [21]
Ring	Calculated, Bussemer, 1993 [22]
Offset	$1/I_o$ included in Fit
Polarisation 1	Eta from key data
Polarisation 2	Zeta from key data
Fraunhofer 1	Atmospheric spectrum, SZA 70°
Fraunhofer 2	Direct solar spectrum, ESM
Fraunhofer 3	Direct solar spectrum, ASM

Table 2: Overview of the included reference spectra in the Heidelberg OClO analysis.

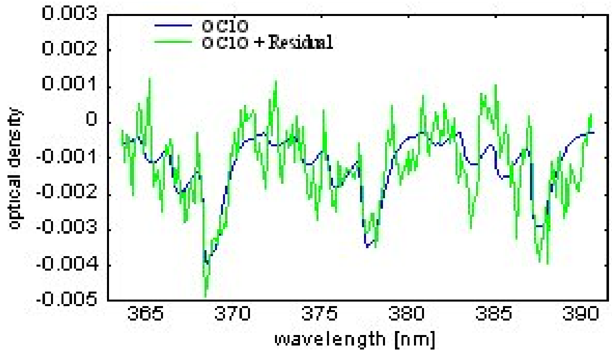

Fig. 1: OClO analysis for a SCIAMACHY spectrum containing high OClO absorption (orbit 7419, SZA: 89°).

From various tests (see e.g. Fig. 2.) it turned out that the inclusion of the polarisation correction spectra is essential for a correct retrieval of OClO. Other parameters that were tested are the wavelength range used for the analysis (fit window), the degree of the polynomial, and the inclusion of the reziprocal of the Fraunhofer Reference ($1/I_0$) in the fit. The latter leads to a correction of a potential intensity-offset. The degree of the polynomial was chosen as 5. While the OClO fit works in many fit windows, we finally chose as wavelength range the same as for GOME, for reason of consistency.
We also examined the influence of the used Fraunhofer-Reference on the quality of the fit. The best results were obtained by using the spectra from the diffuser of the azimuth scanning mirror (ASM-Spectrum) or an Earth Shine reference measured at low latitudes (therefore containing no OClO absorption). The fit with the spectrum from the diffuser of the elevation scanning mirror (ESM-Spectrum) leads to much higher residuals and in many cases also to a larger offset and scatter of the retrieved OClO SCDs.

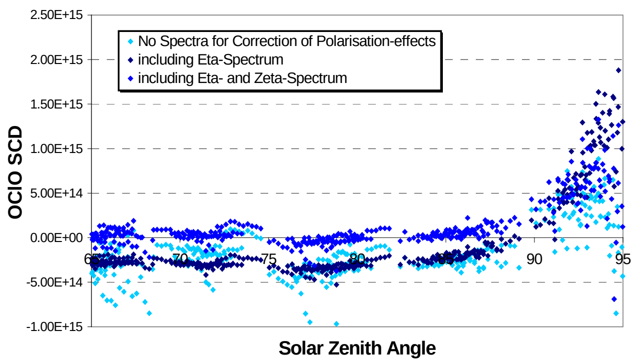

Fig. 2: OClO SCDs as a function of the solar zenith angle (SZA) retrieved for the orbit 2509, either including two, one or no spectra for correction of polarisation features.

4. FIRST RESULTS

SCIAMACHY nadir data are available since August 2002. Here we present first results of the Heidelberg scientific OClO analysis for selected days with chlorine activation in the northern and southern hemisphere. Fig. 3 and 4 show maps of OClO SCDs for some selected days of the Arctic winters 2002/2003 and 2003/2004 and of the Antarctic winter 2003. The regions where high OClO SCDs are observed, coincide with the spatial extension of the polar vortex.

Fig. 3 (top) shows available orbits for the 11th of January, 2003. The early winter 2002/03 was cold, leading to high levels of chlorine activation and therefore large OClO SCDs. In contrast, temperatures in the winter 2003/04 were much higher. Consequently, the OClO SCD map for the 10th of January, 2004 (Fig. 3, bottom) reveals only little level of chlorine activation.

Above the Antarctic, high OClO SCDs are usually observed from mid of may till end of september [10]. An exception was the year 2002, where a major warming caused a rapid increase of the temperatures and OClO SCDs declined one week earlier as usual [14].

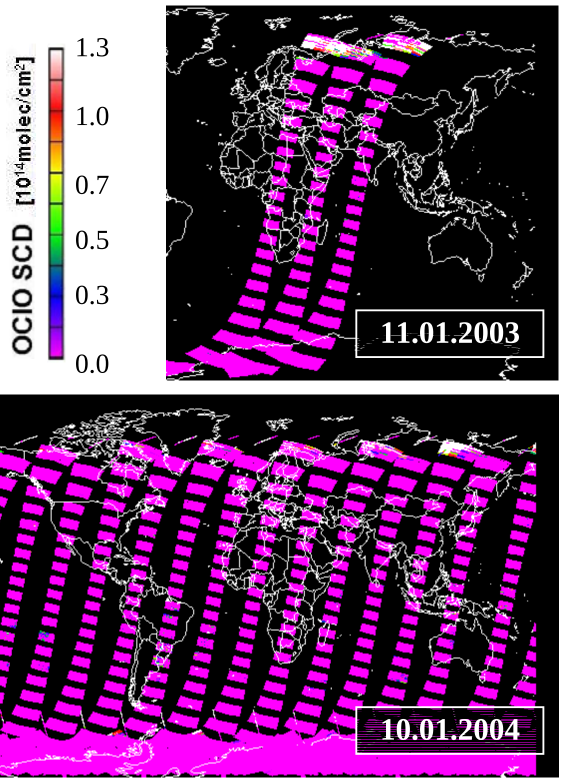

Fig. 3: SCIAMACHY OClO SCDs for the 11th of January 2003, and for the 10th of January, 2004.

Fig. 4: SCIAMACHY OClO SCDs for the 1st, 12th and the 25th of August, and for the 3rd of September 2003.

5. COMPARISON TO GOME RESULTS

To investigate how the SCIAMACHY OClO observations agree with independent measurements, we compared the derived OClO SCDs to the ones obtained from the GOME spectra of the corresponding orbits.
For all examined orbits, the OClO SCDs show a good qualitative and quantitative agreement, see Figs. 5, 6 and 7.
Deviations can be explained by the difference in the measurement time, which for the same geographic location leads to a difference in the SZA, by the smaller pixel size, and by transport of the activated air masses in between the two measurements. Also, the SCIAMACHY OClO SCDs show a larger scatter, possibly due to a still insufficient correction of the polarisation features.

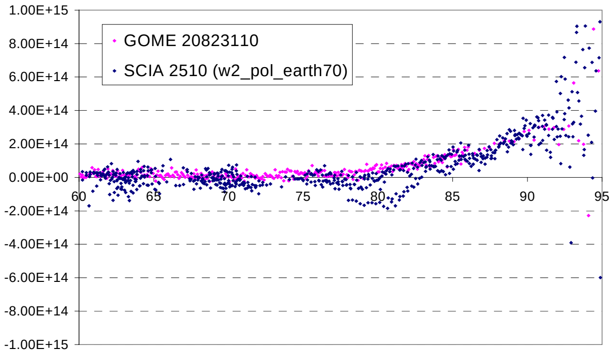

Fig. 5: OClO SCDs as a function of the solar zenith angle (SZA) for the orbit 2510 and for the corresponding GOME orbit.

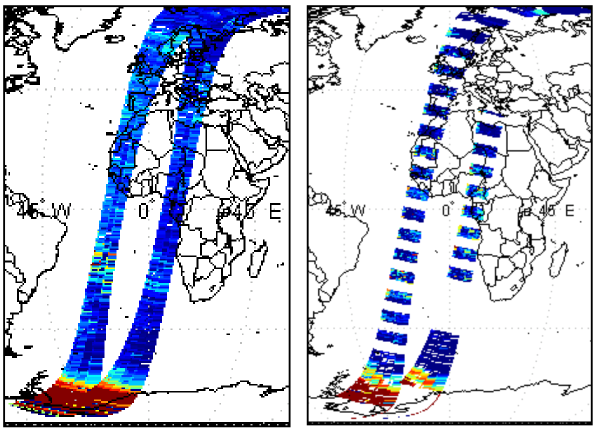

Fig. 6: Comparison of maps of OClO SCDs derived from GOME and SCIAMACHY (scientific algorithms from the University of Heidelberg). Displayed are results for the SCIAMACHY orbits 2509 and 2510 (right) and for the corresponding GOME orbits (left) from the 23rd of August, 2002.

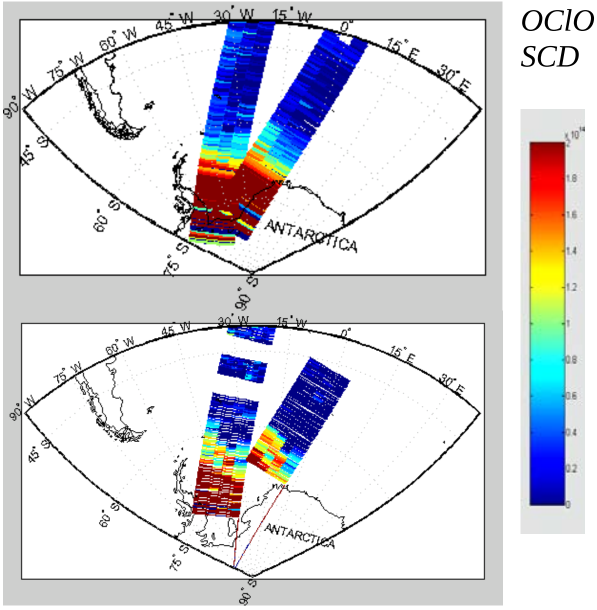

Fig. 7: same as Fig. 6 but in south-pole projection.

6. CONCLUSION & OUTLOOK

First results of the Heidelberg scientific SCIAMACHY OClO analysis were presented. The OClO SCDs derived from SCIAMACHY spectra by the DOAS method are consistent with expectations from stratospheric chlorine chemistry. Large OClO SCDs are observed only for regions inside the polar vortex, their magnitude is in good agreement with independent measurements.
The OClO absorption could clearly be found in the SCIAMACHY spectra. Best results are obtained by using the ASM spectrum or an Earth shine reference (SZA = 70°) as Fraunhofer reference. The correction of the polarisation features by including the Eta and Zeta spectra from key data is essential.
For a few orbits the OClO SCDs have been compared to the ones retrieved from GOME spectra for the respective orbits and a good agreement (qualitatively as well as quantitatively) was found. Differences can be attributed to transport, the different pixel size and the different SZA.
The difference in the OClO SCDs due to different solar zenith angles may be very useful to investigate the photochemistry of OClO. Also, limb measurements from SCIAMACHY will provide information about the vertical profile of OClO. This will allow for a proper calculation of OClO air mass factors also for high solar zenith angles. With the correct air mass factors, the OClO SCDs can then be converted to vertical column densities.

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