COMPARISON OF MODELLED AND MEASURED CHLORINE DIOXIDE SLANT COLUMNS FOR THE ARCTIC WINTER 2004/2005

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ABSTRACT

In this paper, OClO measurements from SCIAMACHY are presented and validated with ground-based DOAS observations. In addition, the different measurements are compared to model calculations including the photochemical change along the light path to investigate the degree of overall consistency.

Although OClO does not participate directly in the destruction of Ozone, its accurate measurement as well as modelling is crucial to understand the highly perturbed chlorine chemistry in the polar vortices.

SCIAMACHY OClO slant columns for the spring 2005 have been validated by comparison with measurements in Ny-Ålesund (79°N, 12°E), Summit (73°N, 38°W), and Bremen (53°N, 9°E). Also, modelled OClO slant column densities, synchronised to the solar zenith angle of the measurements are included in this comparison.

Overall, a good agreement is found between the SCIAMACHY and the ground-based measurements. However, the model predictions significantly disagree with the measurements by under-estimating the OClO for periods with strong chlorine activation.

1. INTRODUCTION

One of the most important issues in atmospheric science remains the understanding of the stratospheric ozone depletion, especially, in polar regions. In polar spring, inert chlorine species of primarily anthropogenic origin are converted to radicals or their precursors by means of heterogeneous reactions taking place on the surface of polar stratospheric clouds (PSCs). During this process, NO_x (nitric oxide NO and nitrogen dioxide NO_2) is trapped in the PSCs as nitric acid HNO_3 hindering the restoration of reservoir species. The temperature threshold for the formation of PSCs is 195 Kelvin and they are therefore only observed in the winter-time polar stratosphere. The species formed on the surfaces are e.g. Cl_2 and HOCl. In spring, photolysis releases the chlorine radicals initiating the catalytic destruction of ozone resulting in the so-called ozone hole over the springtime pole [1, 2]. Within this context, the ClO-BrO-cycle is a very effective ozone destruction cycle in the lower polar stratosphere [3-5]. In a side channel of the 'BrO+ClO'-reaction chlorine dioxide OClO is produced:

$$\mathrm{BrO} + \mathrm{ClO} \rightarrow \mathrm{Br} + \mathrm{OClO} \quad (1)$$

Eq. (1) is thought to be the predominant production mechanism for atmospheric OClO during daytime [6, 7] and leads to a null cycle in ozone destruction.

The arctic winter 2004/2005 was characterised by extraordinarily cold temperatures in the stratosphere. Hence in contrast to prior years of SCIAMACHY measurements (see Fig. 1 for a monthly average of the OClO slant columns), a large and also persistent vortex developed.

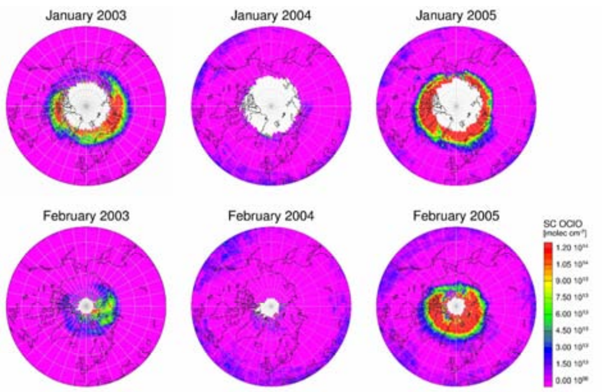

Figure 1. Monthly averages of SCIAMACHY OClO slant column densities over the Arctic for the winters 2003 to 2005.

The aim of this study is to present SCIAMACHY OClO retrievals, to validate them with ground-based measurements, to compare modelled and measured OClO columns and to study the temporal evolution of OClO columns in all three data sets.

2. DATA SETS

Four general problems arise when comparing OClO measurements with each other or with model predictions:

- the rapid photochemistry
- a changing column and profile during twilight
- the change of SZA along the line of sight
- low signals at large SZA

Because of these difficulties, the comparison is best performed directly for the slant columns. Although the viewing geometry is totally different comparing satellite- and ground-based measurements, the air mass factors (AMF), which are the ratio between the slant column density, integrated along the line of sight, and the vertical column density, yield similar values at large

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solar zenith angles. This is shown in Fig. 2 where the AMF modelled for the same vertical profile (modelled OClO profile for Ny-Ålesund at 12:00 UT on 4th March) are shown for both observation geometries and agreement within 4 percent is found between 89° and 91° SZA. Consequently, the slant column densities of OClO from different platforms can be compared directly. For consistency, the modelled OClO profiles are also converted to slant column densities for the given observational geometry assuming arctic back-ground conditions for the aerosol in the radiative transfer calculations. In the following, the three data sets used in this study are described.

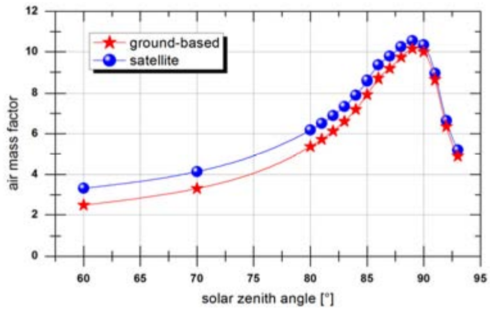

Figure 2. OClO air mass factor for satellite and for ground-based viewing geometry differing by less than 4% between 89° and 91° SZA.

2.1. SCIAMCHY

The SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric CartograpHY) is a spectrometer designed to measure sunlight, transmitted, reflected and scattered by the Earth's atmosphere or surface in the ultraviolet, visible and near infrared wavelength region (240 nm – 2380 nm) at a moderate spectral resolution (0.2 nm – 1.5 nm) [8]. SCIAMACHY was launched on ENVISAT into a sun-synchronous orbit on 1st March 2002 having an equator crossing time of 10 AM local time (descending node). Global coverage is obtained within six days at the equator and within one day at 70° in spring. The spatial resolution varies between 30 km times 30 km and 240 km times 30 km depending on location and season.

SCIAMACHY is in many aspects similar to its predecessor instrument GOME which has already been used extensively for OClO measurements [9-13]. Interpretation of the satellite measurements is complicated by the rapid photochemistry of OClO combined with the sun-synchronous orbit of the satellite. In order to facilitate systematic validation with ground-based measurements, we here compare satellite-measured OClO over the stations with the OClO column measured from the ground at the time of satellite-overpass.

The obtained spectra are analysed with the well-known Differential Optical Absorption Spectroscopy (DOAS) method (see e.g. [14]). The fitting procedure, in a window from 365 to 389 nm, includes, besides the OClO cross section [15] and a polynomial for the compensation of broad-band features, the nitrogen dioxide NO_2 [16], and the oxygen dimer O_4 [17] absorption cross sections as well as a rotational Raman scattering cross section [18]. Additional corrections have to be included to account for undersampling and the polarisation sensitivity of the instrument. As an individual measurement of SCIAMACHY has only a very short exposure time and therefore limited signal to noise at low sun, all measurements within 200 km of a station are averaged over a day. The resulting fitting quality is illustrated in Fig. 3. The overall accuracy of the averaged data is about 30 percent or higher.

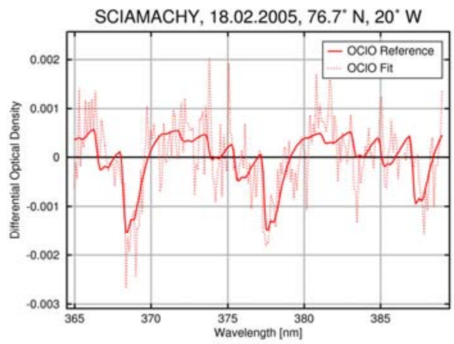

Figure 3. Fit example for SCIAMACHY.

2.2. Ground-based Measurements: BREDOM

The BREDOM (Bremian DOAS Network for Atmospheric Measurements) is a ground-based network of high-quality UV/visible spectrometers for atmospheric observation that has been set up by the Institute of Environmental Physics (IUP), University of Bremen, Germany. All instruments are NDSC/NDACC-approved [19, 20]. The temperature-stabilised spectrometers are equipped with cooled CCD detectors. The spectral resolution is about 0.5 nm to 0.8 nm and about 7 to 12 pixels cover the full width at half maximum depending on the individual instrumental set-up. The instruments are connected to a multi-axis telescope via a quartz-fibre bundle and are described in more detail elsewhere [21-23]. Here, only measurements of light scattered in the zenith are used. The measurement sites include Ny-Ålesund (Svalbard, 79°N, 12°E), Summit (Greenland, 73°N, 38°) and Bremen (Germany, 53°N, 9°E).

Similar retrieval settings as for the SCIAMACHY data are applied to the ground-based spectra. Here, as background spectrum, a measurement at a small solar zenith angle is used. A fit example for an OClO slant column density of approximately 4 x 10^{14} molecules cm^{-2} measured in Ny-Ålesund at 18th February is presented in Fig. 4.

The spectral fit error is usually below 10 percent at 90° SZA. This includes uncertainties introduced by spectral interferences of the different absorption cross sections, by the Ring effect and by the wavelength calibration of the cross sections. For most spectra, the detection limit is less than 1 x 10^{14} molecules cm^{-2} at 90° SZA.

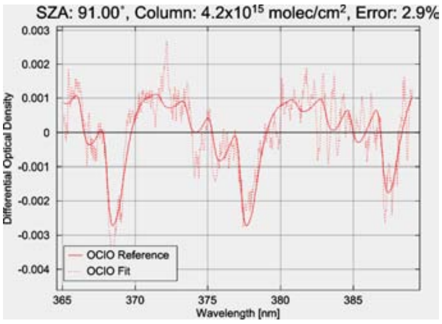

Figure 4. Fit example for Ny-Ålesund, February 18.

2.3. Modelling

The ground-based measurements and SCIAMACHY OClO are compared to modelled slant columns. These are calculated in three steps: First of all, the results of the three-dimensional (3D) chemical transport model SLIMCAT [24] are extracted on a daily basis at 12:00 UT over the stations and thereafter, in a second step, used to initiate a set of one-dimensional (1D) photochemical stacked box models [25] to obtain absorber profiles for the individual species at high temporal resolution.

The OClO profiles as a function of solar zenith angle are then used to derive slant column densities. This third step is accomplished with the full-spherical radiative transfer model SCIATRAN [26, 27] which includes the correct treatment of the photochemistry along the line of sight, i.e. the change of concentration of the absorber with local SZA is taken into account when the light path is simulated. This so-called photochemical enhancement is necessary for photo-labile substances with a short lifetime such as OClO.

3. VALIDATION

In the following the ground-based measurements are averaged over 2° SZA. For SCIAMACHY data, all pixels with their centre within a radius of 200 km around the station are used and then the average SZA is given. The modelled columns on the other hand correspond to the exact angle present at the measurement site.

The figures 5 and 6 show the OClO slant columns for spring 2005 over Ny-Ålesund and Summit. Note that the SZA of SCIAMACHY measurement is changing over the time series since the overpass takes place at a fixed time close to the local noon. So the variation during this time period is mainly caused by the decreasing SZA and the associated increased photolysis rate of OClO.

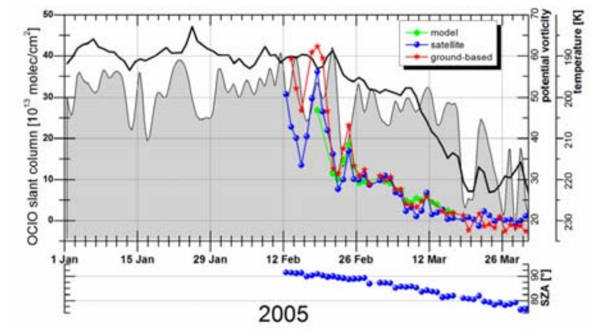

Figure 5. OClO columns over Ny-Ålesund in spring 2005. The ground-based data was sampled at the time of ENVISAT overpass. Also shown are potential vorticity (shaded area) and temperature (black line) at the 475 Kelvin isentropic surface.

In Ny-Ålesund, apart from the first few days, the agreement between ground-based and satellite measured OClO columns is excellent. However, SZAs are rather large at this early time in the year and besides the rapid ongoing photochemistry, also only few photons are available introducing large scatter in the individual measurements.

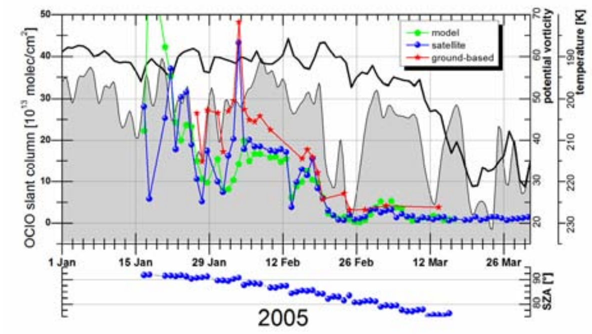

Figure 6. As Fig. 5 but for Summit, Greenland.

It has to be noted that although the radiative transfer model simulations consider the chemical enhancement, the 1D model is not aware of possible differing air masses along the light path, whereas the ground-based and satellite-based measurements in fact investigate an air mass several hundred kilometres away from the ground station. The exact location of this probed air mass in turn depends on the position of the sun but is approximately the same for SCIAMACHY and the ground-based instrument: In polar spring, the sun is always located to the south resulting in a shift of the measurement volume into this direction. In addition, as the SCIAMACHY data is averaged within a radius around the ground station and as there is a lack of measurements towards the polar night, i.e. the north, the majority of the measurements within this circle is shifted southward to smaller SZAs for days early in the year increasing the effect of the solar azimuth. A similar effect can be observed for the ground-based data: The averaging over a 2° range of SZAs results in a bias of the presented data to lower SZAs. In Ny-Ålesund, the SZA of 90° is only reached from February 18th onwards, but the time series already starts on 13th February indicating that the SZA for these days is rather at the lower limit of the accepted range between 89 to 91°.

Over Summit, the agreement is only fair and variable. The ground-based measurements are up to 50 percent larger than the SCIAMACHY data. Whereas SCIAMACHY agrees rather well with the modelled OClO amounts although the large peak on January 3rd is missed. On the other hand, to the end of the chlorine activation the qualitative agreement between model and satellite is excellent despite the fact that measurements are already close to the detection limit: Note the slight enhancement in OClO in the beginning of March. Also the decrease of OClO on February 13th is captured by the model but unfortunately missed by the ground-based measurement due to some equipment problems.

4. SZA DEPENDENCE OF OClO

For the SCIAMACHY validation, only the OClO measurements at time of satellite overpass were used and very good agreement between model and measurements was found. However, usually OClO slant columns at constant SZAs are discussed and it is interesting to investigate the agreement between model and ground-based measurements at different SZAs.

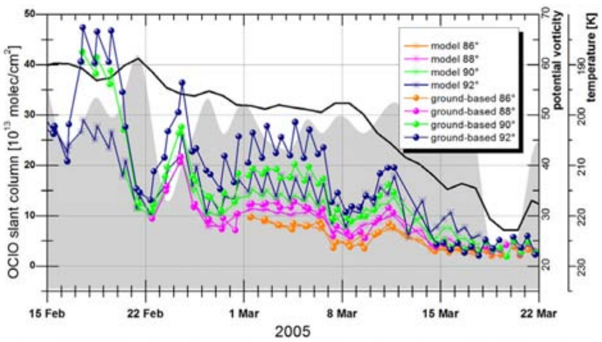

Figure 7. Ny-Ålesund at several SZAs. Potential vorticity (shaded area) and temperature (black line) at the 475 Kelvin isentropic surface are also shown.

Ny-Ålesund is positioned well inside the vortex until March 18th. Fig. 7 shows the ground-based and modelled OClO slant columns for different SZAs. The general evolution of the chlorine activation as well as the AM/PM-variation is captured correctly by the model. In both data sets, also individual events like the peak on February 24th are picked up which actually in this case cannot be explained by neither temperature (as especially on the day before, the temperature was increasing above the formation threshold for PSCs) nor by the potential vorticity being as low as 40 PV units at noon.

However, the model generally underestimates the OClO columns. This effect increases with increasing SZA but also with increasing chlorine activation. Quantitatively, the modelled columns at 88° SZA are about 10 percent too low, at 90° about 20 percent and 30 percent at 92° SZA. This is indication for a problem in the model, either related to photochemistry at low sun or to the formation of OClO which seems to be underestimated.

5. OClO OVER BREMEN

When the vortex gets deformed, it is possible that chlorine activated air masses are transported to midlatitudes, and OClO can be detected at twilight even above Bremen. In Fig. 8, the ground-based and modelled data presented at 90° SZA are compared, including the SCIAMACHY data which were taken at much smaller SZA. As the signal is very small under these conditions, the SCIAMACHY data had to be normalised by subtraction of measurements over the Pacific to remove small instrumental drifts. Several episodes with enhanced OClO are apparent in the three data sets, and two more are apparent in the ground-based data only. It is interesting to note that in spite of the relatively high sun, SCIAMACHY detects enhanced OClO over Bremen during vortex excursions, highlighting the high sensitivity of the measurements.

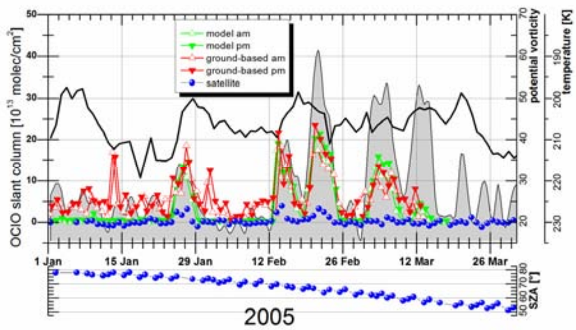

Figure 8. OClO over Bremen: Model and ground-based data at 90° SZA and satellite at the SZA given below, potential vorticity (shaded area) and temperature (black line) at the 475 Kelvin isentropic surface.

Another obvious characteristic in Fig. 8 is the systematic positive bias that occurs in the ground-based measurements when no OClO is present. However, Fig. 5-7 show that the accuracy of the OClO retrieval is much better as even rather low column amounts of less than 0.5×10^{14} molecules cm^{-2} feature less scatter than episodes with non-activated air over Bremen and they are in good agreement with the model indicating that this bias is not a general problem for all measurements but induced by zero OClO.

6. CONCLUSIONS AND OUTLOOK

The presented measurements are the first validation attempt of OClO for SCIAMACHY using ground-based DOAS measurements. The agreement is excellent and OClO could even be detected over the mid-latitude station in Bremen during vortex excursions. It can be concluded that SCIAMACHY is delivering OClO slant column amounts with high accuracy and can thus be used to study the long-term evolution of stratospheric chlorine loading. An interesting addition would be validation in the Southern Hemisphere and a comparison with GOME data in the period of overlapping measurements.

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