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Evaluation of stratospheric chlorine chemistry for the Arctic spring 2005 using modelled and measured OClO column densities

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Abstract. Chlorine dioxide, OClO, column amounts retrieved from measurements of the SCIAMACHY satellite instrument are presented and validated by comparison with simultaneous ground-based DOAS observations. In addition, the measurements are compared to model calculations taking into account the photochemical change along the light path.

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 retrieved during spring 2005 have been quantitatively validated by comparison with slant columns retrieved from measurements made in Ny-Ålesund (79° N, 12° E) and Summit (73° N, 38° W) as well qualitatively for Bremen (53° N, 9° E). Fair to good agreement is found depending on location as well as time of year.

OClO slant column densities modelled with a set of stacked box models and considering the light path through the atmosphere are also included in this comparison. The model predictions differ significantly from the measured quantities. OClO amounts are underestimated for conditions of strong chlorine activation and at large solar zenith angles. Sensitivity studies for several parameters in the stacked box model have been performed and it is inferred that using the chemistry known to date, the observed OClO cannot be adequately reproduced within the range of uncertainties given for the various model parameters.

1 Introduction

One of the most important issues in atmospheric science remains the understanding of the stratospheric ozone depletion, especially, in polar regions and its response to environmental policy and global climate change (WMO, 2007). In the dark, cold polar winter, reservoir 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 cloud (PSC) particles. 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 like chlorine nitrate. The temperature threshold for the formation of PSCs is about 195 K and hence they can usually only be observed in the winter-time polar stratosphere. The species formed on the particle 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 poles (e.g. Chubachi, 1984; Farman et al., 1985). Within this context, the ClO-BrO-cycle is an efficient ozone destruction mechanism in the lower polar stratosphere (Yung et al., 1980; McElroy et al., 1986; Lary, 1997). One of the channels of the BrO + ClO reaction produces chlorine dioxide OClO:

$$BrO + ClO \rightarrow Br + OClO \qquad (R1)$$

Reaction (R1) is thought to be the main production mechanism for atmospheric OClO (Friedl and Sander, 1989; Tung et al., 1986) and assuming that the photolysis primarily leads to O + ClO, this reaction results in a null cycle for ozone destruction.

The first measurements of atmospheric OClO were performed by Solomon et al. (1987a) by means of ground-based UV-visible spectroscopy over Antarctica followed by several other studies for the southern hemisphere (e.g. Sanders et al., 1993; Kreher et al., 1996; Frieß et al., 2005) but also for the Arctic (e.g. Solomon et al., 1988; Perner et al., 1994; Gil et al., 1996; Otten et al., 1998; Tørnkvist et al., 2002) and at mid-latitudes (Aliwell et al., 1997; Richter et al., 1999). The same spectroscopic technique has been applied for balloon and air-borne measurements in order to retrieve profile information of OClO (e.g. Wahner et al., 1989; Schiller et al., 1990; Pommereau and Piquard, 1994; Renard et al., 1997; Riviere et al., 2003).

The first satellite-based remote sensing of OClO became available with the launch of the Global Ozone Monitoring Experiment (GOME-1) in April 1995. These data have been used extensively for OClO studies (Burrows et al., 1999; Wagner et al., 2001, 2002; Kühl et al., 2004a, b; Richter et al., 2005). GOME-1 OClO measurements were followed by observations from the Scanning Imaging Spectrometer for Atmospheric Cartography (SCIAMACHY) on ENVISAT (Kühl, 2005; Kühl et al., 2008) and also by OSIRIS on the Odin satellite (Krecl et al., 2006). Recently, the global presence of night-time OClO has been detected in stellar occultation measurements performed by the GOMOS instrument which also operates on ENVISAT (Fussen et al., 2006).

Other species of the active chlorine family measured in the stratosphere are chlorine monoxide ClO through remote sensing (Solomon et al., 2000), and in-situ measurements (e.g. Brune and Anderson, 1986; Pierson et al., 1999; Avallone and Toohey, 2001; Vogel et al., 2003) and its dimer Cl_2O_2 (Stimpfle et al., 2004; von Hobe et al., 2005). Extensive measurements of ClO from space have been provided by the MLS instruments on UARS and AURA and the SMR instrument on Odin (e.g. Barret et al., 2006; Berthet et al., 2005; Santee et al., 2008).

This study focuses on measurements in northern spring 2005. The Arctic winter 2004/2005 was characterised by extremely cold temperatures in the stratosphere (see e.g. Feng et al., 2007a and references therein). In contrast to the previous years of SCIAMACHY observations (see Fig. 1 for a monthly average of the OClO columns), a large and also persistent vortex developed in the northern hemisphere, leading to chlorine activation and large OClO signals.

The aims of this study are to describe the retrieval of OClO columns from SCIAMACHY observations, to validate them with ground-based measurements, and to compare modelled and measured OClO columns. In addition, the origins of the differences between measurements and model have been investigated. The manuscript is organised as follows: Section 2 describes the technique used for retrieving the OClO columns for the three different data sets. Sections 3 and 4 are dedicated to the validation of the SCIAMACHY OClO columns. The solar zenith angle dependence of the OClO columns is investigated in Sect. 5. In Sect. 6, the sensitivity
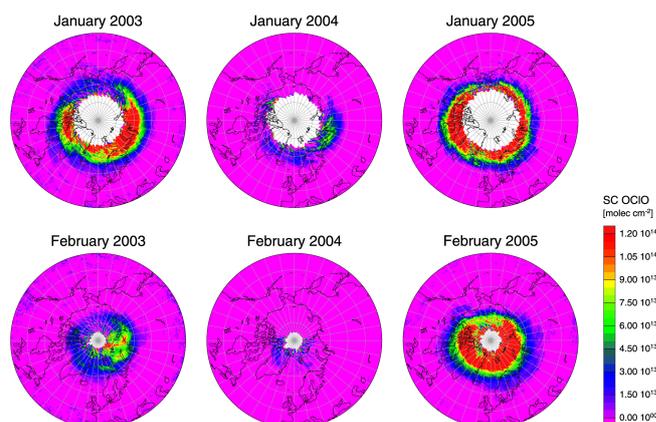
Fig. 1. Monthly averages of OClO slant column densities retrieved from SCIAMACHY observations over the Arctic for the winters 2003 to 2005, top panel shows averages for January und bottom panels for February for the three consecutive years.

of the chemistry model to various parameters is tested and discussed. This study is then summarised in Sect. 7.

2 Data sets

Comparisons of different measurements of OClO with each other or with model predictions require the following issues to be taken adequately into account:

- the photolysis of OClO, which in daylight is rapid,
- the changing column and profile during twilight,
- the change of solar zenith angle (SZA) along the line of sight,
- low signal to noise of the remote sensing of solar scattered radiation at large SZAs.

The comparison is best performed for the slant column densities. The slant column is the absorber density integrated along the light path of the instrument. Although the viewing geometries of the satellite- and ground-based measurements are very different, the air mass factors (AMF), which are the ratio between the slant column densities and the vertical column densities, yield similar values at large solar zenith angles. The AMF modelled for the same vertical profile (model OClO profile for Ny-Ålesund on 4 March, for a description of the models see Sect. 2.3) for the two observation geometries agree within 4% in the SZA range between 89° and 91° and by ∼13% at 80° SZA. Consequently, the slant column densities of OClO from the different platforms can be compared directly. The modelled OClO profiles are also converted to slant column densities for the given observational geometry assuming Arctic background conditions for the aerosol in the radiative transfer calculations. In the following, the three data sets used in this study are described.
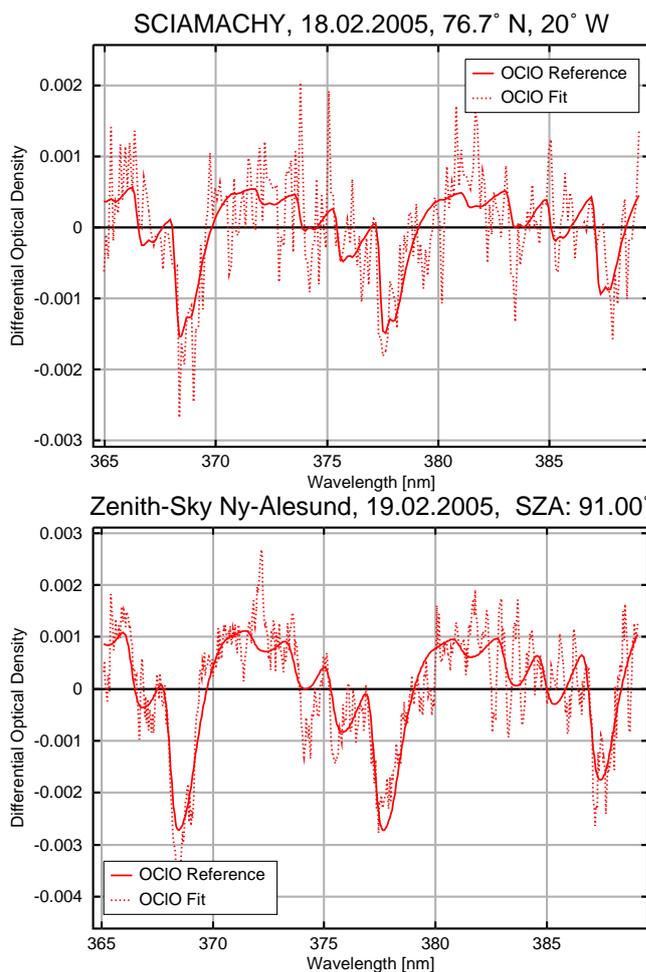
2.1 SCIAMACHY

The SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric CartograpHY) instrument 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) (Bovensmann et al., 1999; Burrows et al., 1995). SCIAMACHY was launched on ENVISAT into a sun-synchronous orbit on 1 March 2002 having an equator crossing time of 10:00 a.m. local time (descending node). Global coverage is obtained within six days at the equator and within one day at 70° latitude in spring. The spatial resolution varies between 30 km × 30 km and 240 km × 30 km depending on location and season.

Interpretation of the satellite measurements is complicated by the rapid photochemistry of OClO combined with the sun-synchronous orbit of the satellite. Along the satellite orbit, the solar zenith angle varies with latitude leading to a latitude dependent change in photolysis rates and thus OClO amounts. In order to facilitate systematic validation with ground-based measurements, the OClO amounts retrieved from the satellite over the stations are therefore compared with the OClO column measured from the ground at the time of satellite-overpass.

The observed spectra are analysed with the well-known Differential Optical Absorption Spectroscopy (DOAS) method (see e.g. Solomon et al., 1987b). The fitting procedure, in a window from 365 to 389 nm, includes in addition to the OClO cross section (Kromminga et al., 2003) and a polynomial for the compensation of broad-band features, the nitrogen dioxide NO_2 (Vandaele et al., 2003), and the oxygen dimer O_4 (Hermans et al., 1999) absorption cross sections as well as a rotational Raman scattering cross section (Vountas et al., 1998). A solar irradiance measurement is chosen as the background spectrum. Additional corrections have to be included to account for under-sampling 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 quality of the resulting OClO fit is illustrated in Fig. 2. The overall accuracy of the averaged slant columns is estimated to be about 30% or higher.

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 observations that has been set up by the Institute of Environmental Physics (IUP), University of Bremen, Germany. The instruments are NDSC/NDACC-approved (Aliwell et al., 2002; Vandaele et al., 2005). The temperature-stabilised spectrome-

Fig. 2. Example of the OClO retrieval fit for SCIAMACHY (top panel) and for ground-based measurement for Ny-Ålesund (bottom panel).

ters are equipped with cooled CCD detectors. The spectral resolution is ∼0.5–0.8 nm and about 7 to 12 detector 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 (Richter et al., 1999; Wittrock et al., 2004; Heckel et al., 2005). In this study, 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° W), and Bremen (Germany, 53° N, 9° E).

Similar settings for the retrieval and the same algorithm as for the SCIAMACHY data are applied to the ground-based spectra to retrieve the OClO slant columns. A measurement recorded at a small solar zenith angle is used as the reference or background spectrum for the whole time series i.e. the measurement at a given SZA is divided by this spectrum of scattered solar radiation. It is assumed that there is no OClO present in the background

spectrum. A fit example for an OClO slant column density of about 4×10^{14} molecules cm^{-2} measured in Ny-Ålesund on 19 February is presented in Fig. 2.

The 1σ spectral fit error is usually below 5% at 90° SZA. This includes uncertainties introduced by spectral interferences of the different absorption cross sections, by the Ring effect, which results in in-filling of Fraunhofer lines and is produced by the inelastic rotational Raman scattering on air molecules, and by the wavelength calibration of the cross sections. The fit error increases towards smaller SZAs. In the following, the 2σ error is quoted to account for possible systematic uncertainties, e.g. uncertainties in the absorption cross section of OClO. The uncertainty in the OClO cross section is estimated to be 7% (Wahner et al., 1987). The overall accuracy is about 20% at 90° SZA. The precision is much better. For most spectra, used in this study, the detection limit is smaller than 5×10^{13} molecules cm^{-2} at 90° SZA.

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 (3-D) chemical transport model SLIM-CAT (Chipperfield, 1999) are extracted on a daily basis at 12:00 UT over the stations and thereafter, in a second step, used to initialise a set of one-dimensional (1-D) photochemical stacked box models to obtain absorber profiles for the individual species at high temporal resolution. More details can be found in Sinnhuber et al. (2002, 2005) where an almost identical model is used to simulate stratospheric bromine chemistry.

The OClO profiles as a function of solar zenith angle are then used to derive slant column densities for the ground-based observation geometry. This third step is accomplished with the full-spherical radiative transfer model SCIATRAN (Rozanov et al., 2001, 2005), 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. It has been shown before that SCIATRAN is suitable to interpret ground-based scattered sunlight measurements up to a SZA of 93° work (Wittrock et al., 2004; Hendrick et al., 2006; Wagner et al., 2007).

In more detail, SCIATRAN simulates the paths of the photons from the sun into the telescope. Along this light path, the SZA changes due to the curvature of the earth. In higher altitudes and towards the sun, the SZA is smaller than the one at the measurement site causing a changing photochemistry for atmospheric trace gases. In SCIATRAN for each local SZA, the corresponding absorber profile from the output of the photochemical model is selected and the absorber den-
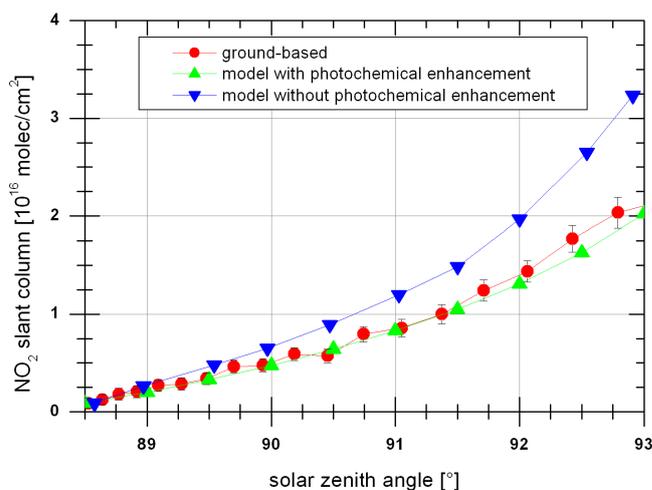

Fig. 3. Measurements (in red) and model calculations of NO$_2$ slant columns at Ny-Ålesund (79° N, 12° E) for 24 February as a function of SZA. The error bars represent the 2σ error of the measurements. The model simulations with photochemical enhancement (in green) are smaller than the ones without (in blue) due to the changing SZA along the line-of sight of the measurements.

sity is integrated to yield the column density along the light path. For illustration an example of NO$_2$ slant column densities is presented in Fig. 3. Shown are measurements and simulations for Ny-Ålesund of the afternoon of 24 February. Due to the on average smaller effective SZA, the simulations including the photochemical enhancement result in smaller slant column densities which agree very well with the measurements.

3 Validation

In the following comparison, 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 ground-based measurements are averaged over 2° SZA, i.e. ±1° SZA around the average SCIAMACHY SZA. The modelled columns on the other hand are calculated at the exact angle. Figure 4 shows the OClO slant columns for spring 2005 over Ny-Ålesund and Summit. Note that the SZA of the SCIAMACHY measurements is changing over the time series since the overpass takes place at a fixed time close to the local noon. Therefore, the variation in OClO during this time period is mainly caused by the decreasing SZA and the associated increased photolysis rate of OClO.

In Ny-Ålesund in the first two weeks until 25 February with SZAs larger 89°, the agreement between ground-based and satellite-measured OClO columns is only fair with the ground-based instrument in general seeing higher values than the satellite. SZAs are rather large this early in the year and rapid changes in photochemistry take place. The
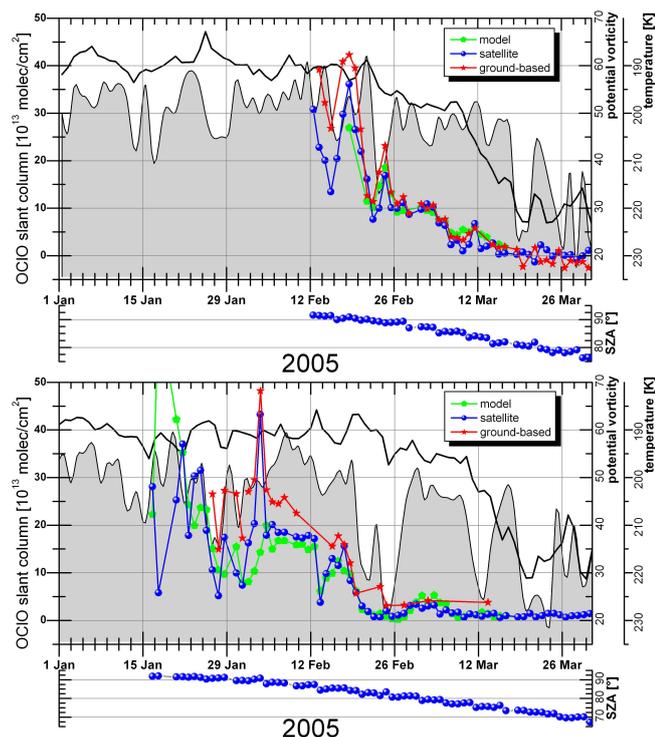
Fig. 4. Top: OClO slant columns over Ny-Ålesund (79° N, 12° E) in spring 2005 (axis on the left): Model data in green, satellite in blue and ground-based data in red. The ground-based data was sampled at the time of ENVISAT overpass. Also shown are potential vorticity (shaded area; axis on the right) and temperature (black line; axis on the right) at the 475 K isentropic surface. Bottom as top panel but for Summit, Greenland (73° N, 38° W).

ground-based and satellite-based measurements probe the atmosphere several hundred kilometres away from the ground station but also not necessarily the same air mass. The exact location of the probed air depends on the position of the sun: In polar spring, the sun is always located towards the south resulting in a shift of the measurement volume into this direction. In addition, as the SCIAMACHY data is averaged within a radius of 200 km 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 leading to a low bias in the data. An opposite 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 higher SZAs. In Ny-Ålesund, SZAs of 90° and smaller are only reached from 18 February onwards, but the time series already starts on 13 February indicating that the SZA for these days is rather at the upper limit of the accepted range given by the SCIAMACHY measurement and hence biased to higher OClO. In contrast, it should be noted that although the radiative transfer model simulations consider the photochemical enhancement, the 1-D model cannot

reproduce possible horizontal gradients along the light path which can result from varying chlorine activation or different air mass origins as described above. Following these initial two weeks of measurements, the agreement between the three data sets is very good in Ny-Ålesund including the time period from about 16 March onwards when all three data sets agree on that there is no more OClO at the small SZAs of the SCIAMACHY overpass.

Over Summit, the agreement is only fair and variable. The ground-based measurements are up to 50% larger than the SCIAMACHY data whereas SCIAMACHY columns agree rather well with the modelled OClO amounts, although the large peak on 3 February is missed. On the other hand, to the end of the chlorine activation the qualitative agreement between model and satellite is better 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 13 February is captured by the model but unfortunately missed by the ground-based measurement due to some equipment problems on these days.
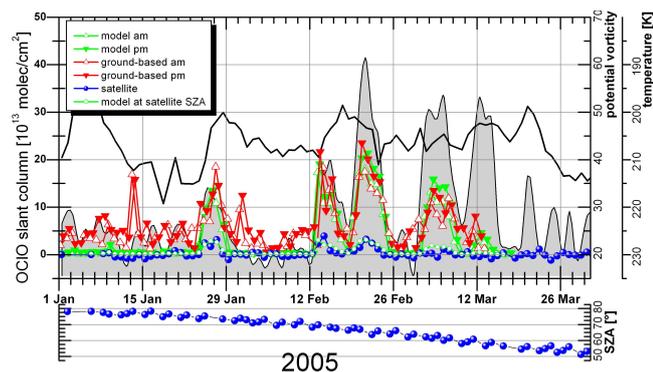
4 OClO over Bremen

When the polar vortex becomes deformed and elongated it is possible that chlorine-activated air masses are transported to mid-latitudes. This provides an opportunity to detect OClO above Bremen as well. In Fig. 5, the ground-based and modelled data presented at 90° SZA are compared, including the SCIAMACHY data which was taken at much smaller SZAs and the corresponding modelled data at the time of over-flight. As the OClO signal is 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 data sets and good agreement is found between measurements and model results with differences around 1×10^{13} molecules cm^{-2} or less.

It is interesting to note that despite the relatively high sun, SCIAMACHY detects enhanced OClO over Bremen during vortex excursions at SZAs as small as 65°. This illustrates the low detection limit of the measurements in spite of the offset problems which necessitate normalisation of the data. Unfortunately, the ground-based instrument in Bremen is not sensitive enough to detect these low amounts of OClO present at these small SZAs, but modelled OClO columns reproduce the observations from satellite. This is confirmation for the ability of the model to accurately reproduce OClO columns at high sun.

5 SZA dependence of OClO

For the SCIAMACHY validation, only the OClO data at the time of the satellite overpass was used and good agreement between model and measurements was found (within $\sim 4 \times 10^{13}$ molecules cm^{-2} at Ny-Ålesund, $\sim 6 \times 10^{13}$
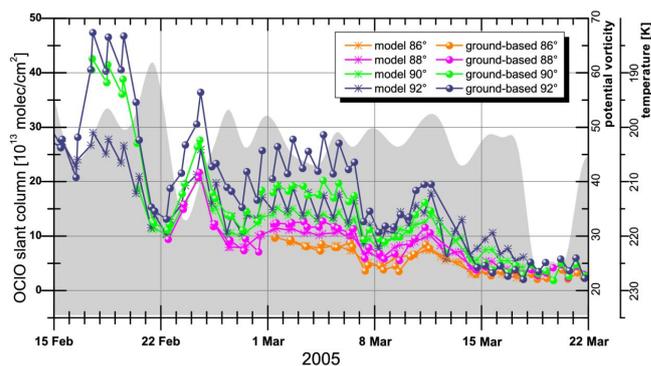
Fig. 5. OClO over Bremen (53° N, 9° E; axis on the left): Model (green triangles) and ground-based data (red triangles) at 90° SZA and satellite (blue dots) at the SZA given below as well as model at the SCIAMACHY SZA (green circles), potential vorticity (shaded area) and temperature (black line) at the 475 K isentropic surface.

Fig. 6. Model (asterisks) and measurements (dots) of OClO at Ny-Ålesund (79° N, 12° E) at four different SZAs (see box embedded in figure; axis on the left). Potential vorticity (shaded area) and temperature (black line) at the 475 K isentropic surface are also shown. Note that the zigzag pattern in the curves for high SZAs is caused by the diurnal variation of OClO with higher concentrations in the afternoon.

molecules cm^{-2} at Summit, and $\sim 1 \times 10^{13}$ molecules cm^{-2} at Bremen for SZAs <90° and for chlorine activated air masses only). However, it is also interesting and conventional to investigate the agreement between model and ground-based measurements at different SZAs.

In 2005 Ny-Ålesund was positioned well inside the vortex until 18 March. After this day the potential vorticity significantly decreased. Fig. 6 shows the ground-based and modelled OClO slant columns for different SZAs. There seems to be a positive offset of 4×10^{13} molecules cm^{-2} in the measurements after the potential vorticity dropped. This could either be caused by some remaining chlorine activation or by a known problem for the OClO retrievals with the DOAS method: The proof of zero OClO is very difficult, and often a small positive offset is found even in situations where no chlorine activation is expected. This can also be observed in the data from the measurements in Bremen (Fig. 5) and previous works suggest a small positive offset as well (e.g. Fig. 6 in Aliwell et al. (1997) where the majority of data points is above 0; and Fig. 10 in Frieß et al. (2005) where OClO at Neymayer station is clearly above 0 in February and March). Whether or not this offset is also present in measurements with high OClO columns is not entirely clear; judging from the behaviour of OClO columns with SZA this appears not to be the case.

The general evolution of the chlorine activation, as well as the AM/PM-variation, is captured correctly by the model. In both data sets individual events like the peak on 24 February are also picked up. However, the model generally underestimates the OClO columns until 11March. This effect increases towards larger SZA but also with increasing chlorine activation. This is illustrated in Fig. 7, top panel for the time series including data from 24 February until 8 March as given in Fig. 6. On average, over the time period of strong chlorine activation until 8 March, the measurements exceed the model columns by (5 ± 12)% at 88° SZA, (22 ± 7)% at 90°

and (26 ± 15)% at 92° SZA. The uncertainties stated here are the standard deviations of the averaging over all days. However, the differences to the measurements depend on the measurement error as well. As stated above, the 2σ measurement uncertainty is about 10% at 90° SZA. The discrepancies between model and measurements are interpreted as indicating missing chemistry in the model, either related to photochemistry at low sun or to the formation of OClO, which seems to be underestimated. The next section will investigate these model and measurement differences by examining the sensitivity of the results towards changes in certain model parameters.

It is also interesting to note that after 14 March, the model overestimates the measured OClO columns at large SZA over Ny-Ålesund. At this time, potential vorticity is still high, temperature is increasing and measurements show little OClO. The model overestimation could indicate that the parameterisation of chlorine activation in the SLIMCAT model is producing too strong chlorine activation at this time of the year.

6 Model studies

The box model simulations as well as the initialisation of it, presented in Sects. 3 to 5, were performed using the JPL 2002 (Sander et al., 2003) recommendations for the kinetic and photochemical parameters including the reaction of BrONO$_2$ with O(^{3}P) (Soller et al., 2001).

Uncertainties in chemistry models originate from the limited accuracy of our knowledge of:
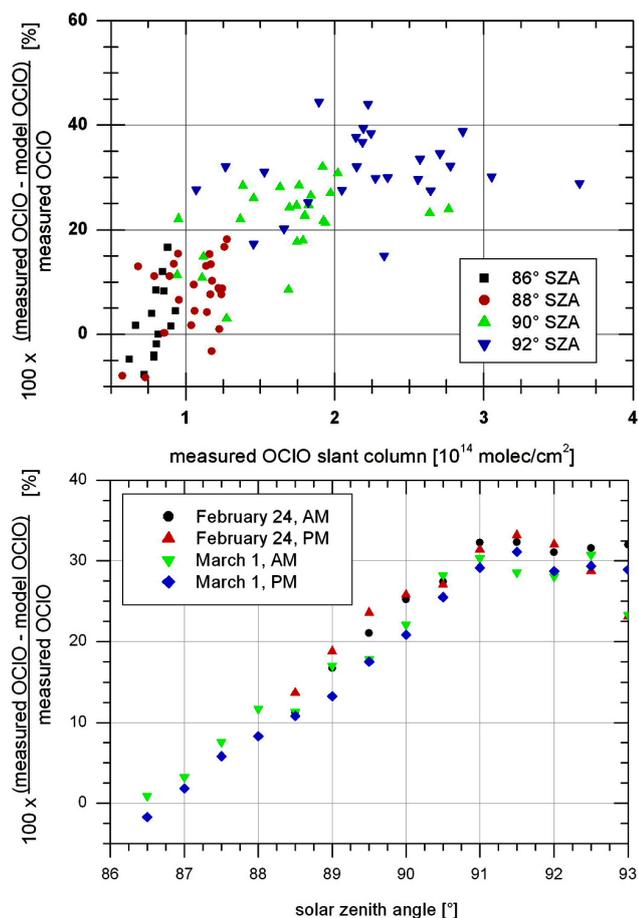
Fig. 7. The relative differences between modelled OClO columns and ground-based data for Ny-Ålesund as a function of OClO (top) and SZA (bottom). Top: all data from 24 February until 8 March as given in Fig. 6 colour-coded for the four different solar zenith angle bins. Bottom: differences for two selected days as stated in the embedded box. The relative differences between modelled and measured OClO increase with chlorine activation as well as with SZA.

– the involved rate and equilibrium constants

– the absorption cross sections and quantum yields

– the photolysis frequencies of molecules

– the initialisation amount of trace species in the model

– the meteorology

Recently, several sensitivity studies of stratospheric chlorine chemistry suggested the need for adjusting some of the reaction rates as well as the absorption cross sections and consequently the photolysis rates of certain gases. These will be discussed in the following sections. The JPL recommendations have partly been updated (Sander et al., 2006, in future referred to as JPL 2006). Here, sensitivity tests are performed for the stacked box model simulations only and not

for the simulation of the radiative transfer since good agreement was found for the simulations of NO_2 slant columns (see Fig. 3). Several scenarios will be investigated. The focus is on 24 February in Ny-Ålesund. At 90° SZA, the measurements exceed the modelled columns by about 26% on this day. The relative differences are shown to increase with increasing SZA (see Fig. 7, bottom panel and Fig. 8) and as described above are in general on average $22 \pm 7\%$ at 90° SZA showing that 24 February is a typical day.

6.1 ClO-dimer cycle chemistry

Comparisons of OClO measurements with model results are rather sparse (e.g. Butz et al., 2007; Fussen et al., 2006). Studies mainly concentrate on the simulation of measured ClO (e.g. Schofield et al., 2008), sometimes in combination with Cl_2O_2 measurements (e.g. von Hobe et al., 2005) testing the ClO-dimer cycle chemistry. In general, it has been found that modelled chlorine monoxide is too low (e.g. Pierson et al., 1999; Solomon et al., 2000). Alongside the ClO-BrO catalytic cycle, the ClO-dimer cycle is a very efficient ozone depleting mechanism which is initiated by the ClO-self-reaction. The main product has been shown to be in the form of chlorine peroxide ClOOCl, which is the most stable one of the three possible isomers of the molecule Cl_2O_2. In future, Cl_2O_2 refers to ClOOCl unless stated otherwise. The ClO-dimer Cl_2O_2 is thermally decomposed in the presence of a third body M:

$$ClO + ClO \overset{M}{\rightleftarrows} Cl_2O_2 \tag{R2}$$

or removed by photolysis:

$$Cl_2O_2 + h\nu \rightarrow Cl + ClOO. \tag{R3}$$

To increase the ClO and hence the OClO concentrations, the partitioning within the active chlorine family ClO_x (i.e. $ClO + Cl_2O_2$) has to be shifted in favour of the ClO. This can be achieved in three ways: Either by (a) increasing the photolysis rate or by (b) speeding up the thermal decomposition of Cl_2O_2 or by (c) decreasing the forward rate constant of Reaction (R2). These three scenarios will be discussed in more details in the following:

a. The JPL 2002/06 recommendations for the ClOOCl absorption cross section are an average of several values (Cox and Hayman, 1988; Burkholder et al., 1990; Permien et al., 1988; DeMore and Tschuikow-Roux, 1990). Some studies (Huder and DeMore, 1995; Pope et al., 2007) obtain significantly lower values in the tail region (see Fig. 5 in von Hobe et al., 2007) and overall, the spectra disagree by a factor of up to 20. The recent study by Chen et al. (2009) confirmed the absorption cross section as obtained by Burkholder al. (1990) at 351 nm. Here, the extremes are tested: The Pope et al. (2007) cross section is the smallest available and the

Burkholder et al. (1990) absorption cross section represents the upper limit of the set. Both have been extended to longer wavelengths by a log-linear extrapolation. The impact of using the different absorption cross sections for Cl_2O_2 in modelled OClO slant columns are large (see Fig. 8): up to 11% at 90° SZA for the Burkholder et al. (1990) cross section and up to −33% for the Pope et al. (2007) values. However, the change in absorption cross section causes simply an offset relative to the original model and does not explain the diurnal behaviour of the OClO. Table 1 shows the differences at 90° SZA also for 4 March. On this day, the OClO measurements at 90° SZA are too high by about 30% and this day is hence at the upper limit of the variations for the differences. However, the changes caused by changing the Cl_2O_2 absorption cross section lead to similar values as for 24 February, i.e. 12% and −36%.

b. During the daytime, at smaller SZA, photolysis dominates over the thermal decomposition of Cl_2O_2. However, with increasing SZAs, the thermal decomposition becomes more important. Several laboratory studies determining the equilibrium constant between ClO and Cl_2O_2 are available (Basco and Hunt, 1979; Cox and Hayman, 1988; Horowitz et al., 1994; Nickolaisen et al., 1994; Plenge et al., 2005; Bröske and Zabel, 2006). The JPL 2002/2006 recommendations are an average of Cox and Hayman (1988) and Nickolaisen et al. (1994), which were then extrapolated to the temperatures prevailing in the atmosphere. The recent photo-ionisation mass spectroscopy study by Plenge et al. (2005) suggests that the ClOOCl is by a factor of 0.3 less stable than previously assumed. This observation is confirmed at atmospheric temperatures by several studies based on air-borne in-situ measurements (Brune et al., 1991; Pierson et al., 1999; Avallone and Toohey, 2001; Stimpfle et al., 2004; von Hobe et al., 2005) and nighttime Odin satellite/ Osiris measurements (Berthet et al., 2005). By changing the equilibrium constant to the most recent value obtained by Bröske and Zabel (2006), a maximum increase in OClO of 3% at 90° SZA is achieved. As expected, the difference increases towards larger SZAs.

c. Another way to shift the partitioning within the Cl_y family in favour of ClO in the model simulations is achieved by decreasing the forward rate constant for the three-body formation of Cl_2O_2. JPL 2006 presents an average of Bloss et al. (2001), Nickolaisen et al. (1994), and Trolier et al. (1990). The more recent study by Boakes et al. (2005) rather increased the rate for this reaction decreasing the OClO by 6%. However, adjusting the rate constant to the lower limit of the JPL recommendations increases the OClO column by 5% at 90° SZA and yields similar values to using Nickolaisen et al. (1994) alone.
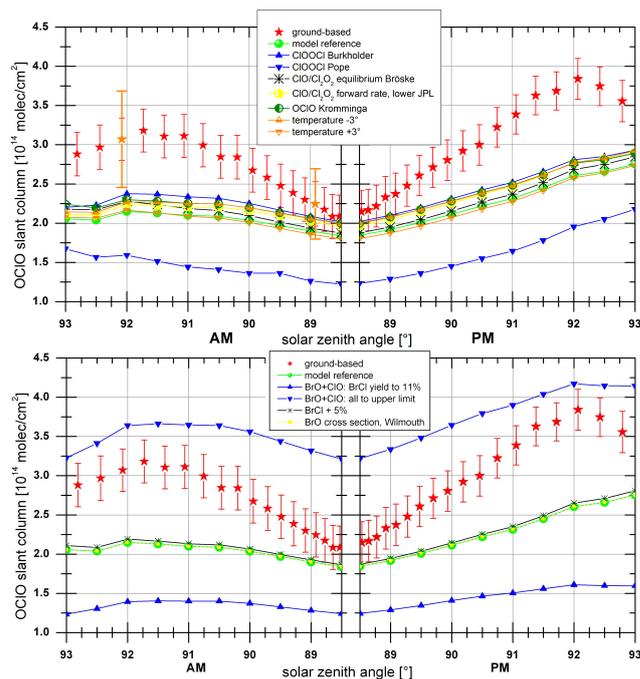
Fig. 8. Sensitivity Studies: measurements and model calculations of OClO slant columns at Ny-Ålesund for 24 February. The error bars represent the 2σ error of the measurements. Exemplarily, two error bars have been added to the top panel indicating the overall measurement uncertainty of 20%. Sensitivity studies have been undertaken by changing the mechanism. The different scenarios are indicated in the box embedded in the figure and are explained in Sect. 6.

Schofield et al. (2008) retrieved a possible range for the combinations of the three model parameters from airborne measurements of ClO and they propose using a decreased forward rate constant for the Cl_2O_2 formation in combination with a smaller equilibrium constant in comparison to the JPL recommendations. Von Hobe et al. (2007) also reviewed the available laboratory references as well as rate theory calculations for the equilibrium constant between ClO and Cl_2O_2. They concluded that the best overall consistency with atmospheric observations as well as rate theory calculations can be found for the combination of the photolysis rates based on the Cl_2O_2 absorption cross section in the range of Burkholder et al. (1990) and JPL 2006, the equilibrium constant by Plenge et al. (2005), and the Cl_2O_2 formation rate constant by Nickolaisen et al. (1994). Although OClO columns are enhanced by up to 20%, this is still not sufficient to explain the ground observations of OClO, reported in this study.

6.2 BrO-ClO cycle chemistry

As the amount of BrO determines how much OClO is produced (Schiller and Wahner, 1996), the implementation of the correct bromine load of the atmosphere is a crucial parameter for accurate modelling of the chlorine chemistry.

Table 1. Summary of the sensitivity studies of the box model in comparison to the JPL 2002 simulation at a SZA of 90°. Texts in bold characters represent scenarios visualised in Fig. 8. More details can be found in the Sect. 6.

Parameter	Study	Differences in OClO to the reference scenario at 90° SZA			
		24 February 2005		4 March 2005	
		AM	PM	AM	PM
ClOOCl absorption cross section	**Burkholder et al. (1990)**	+11%	+9%	+12%	+9%
	Pope et al. (2007)	−33%	−31%	−36%	−31%
ClO/Cl$_2$O$_2$ equilibrium constant	**Bröske and Zabel (2006)**	+3%	+2%	+3%	+1%
ClO/Cl$_2$O$_2$ forward rate constant	**lower JPL limit/** Nickolaisen et al. (1994)	+5%	+5%	+5%	+5%
	Boakes et al. (2005)	−6%	−6%	−6%	−6%
Combination according to von Hobe et al. (2007)	Burkholder et al. (1990) + Plenge et al. (2005) + Nickolaisen et al. (1994)	+19%	+17%	+20%	+15%
Br$_y$ initialisation	+ 3 ppt	+14%	+14%	+14%	+14%
	−3 ppt	−14%	−14%	−14%	−14%
BrO cross section	**Wilmouth et al. (1999)**	<< 1%	<< 1%	<< 1%	<< 1%
BrO + ClO rate constants	**BrCl yield to 11%**	−33%	−33%	−29%	−30%
	all react. to upper limit	+75%	+72%	+84%	+79%
BrCl absorption cross section	**+5%**	+1%	+1%	+1%	+1%
OClO absorption cross section	**Kromminga et al. (2003)**	+8%	+8%	+8%	+8%
Temperature initialisation	**−3 K**	+8%	+8%	+9%	+9%

Generally, the inorganic bromine loading is believed to originate from a combination of long-lived bromine species with contribution of ~16 ppt$_v$ (ppt$_v$: parts per trillion by volume hereafter referred to as ppt) and very short-lived bromine source gases of 3 to 8 ppt (WMO, 2007). In the model, the overall Br$_y$ (=Br + BrO + BrONO$_2$ + HOBr + BrCl + HBr) volume mixing ratio is 21 ppt which is achieved by scaling methyl bromide CH$_3$Br to represent all bromine sources. This can underestimate the bromine load in the lower stratosphere (Hendrick et al., 2007; Theys et al., 2007; Schofield et al., 2006; Feng et al., 2007b). In order to test the effects towards the Br$_y$ initialisation, the profiles of the individual bromine species are scaled to yield a maximum Br$_y$ loading of 24 ppt or 18 ppt. The difference on the OClO columns is symmetrical around the reference simulation with 14% at 90° and it shows only a slight SZA dependence. This is still far off the required increase of OClO by ~30%.

The JPL 2006 recommendations for the BrO cross section were updated from the one reported by Wahner et al. (1987) to the high-resolution data set by Wilmouth et al. (1999) resulting in negligible effects of less than 1% in the OClO concentration. Bromine chloride BrCl is the product in one of the three channels of the BrO + ClO-reaction. It is the main inorganic bromine species during the night in periods of chlorine activation (Sinnhuber et al., 2002). On the basis of a night-time OClO profile measurement, Canty et al. (2005) suggest an increase in the BrCl yield from 7% to 11% is required. This value is consistent with the error bars of 63% of the rate constant at 195 K given by JPL 2002/2006. Atkinson et al. (2000) found a constant partitioning of 8% for this yield over a wide temperature range motivating Sinnhuber et al. (2002) to increase the rate constants of all three branches. As expected, changes in the rates of the directly involved reactions lead to the most dramatic effects of up to 84% and −33% for increasing all or just one rate constant, respectively. However the increase and decrease in the OClO column densities stay constant over a SZA range of up to about 91° resulting in much poorer agreement between model simulation and the measurements at local noon.

Increasing the photolysis rate of BrCl will shift the partitioning of bromine to active forms such as BrO during daytime but would also cause a faster increase of BrO in the morning. The model takes into account the temperature dependence of the BrCl absorption cross section as suggested by Maric et al. (1994). Tellinghuisen (2003) reports the largest of the available cross sections with a peak height

exceeding Maric et al. (1994) by about 2.5% around 375 nm whereas the cross section by Hubinger and Nee (1995) is about 3.5% smaller in this wavelength region. Since the absorption cross sections exhibit a rather smooth distribution with wavelength, a simple scaling by 5% seems to be appropriate in order to simulate larger cross section. However, this increase changes the OClO column densities by only 1%.

6.3 Further tests of the modelled OClO sensitivity

The absorption cross sections for OClO at a temperature of 204 K, recommended by JPL 2002/06, are taken from Wahner et al. (1987). The DOAS fits of the measurements presented here are performed applying the cross sections by Kromminga et al. (2003) at 213 K. Kromminga et al. (2003) report band peaks about 8% smaller than Wahner et al. (1987) leading to a constant offset in the slant column densities for OClO when applied in the modelling.

An accurate knowledge of the temperature in the model simulations is crucial since it determines whether chlorine will be activated or not. It is therefore possible that the temperature of an air mass at a higher spatial resolution might locally drop below the threshold for the formation of PSCs. Such effects are missed by the coarser vertical resolution of the model profile. In order to test the sensitivity of the simulations towards the temperature, a constant offset of 3 K has been subtracted. Decreasing the temperature, increases the vertical extent of the layer where chlorine activation is possible leading to higher concentrations of OClO of up to 9% at 90° SZA.

Changes in the ground albedo in the model also have minor impacts of only about 2%. As expected, the photolysis of OClO increases and consequently the concentration decreases towards larger albedo. However, this does not influence the SZA dependence of the OClO columns up to 91° SZA. Furthermore, the photolysis rates of the box model calculated for OClO have been checked for consistency with SCIATRAN which includes full treatment of multiple scattering. The rates of the two models agree within 3%. Also, reducing NO_2 by 5% to impede the formation of the reservoir species chlorine nitrate yields a negligible effect.

6.4 Discussion

Table 1 summarises the contributions from the different scenarios to the OClO slant column densities at 90° SZA for the two days. The SZA dependence is presented only for 24 February in Fig. 8.

Adjusting the rate constant of the BrO + ClO-reaction has the largest influence on the OClO but introduces only an offset in the data. However, to reproduce the measurements a scaling is needed since the columns agree for low SZAs. In summary, none of the selected individual scenarios can fully explain the diurnal variation of the OClO observations or the absolute values at high SZAs. In the following, some possible additional mechanisms are discussed although implementations in the model are beyond the scope of this study.

Laboratory measurements have shown that OClO evaporates from ice surfaces via heterogeneous reactions after being exposed to ClO radicals (McKeachie et al., 2004). It is suggested that this release is initiated by the formation of the ClO · H_2O radical complex (Francisco and Sander, 1995; Galvez and Gomez, 2007). This could potentially increase the OClO columns.

Thornton et al. (2003, 2005) report measurements of ClO in the lowermost stratosphere at high latitude regions. They suggest heterogeneous chlorine activation on cold particulate surfaces as water-rich background aerosols containing sulphate and nitrate.

A chlorine species neglected in the model is Cl_2. If significant amounts of active chlorine are stored in the form of this molecule, then this would give rise to an additional source of a SZA dependent formation of ClO and consequently OClO in the model. However, the explicit treatment of Cl_2 would mainly increase the morning concentrations of OClO but leave the afternoon concentrations unchanged.

Possible roles of the two other Cl_2O_2 isomers chloryl chloride $ClClO_2$ and chlorine chlorite $ClOClO$ have been discussed in the literature before (Plenge et al., 2004; Bloss et al., 2001). Although these two species are much less stable than ClOOCl, an additional source for OClO could arise from their photolysis.

7 Summary

The measurements, described in this study, are the first validation attempt of the OClO retrieved from SCIAMACHY observations made by comparison with ground-based remote sensing DOAS measurements. The agreement is fair to good depending on location and time of year, i.e. the local SZA. OClO could also be detected over the mid-latitude station Bremen during vortex excursions. It can be concluded that SCIAMACHY is delivering OClO slant column amounts with satisfactory accuracy and can thus be used to study the long-term evolution of stratospheric chlorine loading.

The SLIMCAT-initialised stacked box model simulations of OClO show good qualitative agreement with the day-to-day variations of the measurements and also good agreement at the time of satellite overpass. However, they underestimate the measured amount of OClO, in particular at low sun and large chlorine activation. The absolute differences of the model to the measurements depend on the measurement error. The 2σ measurement error is about 10% at 90° SZA and a conservative estimate for the overall uncertainty is 20%. The differences between model and measurements are on average (22 ± 7)% for 90° SZA and increase with SZA reaching values of up to 40%. In general these differences are spread over a wide range depending on the particular day as well as time of day. The modelled amount of OClO can be

varied by changing the chemistry in the model within the uncertainties of absorption cross-sections and rate coefficients. In addition to the overall underestimation, the model does not capture the magnitude of the OClO variation as a function of SZA. None of the sensitivity studies performed leads to a result which was in good agreement with the measurements with respect to the SZA dependence of the OClO column. From the model simulations of the OClO behaviour, it can be concluded that our knowledge of the physical and chemical processing within the vortex is not sufficient to explain the OClO behaviour adequately. This implies that the chlorine chemistry and its relevant mechanisms for the formation of OClO taking into account the range of the accuracies of the laboratory kinetics are not completely understood. Further research especially for the key rate constants of the chemical and photochemical reactions involving the chlorine oxides is needed.

Further validation of SCIAMACHY OClO in the Southern Hemisphere using ground-based measurements and comparisons with models will provide more information with respect to our understanding of the OClO sources and sinks and related halogen chemistry. A comparison of OClO retrieved with GOME-1 and the new GOME-2 data in the period of overlapping measurements would be valuable to produce consolidated data sets.

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