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**Evaluation of
stratospheric
chlorine chemistry
for Arctic spring 2005**

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

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Abstract

Chlorine dioxide, OCIO, 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 OCIO 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 OCIO 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), Summit (73° N, 38° W) and Bremen (53° N, 9° E). Overall, good agreement is found.

OCIO 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. OCIO 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 OCIO 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

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the surface of polar stratospheric cloud (PSC) particles. During this process, NO_x (nitric oxide NO and nitrogen dioxide NO₂) is trapped in the PSCs as nitric acid HNO₃ 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 surfaces are e.g. Cl₂ 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 (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). In one of the channels of the BrO+ClO reaction chlorine dioxide OCIO is produced:



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

The first measurements of atmospheric OCIO 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 OCIO (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 OCIO became available with the launch of the Global Ozone Monitoring Experiment (GOME-1) in April 1995. These data have been used extensively for OCIO studies (Burrows et al., 1999; Wagner et al., 2001, 2002; Köhl et al., 2004a, b; Richter et al., 2005). GOME-1 OCIO measurements were

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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 OCIO 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 Cl₂O₂ (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 OCIO columns), a large and also persistent vortex developed in the Northern Hemisphere, leading to chlorine activation and large OCIO signals.

The aims of this study are to describe the retrieval of OCIO columns from SCIAMACHY observations, to validate them with ground-based measurements, and to compare modelled and measured OCIO columns. In addition, the origins of the differences between measurements and model have been investigated. The manuscript is organised as follows: Sect. 2 describes the technique used for retrieving the OCIO columns for the three different data sets. Sections 3 and 4 are dedicated to the validation of the SCIAMACHY OCIO columns. The solar zenith angle dependence of the OCIO columns is investigated in Sect. 5. In Sect. 6, the sensitivity of the chemistry model to various parameters is tested and discussed. This study is then summarised in Sect. 7.

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2 Data sets

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

- the photolysis of OCIO, 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 geometry 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 OCIO 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 OCIO from the different platforms can be compared directly. The modelled OCIO 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,

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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. LT (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 OCIO 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 OCIO amounts. In order to facilitate systematic validation with ground-based measurements, the OCIO amounts retrieved from the satellite over the stations are therefore compared with the OCIO 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 OCIO cross section (Kromminga et al., 2003) and a polynomial for the compensation of broad-band features, the nitrogen dioxide NO₂ (Vandaele et al., 2003), and the oxygen dimer O₄ (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 resulting fitting quality for OCIO is illustrated in Fig. 2. The overall accuracy of the averaged slant columns is estimated to be about 30% or higher.

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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 spectrometers are equipped with cooled CCD detectors. The spectral resolution is $\sim 0.5\text{--}0.8$ 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°) 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 OCIO 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 solar scattered radiation. It is assumed that there is no OCIO present in the background spectrum. A fit example for an OCIO slant column density of about 4×10^{14} molecules cm^{-2} measured in Ny-Ålesund on 19 February is presented in Fig. 2.

The spectral fit error is usually below 10% at 90° SZA (1σ error). 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. Not included are systematic errors e.g. uncertainties in the absorption cross section of OCIO. The overall accuracy is about 20% at 90° SZA. The precision is much better. For most

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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 OCIO 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 SLIMCAT (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 OCIO 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 OCIO. It has been shown before that SCIATRAN is suitable to interpret ground-based scattered sunlight measurements up to a SZA of 93° (Wittrock et al., 2004; Hendrick et al., 2006; Wagner et al., 2007).

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. $\pm 1^\circ$ SZA around the

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SCIAMACHY SZA. The modelled columns on the other hand are calculated at the exact angle.

Figure 3 shows the OCIO 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 OCIO during this time period is mainly caused by the decreasing SZA and the associated increased photolysis rate of OCIO.

In Ny-Ålesund, apart from the first few days, the agreement between ground-based and satellite-measured OCIO columns is excellent. As SZAs are rather large this early in year and in addition due to the rapid changes in photochemistry, only few photons are available reducing the signal to noise and introducing large scatter in the individual data of the ground-based measurements.

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. In contrast, the ground-based and satellite-based measurements in fact probe the atmosphere several hundred kilometres away from the ground station. The exact location of the probed air 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 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 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 18 February onwards, but the time series already starts on 13 February indicating that the SZA for these days is rather at the lower limit of the accepted range given by the SCIAMACHY measurement.

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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 OCIO amounts, although the large peak on 3 January 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 OCIO in the beginning of March. Also the decrease of OCIO 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 OCIO 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 OCIO above Bremen as well. In Fig. 4, 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 overflight. As the OCIO 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 OCIO are apparent in the data sets and excellent 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 OCIO 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 OCIO present at these small SZAs, but modelled OCIO columns reproduce the observations from

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satellite. This is confirmation for the ability of the model to accurately reproduce OCIO columns at high sun.

5 SZA dependence of OCIO

For the SCIAMACHY validation, only the OCIO data at the time of the satellite overpass was used and very good agreement between model and measurements was found (within $\sim 4 \times 10^{13}$ molecules cm^{-2} at Ny-Ålesund, $\sim 6 \times 10^{13}$ molecules cm^{-2} at Summit, and $\sim 1 \times 10^{13}$ molecules cm^{-2} at Bremen for SZAs $< 90^\circ$ 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. Figure 5 shows the ground-based and modelled OCIO 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 individual events like the peak on 24 February are also picked up. However, the model generally underestimates the OCIO columns. This effect increases towards larger SZA but also with increasing chlorine activation. On average, over the time period of strong chlorine activation until 8 March, the modelled columns are too low by about 10% at 88° SZA, about 20% at 90° and about 30% at 92° SZA. This is interpreted as indicating missing chemistry in the model, either related to photochemistry at low sun or to the formation of OCIO, 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.

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

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kinetic and photochemical parameters including the reaction of BrONO₂ with O(³P) (Soller et al., 2001).

Uncertainties in chemistry models originate from the limited accuracy of our knowledge of:

- 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 it has been shown before that SCIATRAN is suitable to interpret ground-based scattered sunlight measurements up to a SZA of 93° (Wittrock et al., 2004; Hendrick et al., 2006; Wagner et al., 2007). Several scenarios will be investigated. The focus is on two days in Ny-Ålesund, i.e. 24 February with very high OCIO columns and 4th March with moderate chlorine activation. At 90° SZA, the measurements exceed the modelled columns by 30% on 24 February and by about 40% on 4 March, respectively.

6.1 ClO-dimer cycle chemistry

Comparisons of OCIO measurements with model results are rather sparse (e.g. Butz et al., 2007; Fussen et al., 2006). Studies mainly concentrate on the simulation of

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measured ClO (e.g. Schofield et al., 2008), sometimes in combination with Cl₂O₂ 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 Cl₂O₂. In future, Cl₂O₂ refers to ClOOCl unless stated otherwise. The ClO-dimer Cl₂O₂ is thermally decomposed in the presence of a third body M:



or removed by photolysis:



To increase the ClO and hence the OCIO concentrations, the partitioning within the active chlorine family ClO_x (i.e. ClO+Cl₂O₂) has to be shifted in favour of the ClO. This can be achieved in three ways: Either by increasing the photolysis rate or by speeding up the thermal decomposition of Cl₂O₂ or by decreasing the forward rate constant of Reaction (R2).

The JPL 2002/2006 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 et al. (1990). 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

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cross sections for Cl_2O_2 in modelled OCIO slant columns are large (see Fig. 6): up to 12% at 90° SZA for the Burkholder et al. cross section and up to -36% for the Pope et al. (2007) values (see Table 1). 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 OCIO.

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; Pier-son et al., 1999; Avallone and Toohey, 2001; Stimpfle et al., 2004; von Hobe et al., 2005) and night-time 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 OCIO of 3% at 90° SZA is achieved. As expected, the difference increases towards larger SZAs.

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. However, adjusting the rate constant to the lower limit of the JPL recommendations increases the OCIO column by 5% at 90° SZA and yields similar values to using Nickolaisen et al. (1994) alone.

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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 Cl₂O₂ 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 Cl₂O₂. 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 Cl₂O₂ absorption cross section in the range of Burkholder et al. (1990) and JPL 2006, the equilibrium constant by Plenge et al. (2005), and the Cl₂O₂ formation rate constant by Nickolaisen et al. (1994). Although OCIO columns are enhanced by up to 20%, this is still not sufficient to explain the ground observations of OCIO, reported in this study (see Fig. 6).

6.2 BrO-ClO cycle chemistry

As the amount of BrO determines how much OCIO 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. 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+BrONO₂+HOBr+BrCl+HBr) volume mixing ratio is 21 ppt which is achieved by scaling methyl bromide CH₃Br 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 OCIO 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 OCIO by 30%.

The JPL 2006 recommendations for the BrO cross section were updated from the one reported by Wahner et al. (1988) to the high-resolution data set by Wilmouth et al. (1999) resulting in negligible effects of less than 1% in the OCIO 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 OCIO 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 OCIO 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 OCIO column densities by only 1%.

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6.3 Further tests of the modelled OCIO sensitivity

The absorption cross sections for OCIO 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. leading to a constant offset in the slant column densities for OCIO 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 OCIO 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 OCIO increases and consequently the concentration decreases towards larger albedo. However, this does not influence the SZA dependence of the OCIO columns up to 91° SZA. Furthermore, the photolysis rates of the box model calculated for OCIO 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 NO₂ 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 OCIO slant column densities at 90° SZA for the two days. The SZA dependence is presented only for 24 February in Fig. 6.

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Adjusting the rate constant of the BrO+ClO-reaction has the largest influence on the OCIO 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 OCIO 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 OCIO 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 · H₂O radical complex (Francisco and Sander, 1995; Galvez and Gomez, 2007). This could potentially increase the OCIO 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 Cl₂. 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 OCIO in the model. However, the explicit treatment of Cl₂ would mainly increase the morning concentrations of OCIO but leave the afternoon concentrations unchanged.

Possible roles of the two other Cl₂O₂ isomers chloryl chloride ClClO₂ 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 OCIO could arise from their photolysis.

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7 Summary

The measurements, described in this study, are the first validation attempt of the OCIO retrieved from SCIAMACHY observations made by comparison with ground-based remote sensing DOAS measurements. The agreement is excellent and OCIO could even be detected over the mid-latitude station Bremen during vortex excursions. It can be concluded that SCIAMACHY is delivering OCIO slant column amounts with high accuracy and can thus be used to study the long-term evolution of stratospheric chlorine loading.

The SLIMCAT-initialised stacked box model simulations of OCIO show very good qualitative agreement with the measurements but underestimate the measured amount of OCIO, in particular at low sun and large chlorine activation. Differences can be 40% or more. The modelled amount of OCIO 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 OCIO 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 OCIO column. From the model simulations of the OCIO behaviour, it can be concluded that our knowledge of the physical and chemical processing within the vortex is not sufficient to explain the OCIO behaviour adequately. This implies that the chlorine chemistry and its relevant mechanisms for the formation of OCIO 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 OCIO in the Southern Hemisphere using ground-based measurements and comparisons with models will provide more information with respect to our understanding of the OCIO sources and sinks and related halogen chemistry. A comparison of OCIO retrieved with GOME-1 and the new GOME-2 data in the

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period of overlapping measurements would be valuable to produce consolidated data sets.

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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. 6. More details can be found in the Sect. 6.

Parameter	Study	Differences in OCIO to the reference scenario at 90° SZA			
		24 Feb 2005		3 Mar 2005	
		a.m.	p.m.	a.m.	p.m.
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%
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%
OCIO absorption cross section	Kromminga et al. (2003)	+8%	+8%	+8%	+8%
Temperature initialisation	−3 K	+8%	+8%	+9%	+9%

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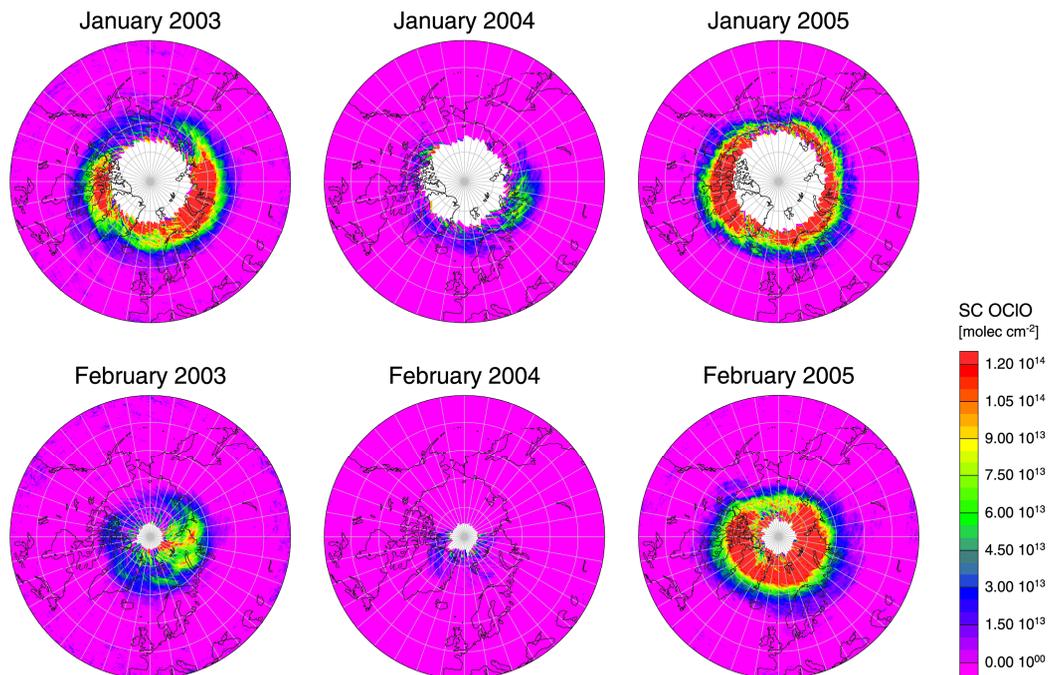


Fig. 1. Monthly averages of OCIO slant column densities retrieved from SCIAMACHY observations over the Arctic for the winters 2003 to 2005, top panel shows averages for January and bottom panels for February for the three consecutive years.

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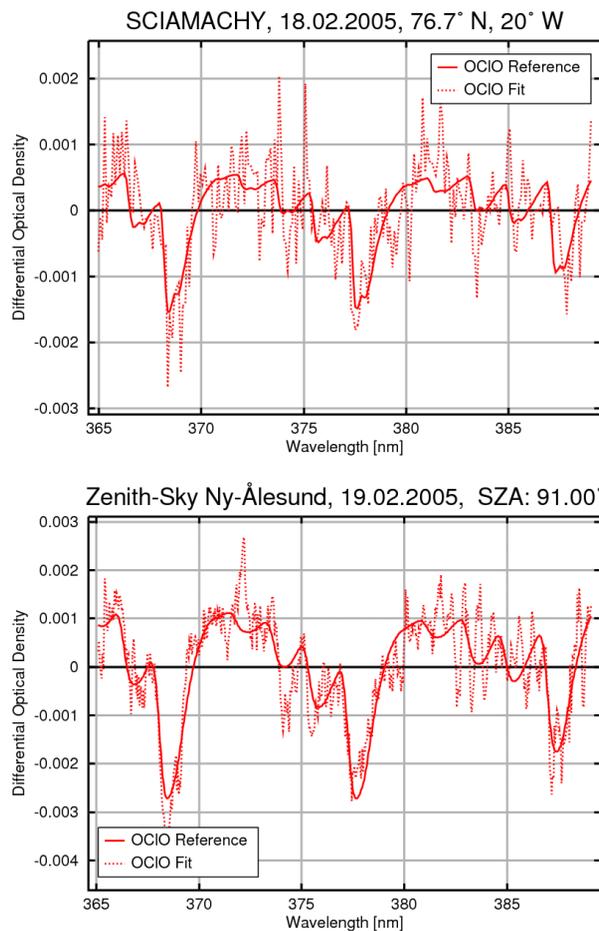


Fig. 2. Example of the OCIO retrieval fit for SCIAMACHY (top panel) and for ground-based measurement for Ny-Ålesund (bottom panel).

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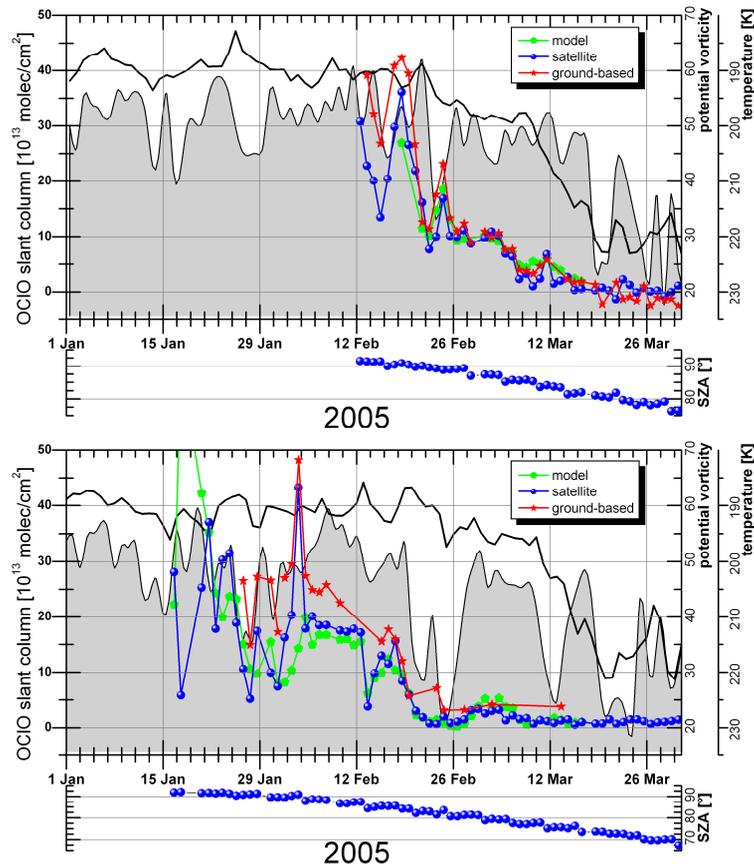


Fig. 3. Top: OCIO slant columns over Ny-Ålesund (79° N, 12° E) in spring 2005 (axis on the left): Model data in green, satellite in blue and ground-based data in red. The ground-based data was sampled at the time of ENVISAT overpass. Also shown are potential vorticity (shaded area; axis on the right) 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).

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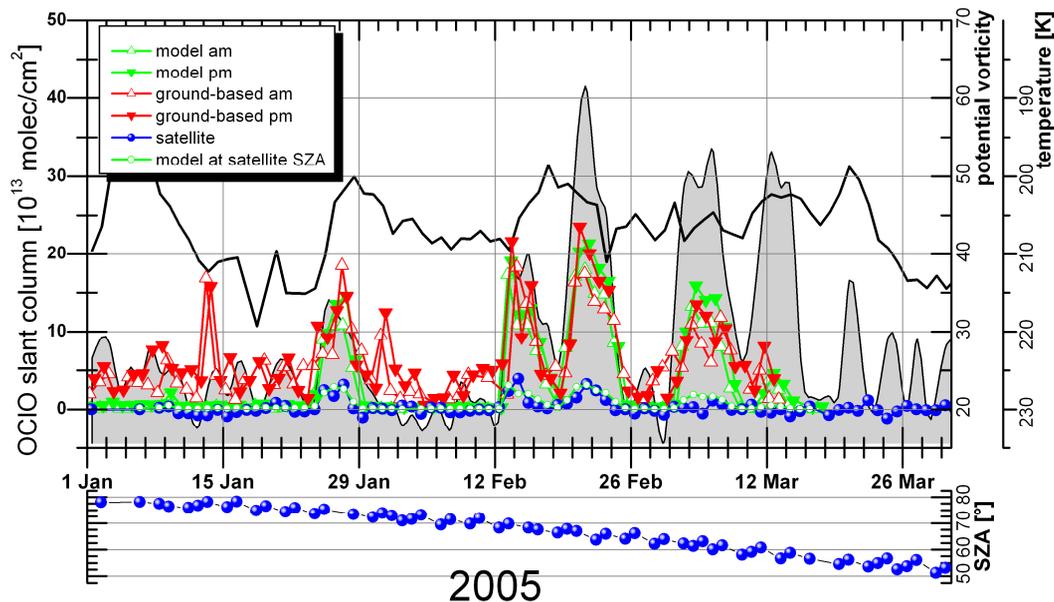


Fig. 4. OCIO over Bremen (53° N, 9° E; axis on the left): Model (green triangles) and ground-based data (red triangles) at 90° SZA and satellite (blue dots) at the SZA given below as well as model at the SCIAMACHY SZA (green circles), potential vorticity (shaded area) and temperature (black line) at the 475 K isentropic surface.

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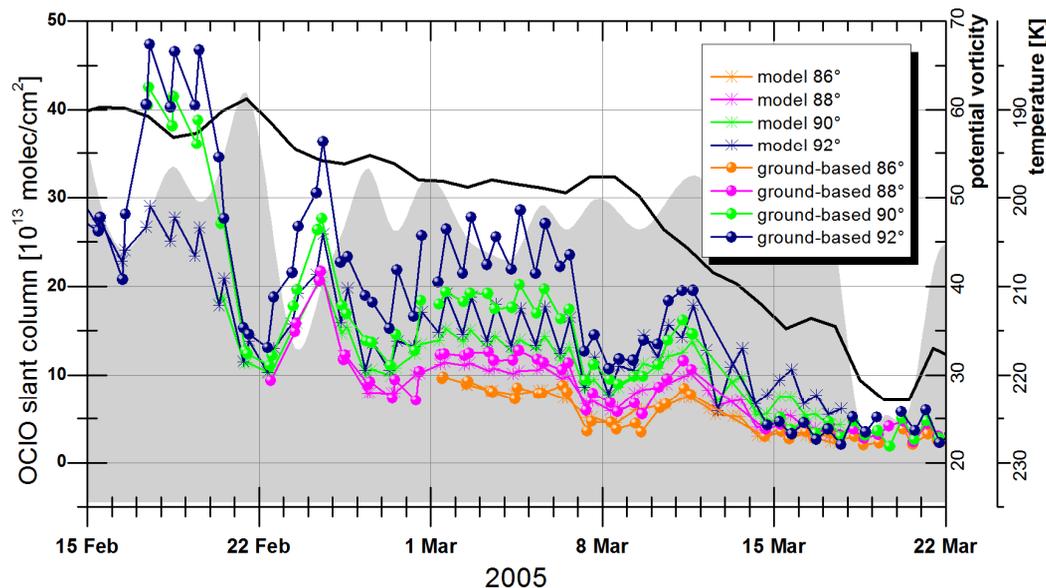


Fig. 5. Model (asterisks) and measurements (dots) of OCIO at Ny-Ålesund (79° N, 12° E) at four different SZAs (see box embedded in figure; axis on the left). Potential vorticity (shaded area) and temperature (black line) at the 475 K isentropic surface are also shown. Note that the zigzag pattern in the curves for high SZAs is caused by the diurnal variation of OCIO with higher concentrations in the afternoon.

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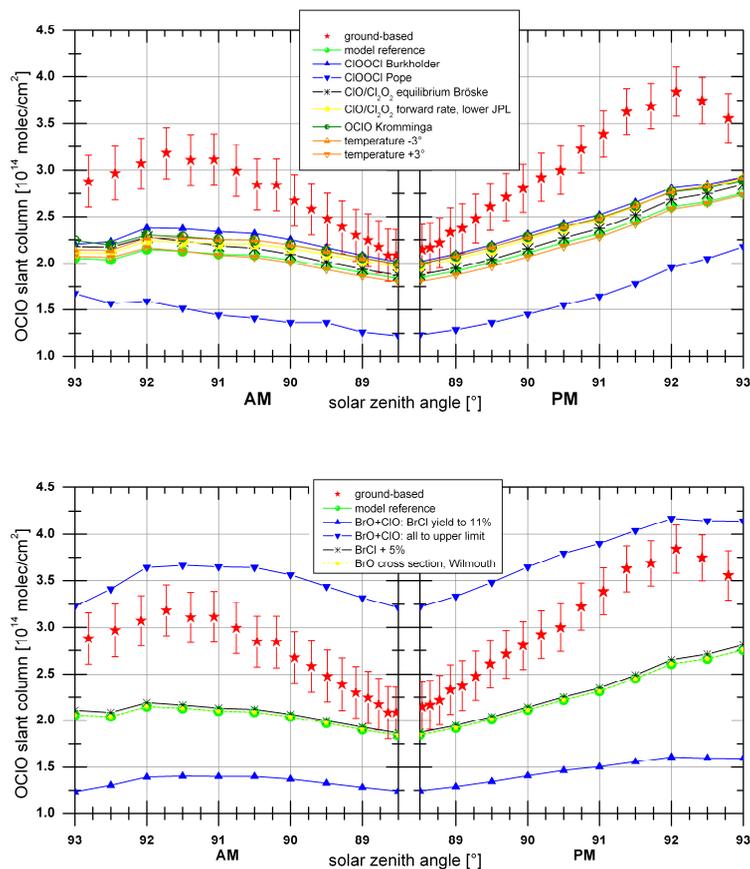


Fig. 6. Sensitivity Studies: measurements and model calculations of OCIO slant columns at Ny-Ålesund for 24 February. The error bars represent the 2σ error of the measurements. Sensitivity studies have been undertaken by changing the mechanism. The different scenarios are indicated in the box embedded in the figure and are explained in Sect. 6.

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