Comparison of Modelled and Measured Chlorine Dioxide Slant Columns for the Arctic Winter 2004/2005

H. Oetjen, T. Medeke, A. Richter, N. Sheode, B.-M. Sinnhuber, F. Wittrock and J.P. Burrows

Institute of Environmental Physics, University of Bremen, Germany

hilkeo@uni-bremen.de

Introduction

One of the important issues in atmospheric science is the stratospheric ozone depletion especially in Polar Regions. The most important halogen radicals involved in the ozone destruction are BrO and ClO. Whereas BrO can easily be detected by UV/visible spectroscopy this is not the case for ClO. But observations of chlorine dioxide (OClO) give a good indicator for chlorine activation in the polar vortex since the concentration of OClO is approximately proportional to the product of the concentrations of BrO and ClO during dawn and dusk.

This study presents ground-based and satellite, i.e. SCIAMACHY, measurements of chlorine dioxide by means of UV/visible spectroscopy over the Arctic for the exceptional winter 2004/2005. This winter was characterised by almost complete chlorine activation (see figure 1). The measured slant columns will be compared to model calculations.

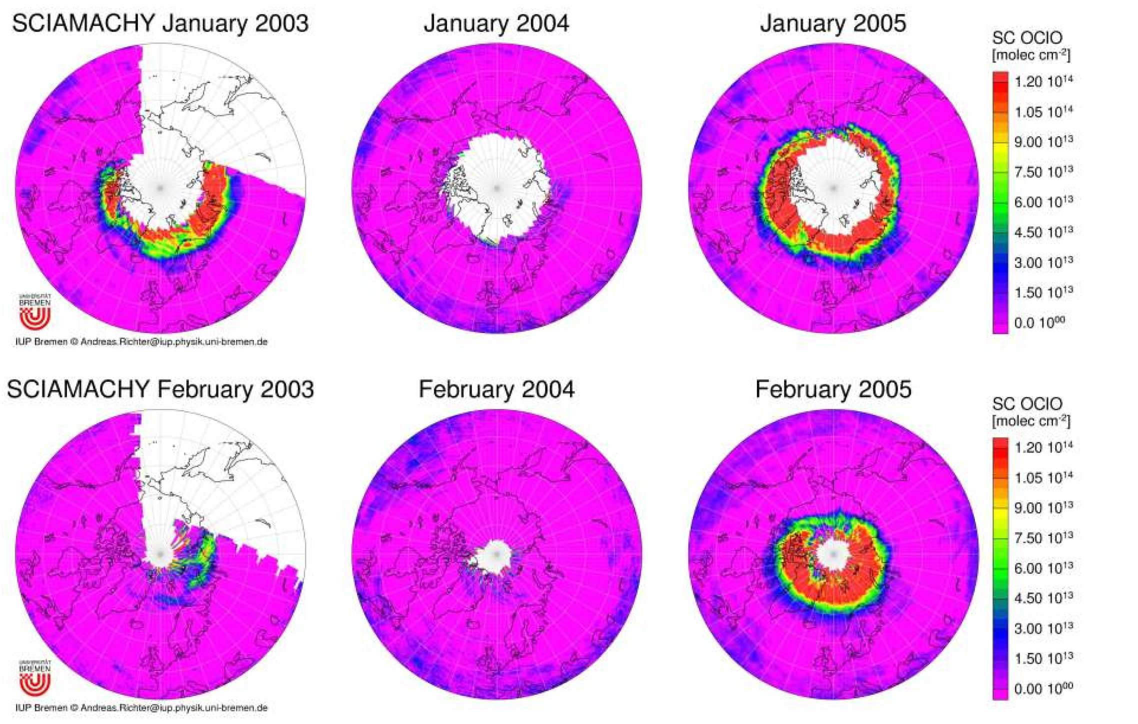

Figure 1: Averaged slant OClO columns from SCIAMACHY for January and February 2003, 2004 and 2005.

Data Sets

Bremian DOAS Network for Atmospheric Measurements (BREDOM)

- High-sensitivity ground-based MAX-DOAS-instruments for stand-alone operation [1] (see figure 2)
- Alternating zenith-sky and 4 off-axis viewing modes.
- Here, data from the instruments in Ny-Ålesund (Svalbard), Summit (Greenland) and Bremen (Germany).
- Spectra analysed with the DOAS method.

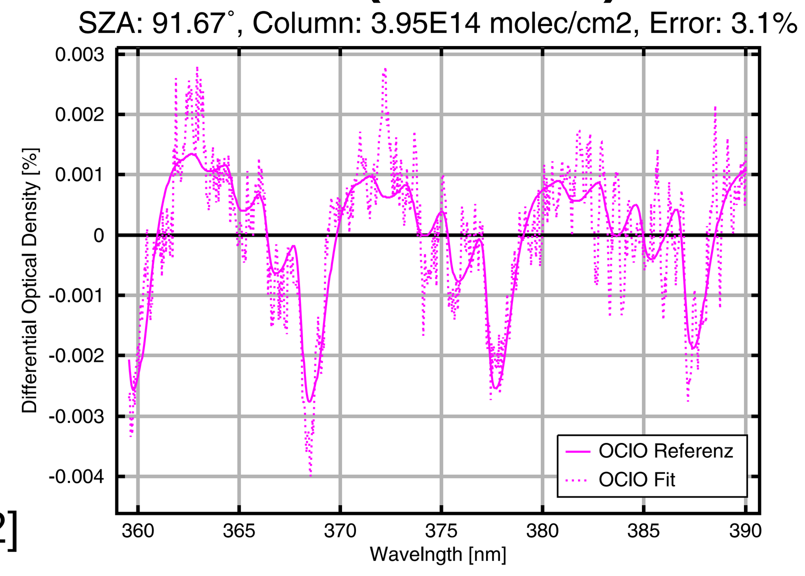

Figure 2: Example of an OClO Fit for the ground-based instrument in Ny-Ålesund.

SCIAMACHY satellite UV/vis instrument [2]

- Sun-synchronous orbits
- Global coverage within 6 days
- Spatial resolution 60x30 km^2
- Pixels with the centre within a radius of 200 km around the station are used.
- Spectra also analysed with the DOAS method.

Model calculations

- 1-D photochemical stacked box model with the photochemical scheme based on SLIMCAT [3] with a few modifications [4].
- 1-D model initialised with SLIMCAT data; pressure and temperature from ECMWF
- Calculations of OClO slant columns from the box model profiles with the radiative transfer model SCIATRAN [5] with 'chemical enhancement'.

Ny-Ålesund (79°N, 12°E)

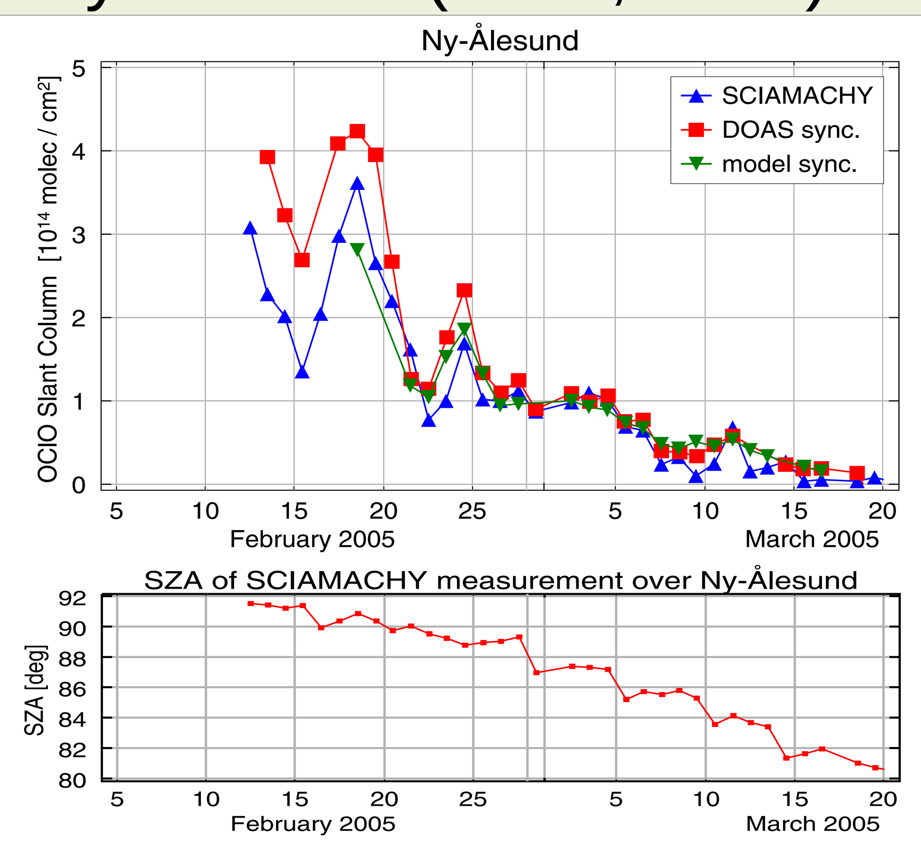

Figure 3: Time series of modelled and measured OClO over Ny-Ålesund for February and March 2005. The slant columns are shown for the SZA of the SCIAMACHY overflight time (see lower panel).

The upper panel of figure 3 shows the OClO slant columns for the winter 2005 over Ny-Ålesund. The ground-based and modelled data are given for the solar zenith angle (SZA) of the SCIAMACHY overpass (see figure 3, lower panel). The time of SCIAMACHY overflight is close to the local noon at this station. The columns from the ground-based and the satellite instruments agree nicely except in the beginning of the time series.

A comparison of ground-based and modelled slant columns for different SZAs shows generally good agreement for low SZAs but also for high SZAs similar columns can be observed when the chlorine activation is low (see figure 4). For situations with high chlorine activation the model underestimates the slant columns. But the

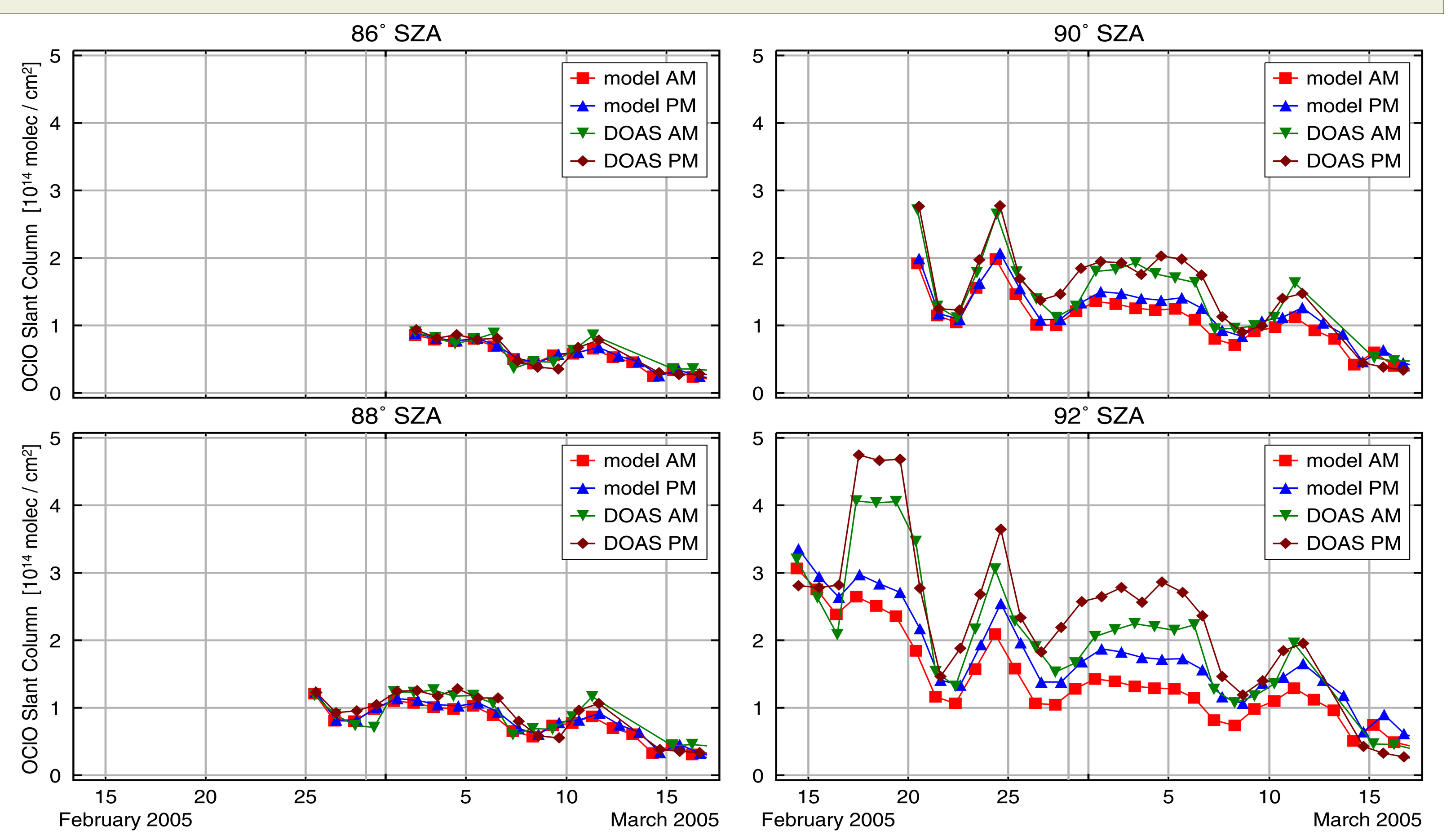

Figure 4: Comparisons of ground-based and modelled slant columns for 86°, 88°, 90° and 92° SZA over Ny-Ålesund.

Bremen (53°N, 9°E)

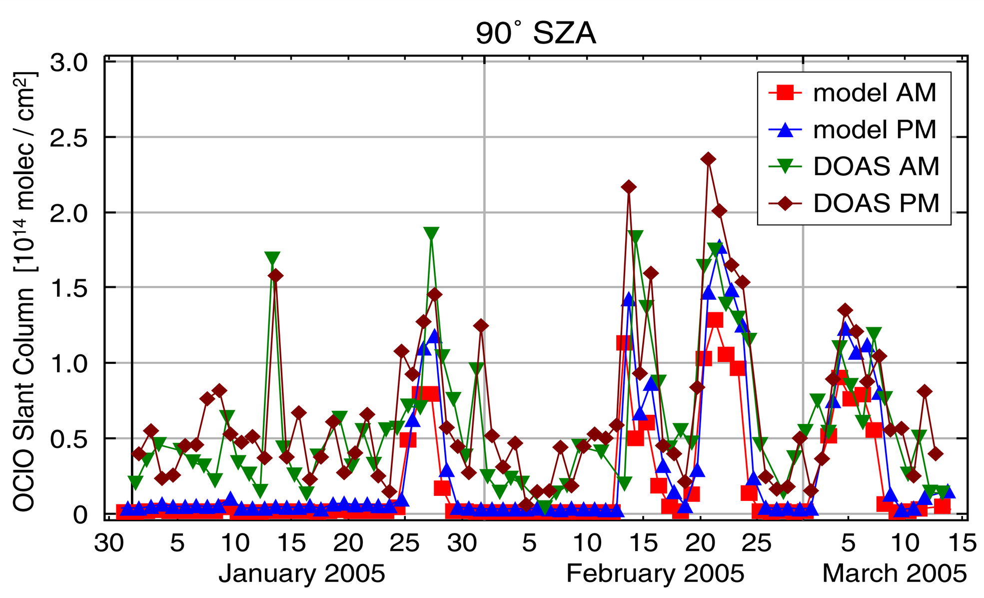

Figure 5: Comparison of ground-based and modelled OClO slant columns over Bremen for 90° SZA.

For Bremen, OClO could not be detected with SCIAMACHY since at the time of overpass, the SZA is smaller than 75° and consequently, the OClO is almostcompletely photolysed.

Figure 5 shows enhanced OClO columns whenever there were polar air masses present over Bremen. This can be observed with ground-based measurements as well as model simulations. The detection limit of OClO is at about $5x10^{13}$ molec/cm^2 for the ground-based OClO measurements.

Summit (72°N, 38°W)

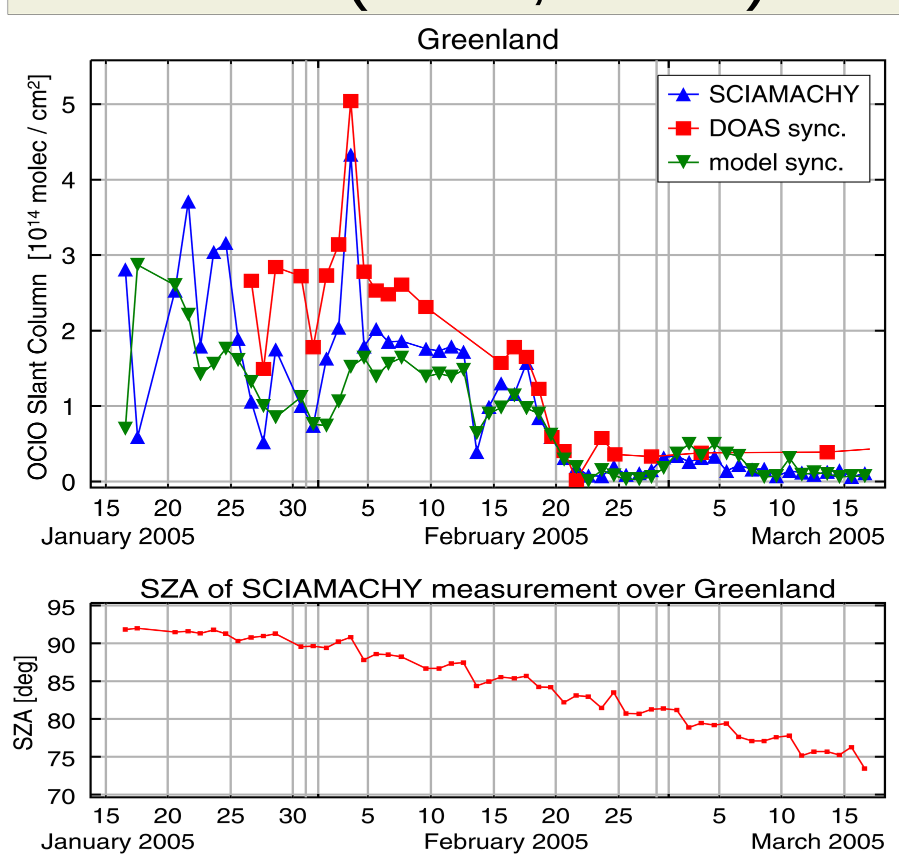

Fig 6: Time series of modelled and measured OClO over Greenland for January to March. The slant columns are shown for the SZA of the time of the SCIAMACHY overflight (see lower panel).

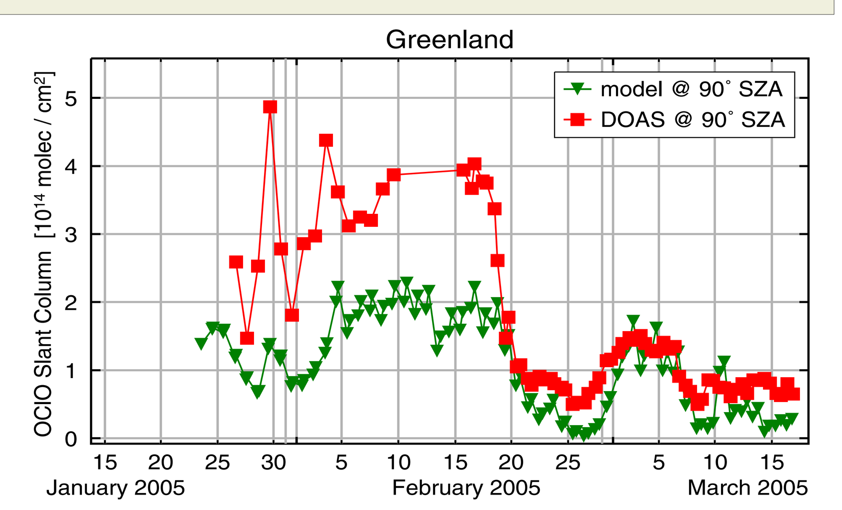

Figure 7: Comparison of ground-based and modelled OClO slant columns over Greenland for 90° SZA.

In Summit, the overall agreement of the three different data sets is not as good as in Ny-Ålesund, e.g. the peak detected by both instruments on April 4 is missed by the model simulation (see figure 6). In figure 7, the OClO columns show a similar behaviour as observed in figure 4: The strong chlorine activation is underestimated by the model.

References

[1] F. Wittrock, H. Oetjen, A. Richter, S. Fietkau, T. Medeke, A. Rozanov, J.P. Burrows: MAX-DOAS measurements of atmospheric trace gases in Ny-Ålesund - Radiative transfer studies and their application, *Atmos. Chem. Phys.*, 4 (2004) 955-966

[2] H. Bovensmann, J.P. Burrows, M. Buchwitz, J. Frerick *et al*.: SCIAMACHY: Mission objectives and measurement modes, *J. Atmos. Sci.*, *56*, 127-150, 1999.

[3] M.P. Chipperfield: Multiannual simulations with a three-dimensional chemical transport model, *J. Geophys. Res.*, *104*, 1781-1805, 1999.

[4] B.-M. Sinnhuber, D.W. Arlander, H. Bovensmann, J.P. Burrows *et al.*: On stratospheric bromine monixide: Intercomparison of measured and modelled slant column densities from a near-global network, *J. Geophys. Res.*, *107*, doi10.1029/2001JD000940, 2002.

[5] A. Rozanov, V.V. Rozanov, and J.P. Burrows: A numerical radiative transfermodel for a spherical planetary atmosphere: combined differential-integral approach involving the Picard iterative approximation, *J. Quant. Spectrosc. Radiat. Transfer*, *69*, 491, 2001.

Acknowledgements

This project has been funded in parts by:

- the German Federal Ministry of Education and Research (BMBF)
- the German Aerospace Agency (DLR)
- the German Research Council (DFG)
- the State of Bremen and the University of Bremen
- the European Union (Quilt EVK2-2000-00545)

We would like to thank the station personal of the Koldewey station in Ny-Ålesund for their assistance.

A big thank you also goes to Martyn Chipperfield for providing the SLIMCAT data.

Summary and Conclusions

- Considering the spatial distances of the ground-based and the satellite measurements, the agreement is excellent.
- At large SZAs, the modelled slant columns are too low compared to the measured ones.
- The discrepancies between model and measurement increase with increasing SZA as well as with increasing chlorine activation. Possible reasons for this are
  - a too high photolysis rate of the OClO in the model,
  - an incorrect branching ratio of the 'ClO + BrO'-reaction in the model
  - or an inaccuarate Br_y initialisation in the model.

Universität Bremen

www.doas-bremen.de