Appendix A

A new approach to derive the BrO absorption of the Fraunhofer spectrum from the comparison of ground based and satellite data

In contrast to satellite observations the Fraunhofer spectrum used for ground based DOAS measurements contains BrO absorption features, because usually no extraterrestrial spectrum measured with the same instrument is available. Commonly a spectrum measured at low SZA is used as Fraunhofer spectrum which contains only small atmospheric absorptions. However, to derive the total SCD from the DOAS analysis, the BrO SCD of the Fraunhofer spectrum (SCD_{Ref}) has to be added to the retrieved difference in the SCDs of the measured spectrum and the Fraunhofer spectrum:

$$SCD_{tot} = SCD_{diff} + SCD_{Ref} \qquad (A1)$$

Here we present a new method for the determination of SCD_{Ref}. Especially for species which are mainly located in the lower stratosphere and with a pronounced diurnal variation (like e.g. BrO and OClO) this method is more accurate than the methods usually used.

Up to now mainly two methods have been used (see e.g. Otten et al. [1998]) for the determination of SCD_{Ref}:
A) The use of a moonlight spectrum as Fraunhofer spectrum. Since during night all BrO is expected to be converted into reservoir species the BrO absorption of a moonlight spectrum is negligible. However, this method is subject to two large uncertainties: First, because of the low light intensity the fitting error is relatively large. Second, because of the large Ring effect also strong systematic errors can occur.
B) The Langley-plot method which is based on the calculation of AMFs. From Equation 5.1 it directly follows:

$$SCD_{tot}(SZA) = VCD \cdot AMF(SZA) \qquad (A2)$$

Combining Equations A1 and A2 we derive:

$$SCD_{diff}(SZA) = VCD \cdot AMF(SZA) - SCD_{Ref} \qquad (A3)$$

Thus, we expect a linear relation between the measured SCD_{diff}(SZA) and the calculated AMF(SZA) for a data set covering different SZA (e.g. measured during a day). If the measured SCD_{diff} (SZA) is plotted as a function of the calculated AMF(SZA) we can derive VCD from the slope and SCD_{Ref} from the y-intersect of the graph. This graph is referred to as Langley plot. Two prerequisites must be fulfilled for the application of the Langley plot method: First, the VCD must be constant for different SZA; second, the AMF must be appropriate for the measurements. For BrO both requirements are not fulfilled. In particular, because of the lack of knowledge about the BrO concentration profile large uncertainties result for the AMF calculation (see section 5).
This can be seen in Figure A1. Using AMFs for slightly different profile heights leads to significantly different SCD_{Ref}.

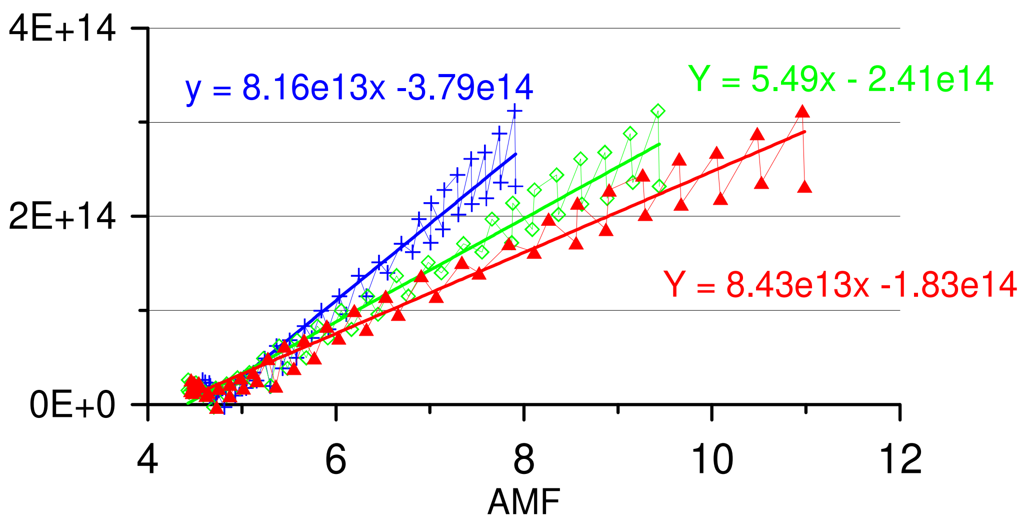

Figure A1 Determination of SCD_{Ref} for ground based measurements of BrO using the Langley plot method. Applying AMFs for only slightly different profile heights leads to significantly different results in SCD_{Ref}.

The new method developed within this PhD-thesis is based on a comparison of ground based and satellite BrO observations. Such a comparison was performed for a period of about 3 months with the ground based measurements at Kiruna for the daily GOME overpass(see section 6.4.1). During this period the SZA for the satellite's overpass changed from about 90° to about 70°.

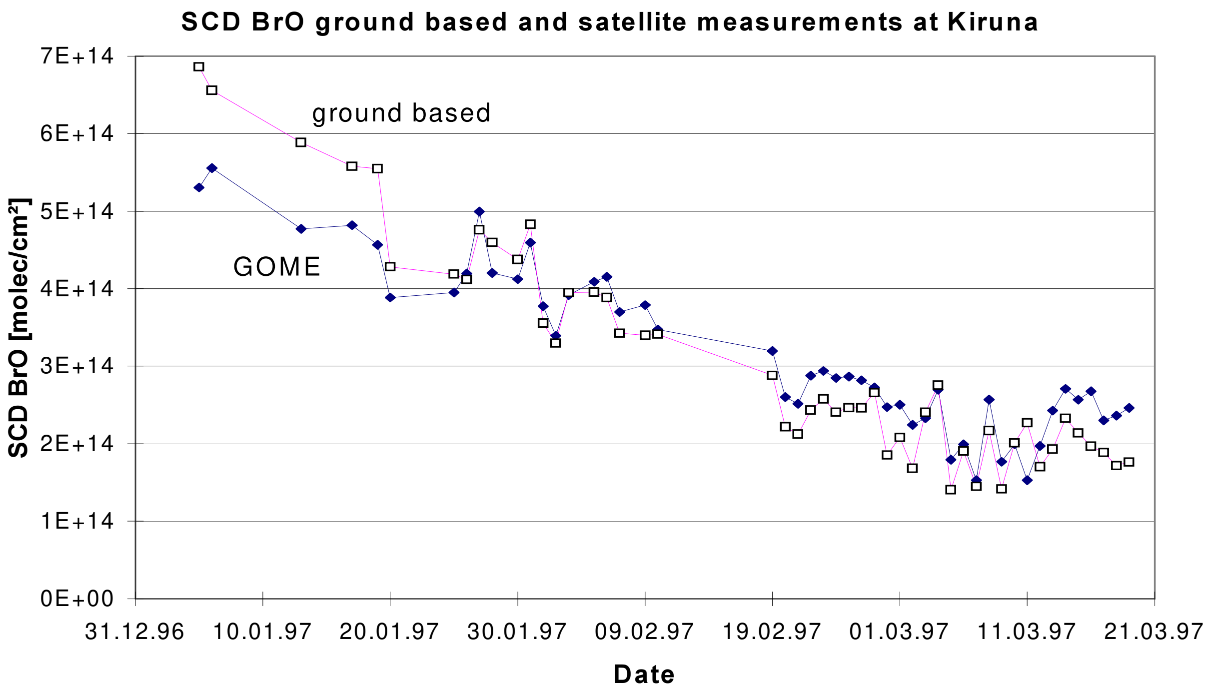

Figure A2 SCD BrO from ground based and satellite observations for the period from January to March 1997 at Kiruna. At the beginning the SZA is about 90°, at the end about 70°.

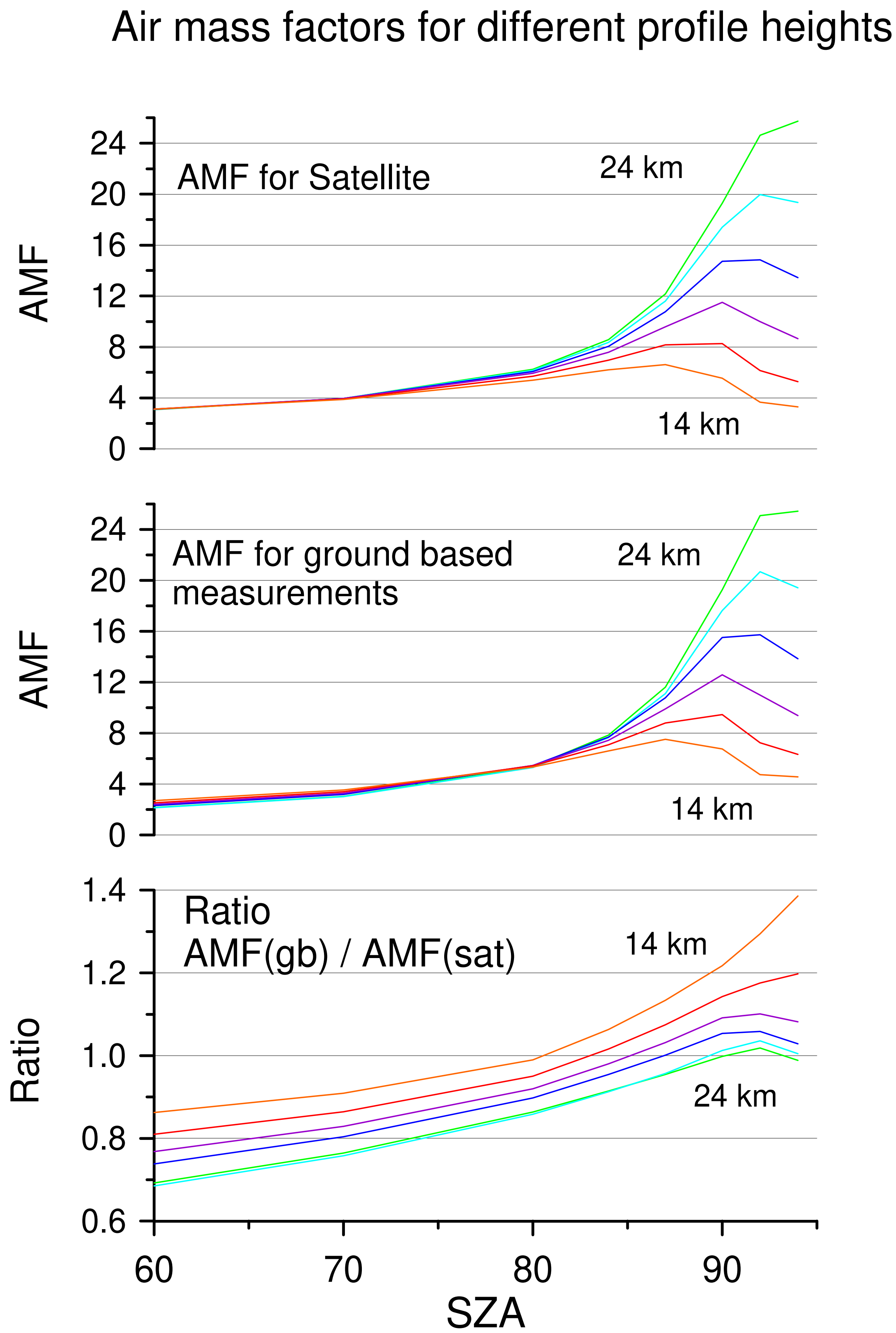

Figure A3 BrO AMFs for satellite and ground based observations calculated for different atmospheric BrO profiles. In the lower panel the ratio of both sets of the AMFs is shown.

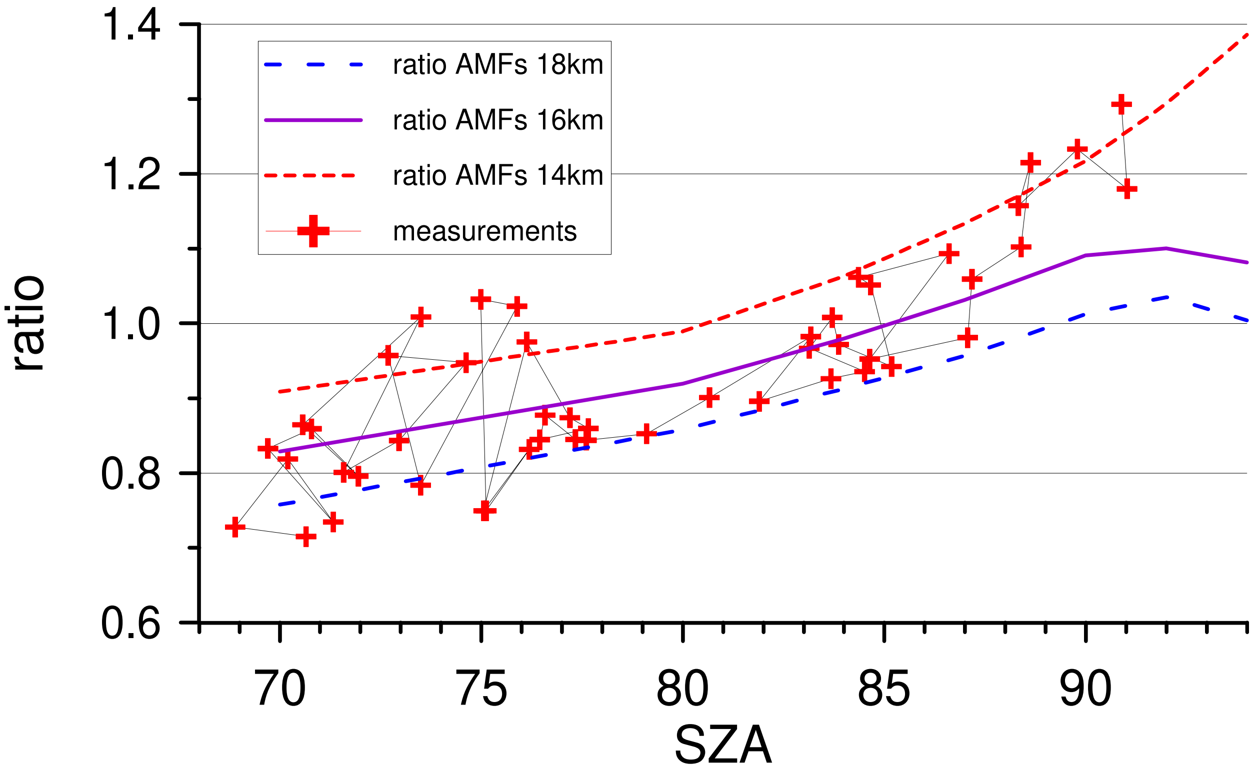

Figure A4 Comparison of the ratio of the ground based and satellite AMFs and the ratio of the measured BrO SCDs.

In Figure A2 the comparison of the BrO SCDs for both data sets is shown. While the long-term decrease of the measured SCDs is due to the changing SZA there are many short time variations which can be found similarly in both data sets. However, there is also a systematic difference of both measurements: At the beginning of the period (for large SZA) the BrO SCDs from the ground based observation are larger, at the end of the period (for small SZA) they are smaller than the BrO SCDs from satellite measurements. This systematic behaviour can be explained by the different atmospheric radiative transport for satellite and ground based measurements. In Figure A3 AMFs calculated for ground based and satellite observations are shown. The calculations were performed for BrO profiles with a Gaussian shape (FWHM: 7.5 km) and different heights of the concentration maximum. Also displayed is the ratio of the ground based AMFs and the satellite AMFs for the different BrO profiles. It is found that for all BrO profiles this ratio depends systematically on the SZA: For large SZAs the AMFs for ground based observations are enhanced compared to satellite observations, for small SZAs vice versa.

In Figure A4 the ratios of the AMFs are compared to the ratios of the measurements from ground and satellite plotted as a function of the SZA.

It can be seen that the measurements fit the AMF calculations well. Towards large SZA the scatter of the ratio of the measurements decreases, thus it is possible to derive information about the most probable profile height of the atmospheric BrO concentration during the period of the measurements. From Figure A4 it turns out that the best agreement is achieved for an assumed height of the BrO concentration maximum of about 14 km. This is in good agreement with BrO balloon measurements made during the same period at Kiruna [Pundt et al., 1998; Harder et al., 1998].

For small SZAs the ratio of the measured BrO SCDs depends strongly on the assumed value for the SCD_{ref} BrO of the Fraunhofer spectrum, because the total SCD BrO is small. For the measurements shown in Figures A1 and A4, the SCD_{Ref} derived from the Langley plot for the BrO profile maximum at 16 km ($SCD_{Ref} = 2.4 \cdot 10^{14}$ molec/cm²) was used.
Figure A5 presents the same comparison as in Figure A4 but with different (total) BrO SCDs for the ground based measurements according to the different SCD_{Ref} derived from the Langley plots for the BrO profile maximum at 14 km and 18 km, respectively. It is found that this comparison is very sensitive to the assumed values for SCD_{Ref}. With this method the SCD_{Ref} was determined as $(2.4 \pm 0.2) \cdot 10^{14}$ molec/cm². Compared to the Langley plot method the uncertainty is reduced by about a factor of three to four. The SCD_{Ref} determined with the new method was used for the ground based BrO data shown in section 6.4.

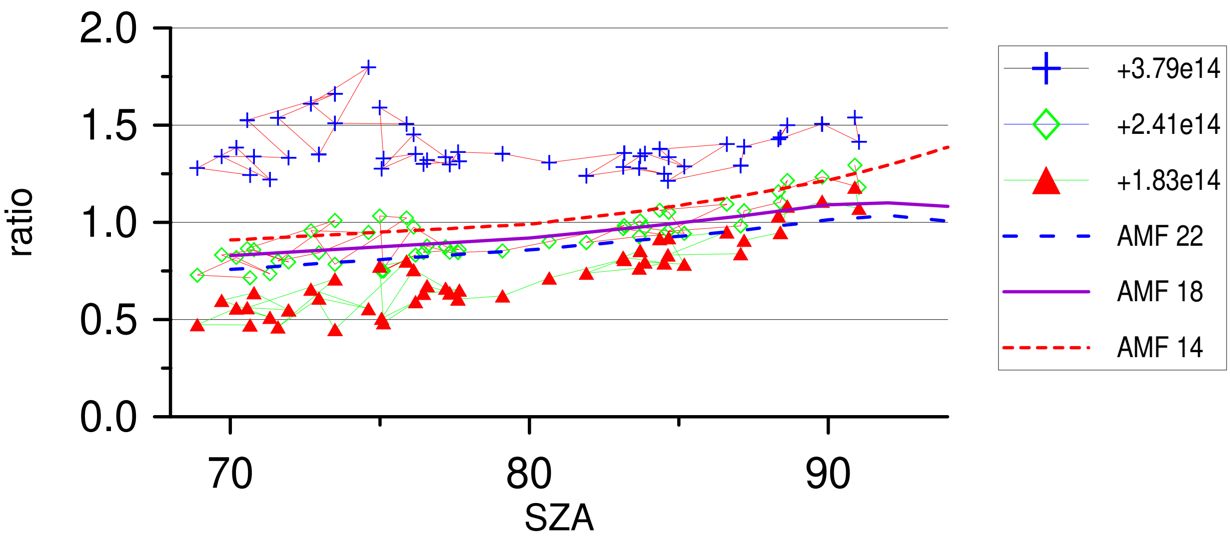

Figure A5 Determination of the BrO absorption of the Fraunhofer spectrum (SCD_{Ref}) for ground based measurements from the comparison to satellite observations. If the different values for SCD_{Ref} derived from the Langley plot method are used (Figure A2) to calculate the ground based BrO SCDs the derived ratios of ground based and satellite BrO SCD differ significantly from the ratios of the AMFs.

Appendix B

Publications

An overview of the author's publications is given in the reference list.

The author also contributed to several further articles:

Friess, U., M.P. Chipperfield, H. Harder, C. Otten, U. Platt, J. Pyle, T. Wagner, and K. Pfeilsticker, Intercomparison of measured and modelled BrO slant column amounts for the Arctic winter and spring 1994/95, *Geophys. Res. Lett., in print, 1999.*

Marquard, L.C., T. Wagner, and U. Platt, Improved Air Mass Factor Concepts for Scattered Radiation Differential Optical Absorption Spectroscopy of Atmospheric Species, *J. Geophys. Res., revised 1999.*

Otten, C., F. Ferlemann, U. Platt, T. Wagner, and K. Pfeilsticker, Groundbased DOAS UV/visible measurements at Kiruna (Sweden) during the SESAME winters 1993/94 and 1994/95, *J. of Atm. Chem., 30, 141-162, 1998.*

Pfeilsticker, K., F. Erle, O. Funk, L. Marquard, T. Wagner, and U. Platt, Optical path modifications due to tropospheric clouds: Implications for zenith sky measurements of stratospheric gases, *J. Geophys. Res., 103, 25323-25335, 1998.*

Platt, U., L. Marquard, T. Wagner, and D. Perner, Corrections for zenith scattered light DOAS, *Geophys. Res. Lett., 24, 1759-1762, 1997.*

Van Roozendael, S.R. Alliwell, P.V. Johnston, A. Richter, M. Van Roozendael, T. Wagner, D.W.Arlander, J.P. Burrows, D.J. Fish, R.L. Jones, K. Karlsen T∅rnkvist, J.-C. Lambert, K.Pfeilsticker and I.Pundt, Analysis for BrO in zenith-sky spectra - an intercomparison exercise for analysis improvement, *to be submitted to JGR, 1999b.*

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