Chapter 5

Modelling of the atmospheric radiative transport

For the analysis of DOAS measurements using direct or scattered solar radiation traversing the atmosphere, the so-called air mass factor concept has been developed (see e.g. Noxon et al. [1979], Solomon et al. [1987b]). Since the measured slant column density (SCD), the integrated trace gas concentration along the light path, strongly depends on the solar zenith angle (SZA), it is advantageous to convert the SCD into a vertical column density (VCD), the vertically integrated trace gas concentration. This conversion is usually performed by dividing the SCD by the air-mass factor (AMF):

$$VCD = SCD(SZA) / AMF(SZA) \quad (5.1)$$

The use of this air mass factor concept for atmospheric observations implies that the 'scalar' AMF contains all information about the viewing geometry of a specific measurement and the actual atmospheric conditions. In particular, it reflects the artificial separation between the spectral DOAS evaluation (in a first step) and the interpretation of the fitting results by applying radiative transport modelling (in a second step). We will refer to this approach as the 'traditional concept' in the following. While this proceeding is convenient and lucid in use, appropriate for many applications and has been widely and successfully used by many groups so far, it should be noted that this separation is not strictly correct [Marquard et al., 1999]. In particular, the spectral structures detected in atmospheric observations of scattered light depend on the radiative transport through the atmosphere (see e.g. Platt et al., [1997], Richter, [1997]). On the other hand also the AMF for a specific measurement depends on some of the arbitrarily chosen properties of the DOAS fit applied [Marquard et al., 1999].
In this study we use the 'traditional' AMF-approach: First the SCDs of the trace gases are derived from the spectral analysis of the measured spectra. Second these SCDs are converted to VCDs by dividing by the AMF. Since BrO and OClO, both species considered here, are only week atmospheric absorbers, the errors caused by the application of the 'traditional' concept are negligible compared to further uncertainties caused by the lack of atmospheric data (see below).

5.1 Air mass factors for ground based and satellite observations

For SZA < about 80° the AMF for direct light observation from ground can be approximately expressed by

$$AMF \approx 1/\cos(SZA) \quad (5.2)$$

(For a nadir viewing satellite instrument like GOME the AMF can be approximately expressed by 1 + 1/cos(SZA)). This relation also approximately describes the AMF for stratospheric species using zenith scattered light (see Figure 5.1). Nevertheless, for the correct interpretation of such measurements, especially at large SZA, radiative transport models are required which take into account the viewing geometry, the atmospheric conditions, the selected wavelength range, the ground albedo and the atmospheric trace gas profiles for a specific measurement.

Usually the calculation of the AMF includes modelling of the intensities received by the spectrometer with and without the atmospheric absorber. The AMF can then be derived (see e.g. [Noxon, 1975; Noxon et al., 1979; Solomon et al., 1987b; Perlsiki and Solomon, 1993; Sarkissian et al., 1995; Marquard et al., 1999]):

$$\mathrm{AMF(SZA)} = \frac{\ln[I(SZA) / I_0(SZA)]}{\sigma} \tag{5.3}$$

where I(SZA) denotes the modelled intensity with the absorber and I_0(SZA) without the absorber, and σ is the absorption cross section of the trace gas.

Recent studies [Marquard et al., 1999] have shown that the AMF not only depends on the concentration profile of an atmospheric absorber but also on the total atmospheric VCD. Additionally, it was found that the AMF is also a function of the strength of the absorption cross section. Most strikingly it turned out that the AMF depends on the specific properties of a DOAS analysis like the kind of high pass filter chosen (see section 4.3). These additional dependencies occur only when scattered radiation is observed; they arise for this kind of measurement technique from the non-linearity between the absorption cross section and the measured optical depth. The errors caused by these 'non linear effects' (NLE) can be about several per cent, in particular for measurements of ozone in the UV spectral range [Marquard et al., 1999].

However, for the satellite borne measurements of BrO and OClO described in this thesis the NLE are not important because both species are only 'weak' atmospheric absorbers and the measurements were performed in spectral ranges where other atmospheric absorptions (e.g. due to O_3 and the oxygen dimer O_4) are rather small, too. Thus the systematic error of the AMF due to the NLE are expected to be below about 1% [Marquard et al., 1999]. Thus they are by far smaller than the uncertainties due to the lack of information about the measurement conditions, i.e. the profile shapes of the absorbing species, the atmospheric aerosol extinction, the cloud cover and the ground albedo.

The variability of these parameters influences the AMFs in such a way that it limits the accuracy of satellite measurements for many cases. In particular, the huge amount of data excludes a detailed consideration of these parameters (if available at all) for each single observation. In section 5.2.2 AMFs for satellite observations are calculated taking into account the variations of these parameters. It turned out that for the majority of the GOME measurements the AMF for BrO and OClO can be determined within an uncertainty of about 10% (see Table 5.2).

It should also be noted here that the atmospheric concentrations of photoreactive trace gases like BrO and especially OClO vary with the intensity of the solar radiation which in particular depends on the SZA. Because of this dependence the usefulness of the conversion of SCDs into VCDs is limited: Even if the AMF for a specific measurement condition is modelled correctly the derived VCD for the respective SZA can not directly compared to that of another SZA. Moreover, since the light detected by the instrument has traversed through the atmosphere at different (local) SZAs the derived SCD can not simply be assigned to a specific SZA. This is in particular important for SZA around 90°. For the correct interpretation of the measurements of photoreactive compounds usually radiative transport models and photochemical models have to be combined [Roth, 1992; Brandtjen, 1994; Fish et al., 1997; Otten et al., 1998; Erle et al, 1999; Friess et al., 1999]. Such a treatment, however, is beyond the scope of this work because of the huge amount of data. It rather should be applied to case studies in future work.

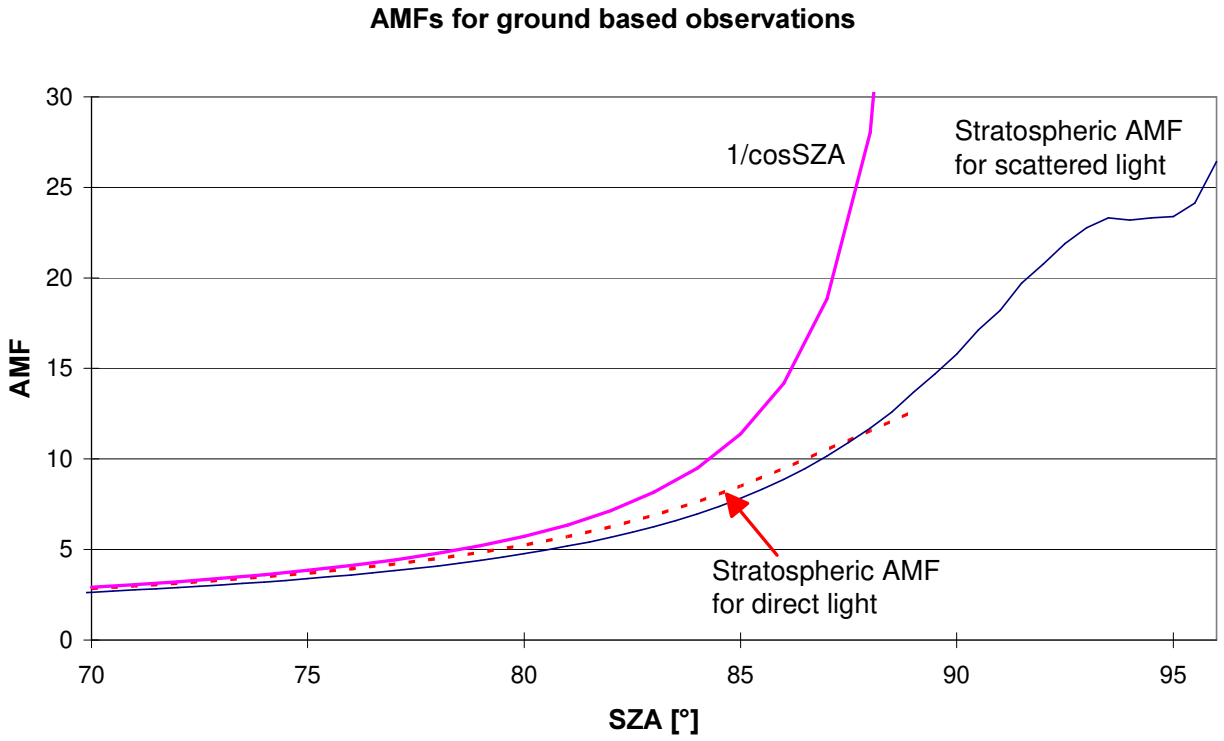


Figure 5.1 Geometric approximation for the AMF (1/cos[SZA]) compared to stratospheric AMFs for direct and scattered light for ground based observations (The maximum concentration of the assumed trace gas concentration profile is located at 16 km).

5.2 Calculation of air mass factors for GOME

The AMFs used in this work have been calculated with the Monte Carlo radiative transport model AMFTRAN. This model was developed on the University of Heidelberg by Heinz Frank and Lutz Marquard [Marquard et al., 1997; Marquard, 1998]; it takes into account fully spherical geometry and multiple scattering processes in the atmosphere. Also variations in the atmospheric aerosol load and the ground albedo can be considered. It can be applied to the measurements of direct and scattered radiation and different viewing geometries. Thus it is well suited for the calculation of satellite AMFs because it especially.

The main focus in this section is spent on AMFs for BrO, because the high accuracy of the developed algorithm for the determination of the BrO SCD (see section 4.3.7). Thus it is useful to achieve a similar accuracy also in the AMF calculation. In addition, recent balloon borne measurements and modelling studies provide atmospheric BrO profile data [Pundt, 1997; Pundt et al., 1998b, 1999; Harder et al., 1998] which are a prerequisite for the precise determination of the AMF.

For OClO the situation is completely different. First, larger relative uncertainties in the determination of the OClO SCDs appear. Second, the knowledge about the stratospheric OClO concentrations is still very uncertain. Only very few OClO profiles have been measured during daylight so far [Pundt et al., 1998b].

In general, the OClO results in this study are expressed as slant column densities.

5.2.1 Air mass factors for stratospheric BrO

The large amount of satellite data (about 30 000 spectra per day) and in particular the high variability of the atmospheric conditions (like the height profiles of temperature, pressure, ozone and BrO concentration as well as aerosol extinction) and the ground albedo for different latitudes and seasons makes the determination of appropriate AMFs a great challenge. First, to date it is still impossible to perform individual calculations for each measurement. This would even be impossible if the required input information would be available which is not the case. Thus the most useful solution is to calculate 'standard' AMFs for several 'typical' atmospheric height profiles. This allows to get an estimate about the range of variation of the AMF for stratospheric BrO measurements. For these 'standard' AMFs sensitivity studies were performed to determine the dependencies of these AMFs from the ground albedo and the height profiles of temperature, pressure, ozone and BrO concentration as well as aerosol extinction.

Stratospheric profiles of the BrO concentration

The height of the tropopause changes systematically from polar regions to the tropics. As can be seen in Figures 5.2 and 5.3 e.g. the height profiles of stratospheric O_3 closely follow these height variations. Although this dependence can not in general be expected to be valid for other trace gases for the calculation of the BrO AMFs we assume as a first guess that the height profiles of the BrO mixing ratios are shifted according to the tropopause height. This dependence is in general agreement with the current understanding of the release of reactive bromine from the source gases [Wamsley et al., 1998] and was also observed for some balloon measurements of BrO [Harder et al., 1998].

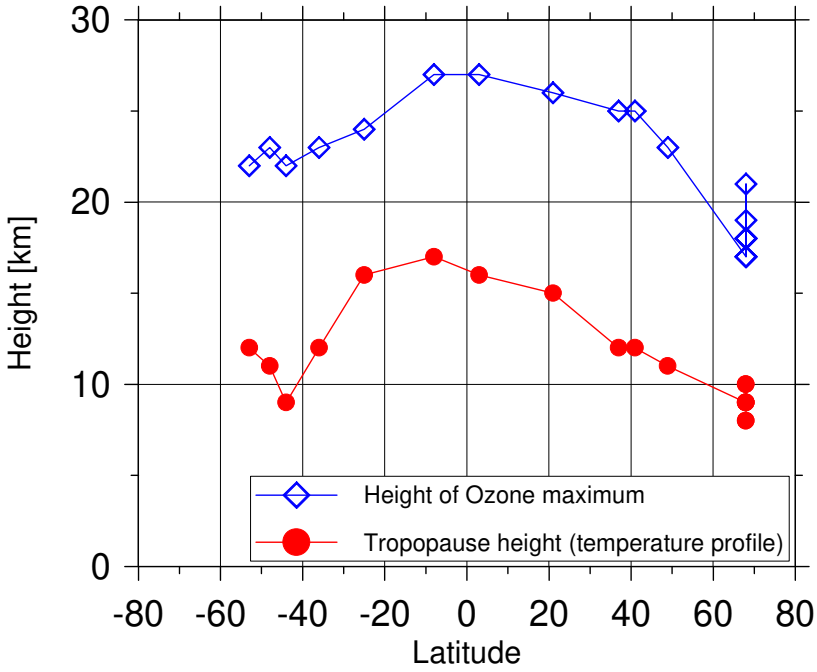


Figure 5.2 Variation in the tropopause height (derived from the temperature profiles) and the height of the ozone concentration maximum derived from ozone sondes measured on a ship cruise across the Atlantic during October and November 1993 (see e.g. Senne et al. [1995]).

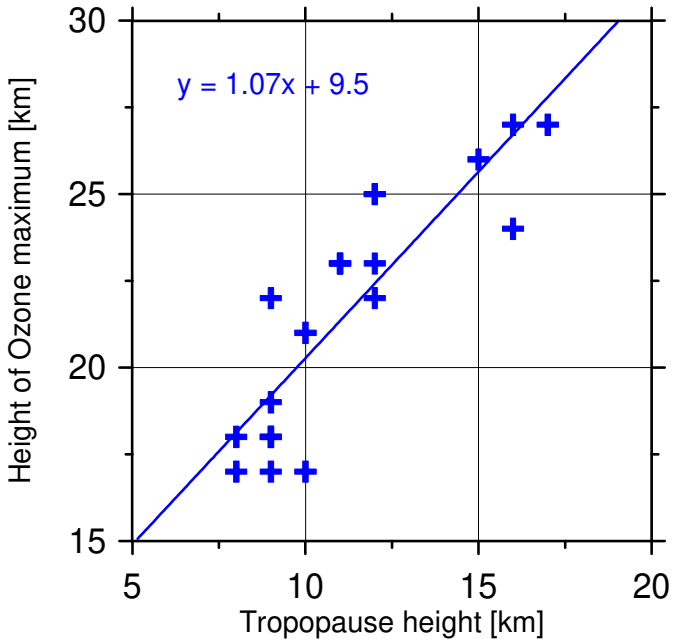


Figure 5.3 Correlation of the height of the tropopause and maximum of the ozone layer; same data as shown in Figure 5.2.

The stratospheric BrO concentration profiles were calculated according to a BrO mixing ratio increasing from about zero to about 12 ppt within the first 10 kilometres above the tropopause (similar to the measurements of Harder et al. [1998] and Pundt et al. [1999]).
The resulting BrO concentration profiles and also the total BrO VCD depend strongly on the height of the tropoause (see Figure 5.4).
These profiles were used as input for the AMF calculation. The resulting AMFs (hereafter referred to as 'standard' AMFs) are displayed in Figure 5.5. While for SZA < 75° the profile shape has negligible influence on the AMF this changes for SZA > about 75°. For example, at a SZA of 90° the AMF varies by a factor of about three.

Because GOME measurements cover a wide range of different atmospheric conditions and because for most of the measurements information about these conditions is not available in sufficient quality, it is useful to study the sensitivity of the standard BrO AMFs with respect to variations in these atmospheric conditions. The sensitivity studies presented in the next sections include variations in the ground albedo, the aerosol load, the ozone profile, as well as temperature and pressure profiles. The AMF calculations were performed for SZA up to 92°. However, it should be noted that for the BrO results presented in section 6 only measurements for SZA ≤ 90° were taken into account. For these SZA the uncertainties are in general much smaller than for SZA > 90°.

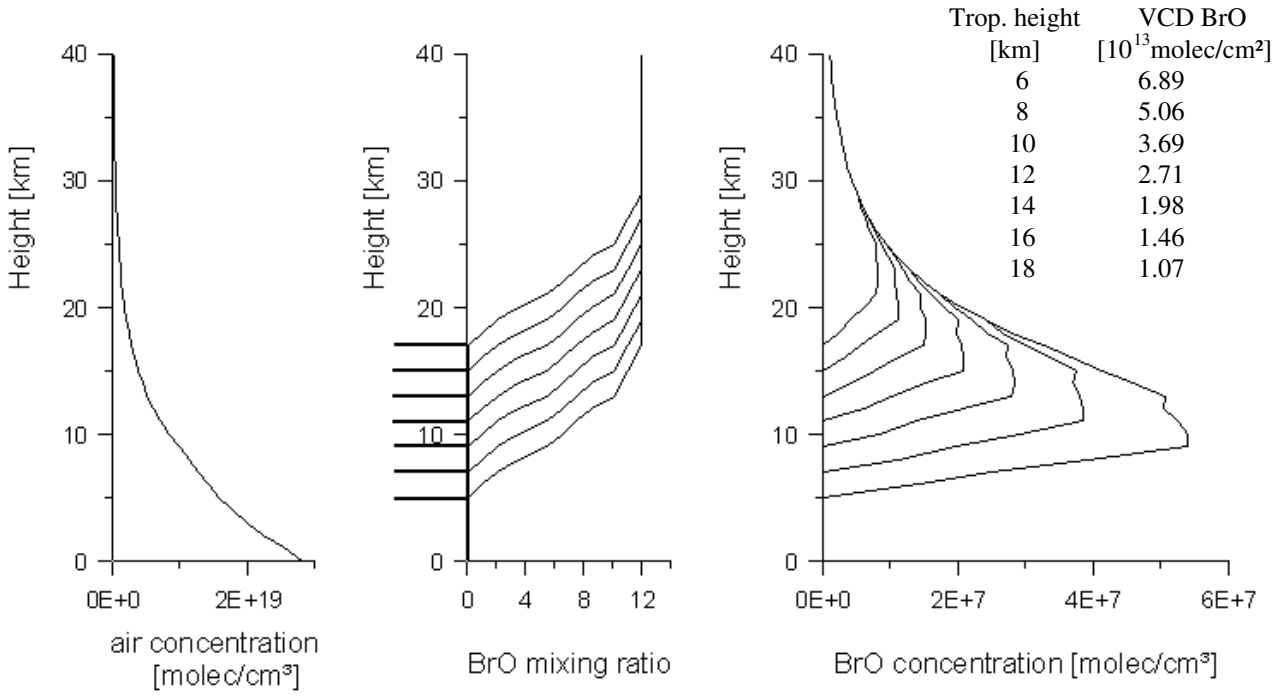


Figure 5.4 Calculation of the stratospheric BrO concentration profiles used for the AMF calculation. Left: height profile of the air concentration (derived from a radio sonde from mid latitudes). Center: profiles of the BrO mixing ratio for different tropopause heights (at 6, 8, 10, 12, 14, 16, and 18 km, indicated by the horizontal bars). Right: The resulting concentration profiles for BrO concentrations. Also displayed are the BrO VCDs for the different tropopause heights.

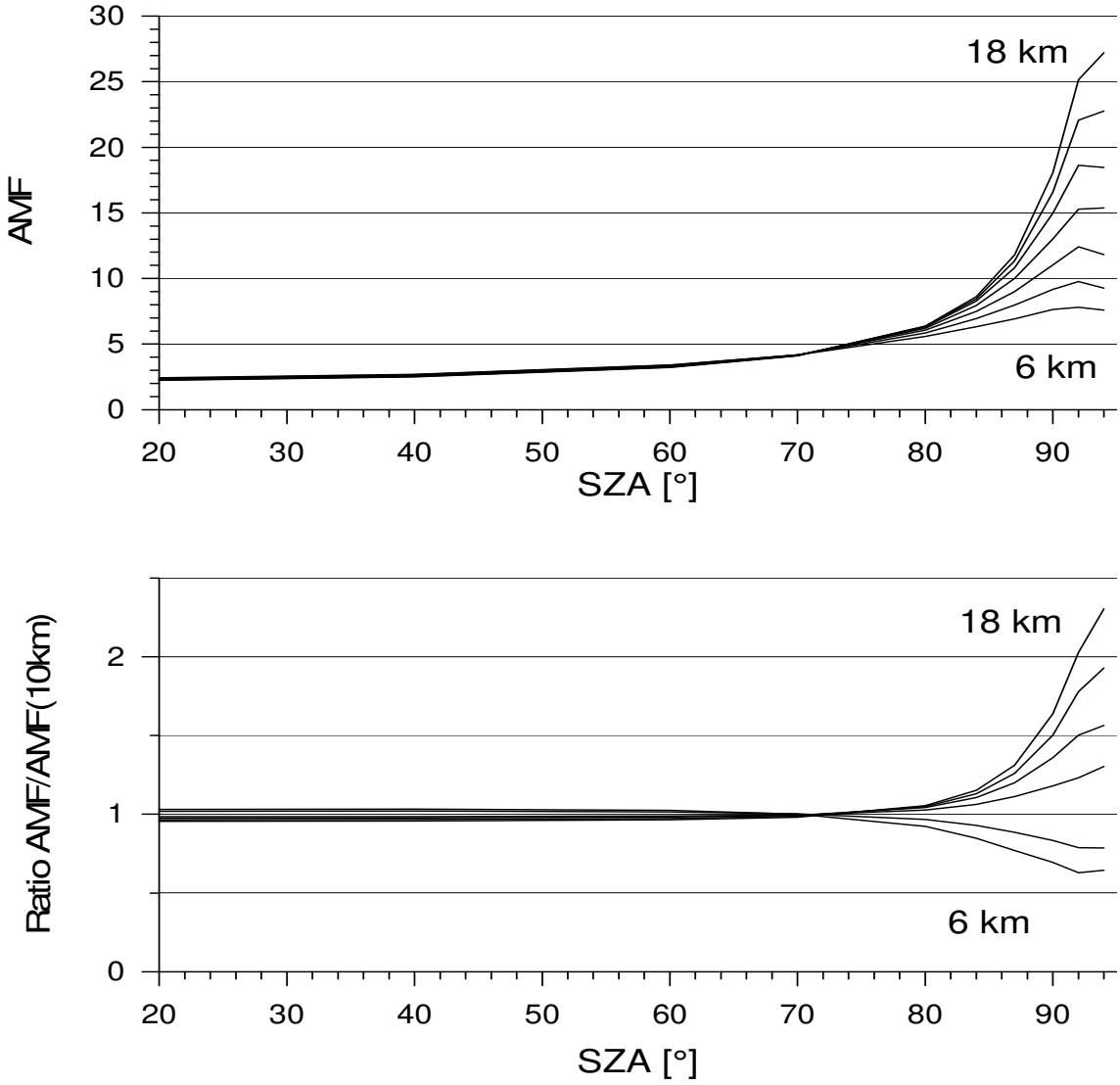


Figure 5.5 top: AMFs calculated for the BrO profiles shown in Figure 5.4. These AMFs were calculated for 'average' atmospheric conditions (see below) and are referred to as BrO 'standard' AMFs in the following. bottom: Ratio of each AMF shown in the top panel with the AMF for a tropopause height of 10 km.

5.2.1.1 Influence of the ground albedo

Especially for satellite measurements the ground albedo is expected to have a large influence on the AMF. This influence increases with decreasing SZA and decreasing height of the atmospheric trace gases. For the standard AMFs (see Figure 5.5) an albedo of 0.8 was chosen, because specific interest of this study concerns polar regions during winter and spring time. Nevertheless, as can be seen in Figure 5.6 the uncertainty in the AMFs for stratospheric BrO caused by variations of the ground albedo is in the range of only a few percent. Especially for low latitudes where the tropopause is high the influence of the ground albedo is negligible compared to other uncertainties (see Table 5.2).

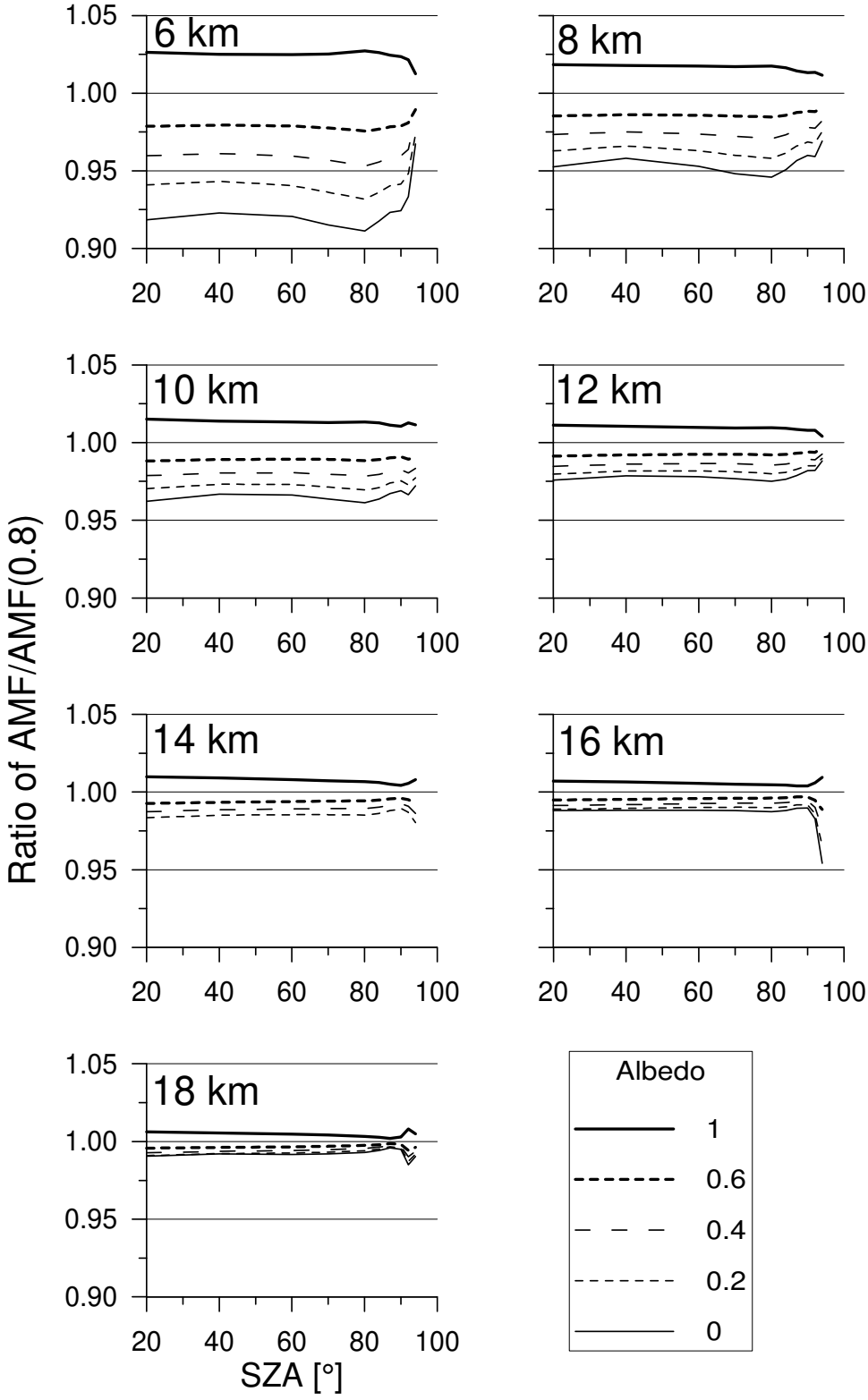


Figure 5.6 Influence of variations of the ground albedo on the BrO standard AMFs for different tropopause heights (6 to 18 km, see Figure 5.4). Displayed is the ratio of the AMFs calculated for different albedos and the BrO standard AMF calculated for an albedo of 0.8.

5.2.1.2 Influence of the atmospheric aerosol profile

In this section the influence of aerosol extinction on the BrO standard AMFs is investigated. For satellite observations aerosol scattering can have different effects: On the one hand the absorption paths can be elongated due to multiple scattering, on the other hand thick aerosol layers can hide the 'view' of the instrument down to the atmosphere below the aerosol layer. GOME measurements started in mid 1995 after most of the aerosol loading from the eruption of Mount Pinatubo had disappeared. For the calculation of the BrO standard AMFs, aerosol profiles from the LOWTRAN data base for fall/winter [Isaacs et al., 1986, 1987; Kneizys et al., 1988] were used. In this data set the tropopause is placed at 10 km altitude.
Thus it is necessary to adapt the aerosol profile according to the tropopause heights used for the calculation of the BrO standard AMFs (see Figure 5.4). We performed an analysis of the stratospheric aerosol data measured by SAGE-II at different latitudes and seasons for the years from 1985 to 1990 [SAGE II, 1993]. During these years (before the Pinatubo eruption) background values can be expected for the stratospheric aersol loading. From our study it became obvious that the variability of the aerosol profiles was significantly smaller than the respective variation of the tropopause height. To account for this finding it seems to be more reasonable to vary the stratospheric aerosol profile for the calculation of the standard BrO AMFs less than the variation of the tropopause height. For the calculation of the standard BrO AMFs we shifted the LOWTRAN aerosol profile by half the amount of the shift of the tropopause (relative to a tropopause height of 10 km).
Table 5.1 summarises the shifts of the LOWTRAN aerosol profile for the different heights of the tropopause. The different aerosol profiles used for the AMF calculation as well as average aerosol profiles from SAGE-II observations are shown in Figure 5.7.

Height of the tropopause [km]	Shift of the stratospheric aerosol profile (LOWTRAN, fall/winter) [km]
6	-2
8	-1
10	0
12	1
14	2
16	3
18	4

Table 5.1 Shift of the stratospheric aerosol profiles compared to the original LOWTRAN aerosol profile according to the tropopause heights used for the calculation of the standard BrO AMFs.

To investigate the sensitivity of the standard BrO AMFs to the aerosol extinction the aerosol profiles were varied by dividing and multiplying by a factor of three (see Figure 5.7). It was found that for these considerably strong variations in the aerosol extinction the AMF varies only within a few percent for SZA < 90° (see Figure 5.8).

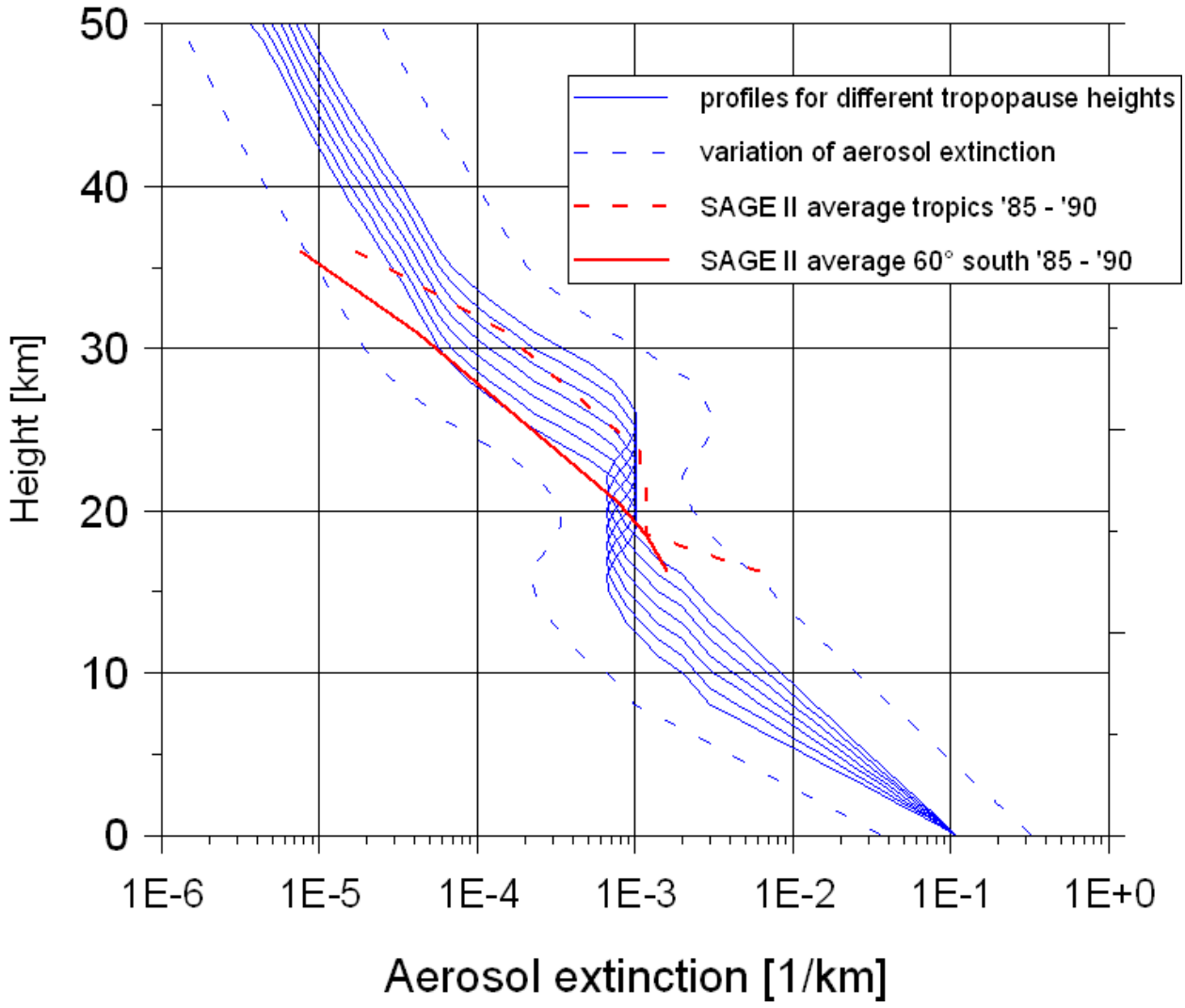


Figure 5.7 Aerosol extinction profiles used for the calculation of the BrO AMFs (continuous thin lines). Also displayed are average aerosol profiles from SAGE-II observations for the tropics (continuos thick line) and at 60° south (dashed thick line) [SAGE II, 1993]. The SAGE II data were measured during the years 1985 to 1990 and are characteristic for stratospheric background aerosol profiles. To investigate the sensitivity of the standard BrO AMF to the aerosol extinction, the aerosol extinction was varied by dividing and multiplying by three (thin dashed lines).

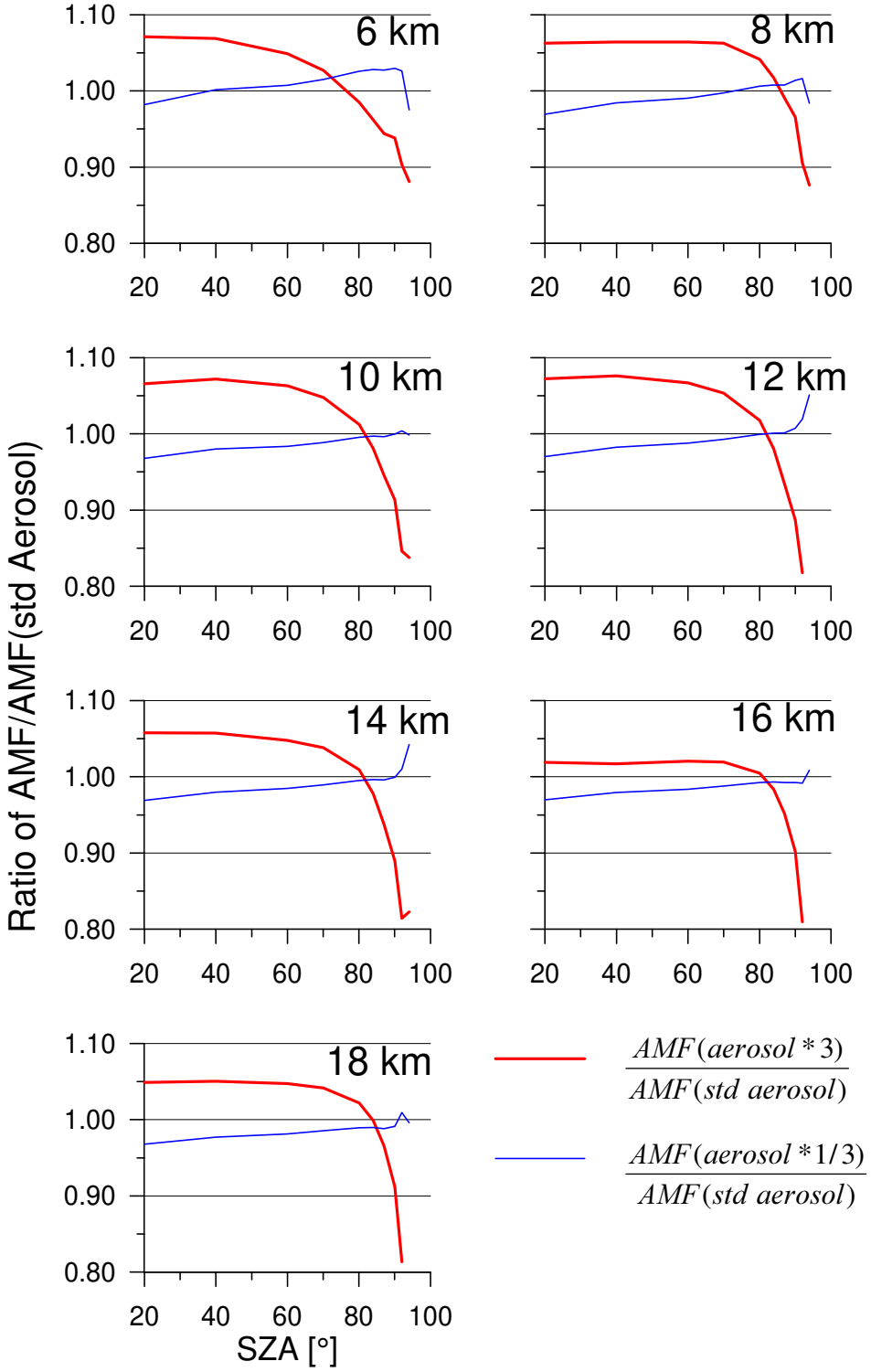


Figure 5.8 Influence of variations in the aerosol extinction on the BrO standard AMFs for different tropopause heights (6 to 18 km, see Figure 5.4). Displayed is the ratio of the AMFs calculated for enhanced (multiplied by a factor of three) and decreased (divided by a factor of three) aerosol extinctions and the BrO standard AMF calculated for the LOWTRAN profile.

5.2.1.3 Influence of the atmospheric temperature and pressure profile

To investigate the dependence of the BrO standard AMFs on variations of atmospheric temperature and pressure profiles, AMFs were calculated for data from radio sondes for different latitudes and seasons (see Figure 5.9). It can be seen that for SZA ≤ 90° the variations of the AMF are within about 5 %. It is important to note that for GOME observations large SZAs occur only at high latitudes. Since the temperature and pressure profiles used for the calculation of the standard AMFs were taken from such conditions, the errors of the AMF are expected to be even smaller than 5% for most of the measurements.

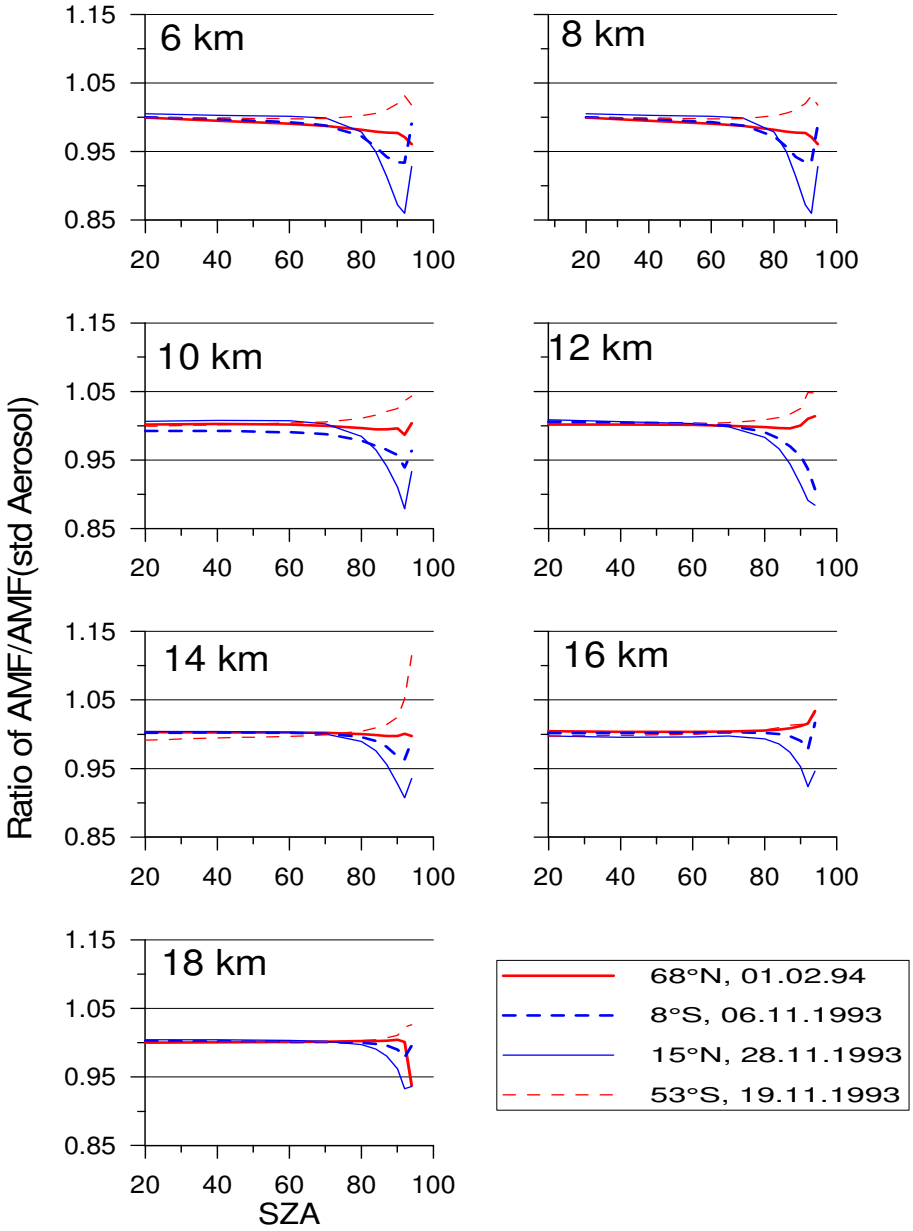


Figure 5.9 Influence of variations in the atmospheric temperature and pressure profiles on the BrO standard AMFs for different tropopause heights (6 to 18 km, see Figure 5.4). Displayed is the ratio of the AMFs calculated for several selected radio sonde data and the BrO standard AMF.

5.2.1.4 Influence of the atmospheric ozone profile

As already shown in Figure 5.2 and 5.3 the atmospheric ozone profile varies systematically for different locations and seasons. In particular under ozone hole conditions the profiles are additionally deformed due to photochemical ozone destruction (see Figure 2.12). Thus the influence of such variations on the BrO standard AMF was studied. In Figure 5.10 two 'extreme' O_3 profiles are displayed together with the O_3 profile used for the calculation of the BrO standard AMFs. Despite the large discrepancies between these profiles the respective AMF changes only negligible (see Figure 5.11.).

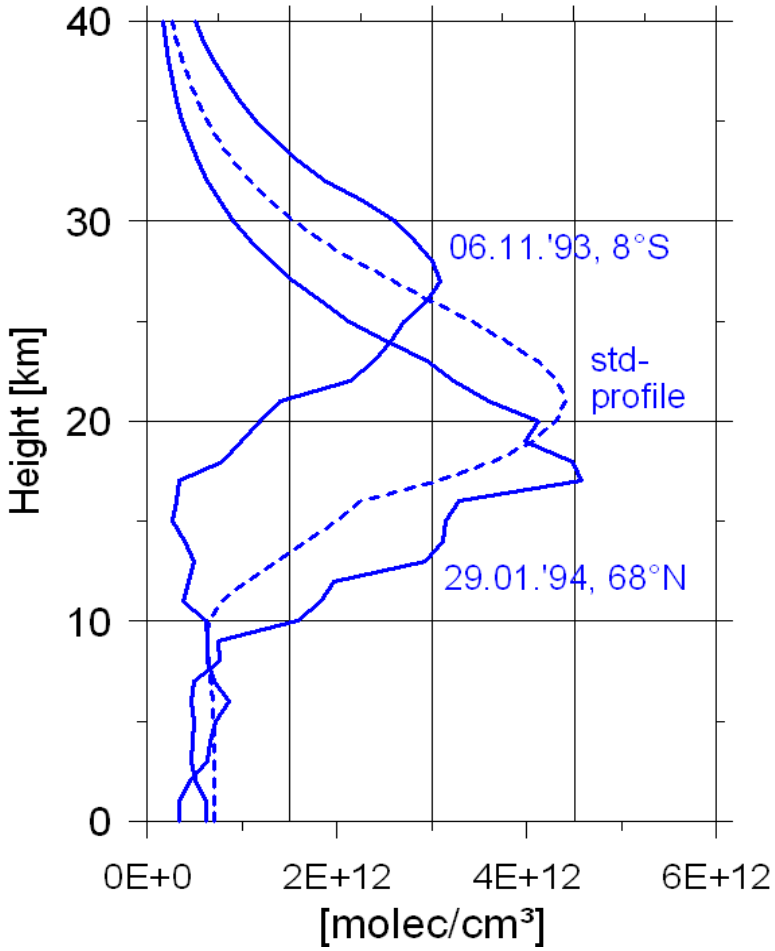


Figure 5.10 Selected 'extreme' ozone profiles as well as the profile used for the calculation of the BrO standard AMFs.

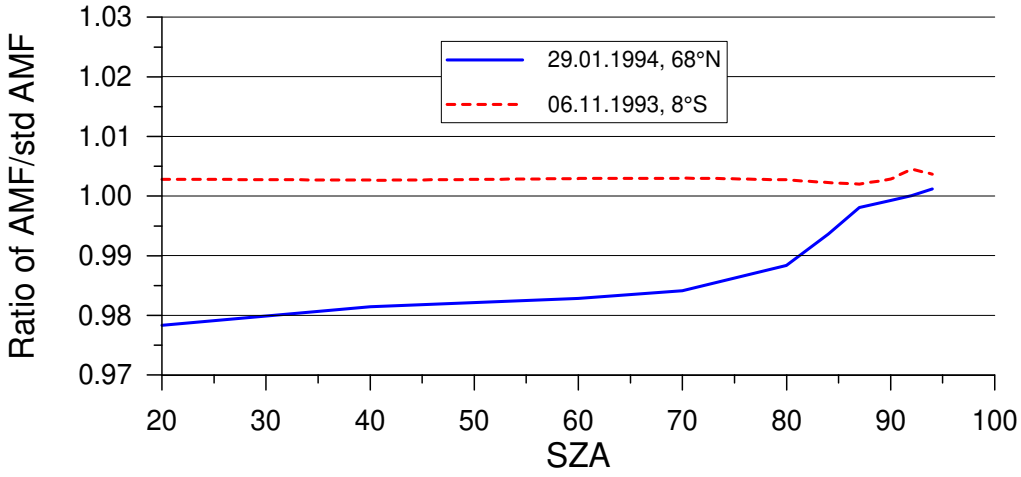


Figure 5.11 Influence of variations of the atmospheric ozone profile on the BrO standard AMF for a tropopause height of 10 km. Displayed is the ratio of the AMFs calculated for the selected radio sonde data and the BrO standard AMF.

5.2.1.5 The uncertainty of the air mass factor

Based on the sensitivity studies above it can be concluded that for SZA below 90° the stratospheric 'standard' BrO AMFs can be calculated with an accuracy of about 10% if the height of the BrO profile is known (see Table 5.2). Without this knowledge the uncertainty of the BrO AMF increases strongly for SZA above 80°, up to more than 100 % (see Figure 5.5). On the other hand we find that for SZA below 78° the height of the BrO profile has only negligible influence on the AMF.

	uncertainty of the AMF [%]		
parameter	SZA = 20°	SZA = 80°	SZA = 90°
ground albedo	6	5	4
aerosol extinction	6	6	6
Temperature & pressure	1	4	3
O_3 profile	2	2	1
Total	9	9	8

Table 5.2 Summary of the uncertainties of the standard BrO AMF with respect to variations of different measurement parameters as described above. The total uncertainty is calculated by square addition of the different contributions.

5.2.2 Air mass factors for tropospheric BrO

AMFs for stratospheric absorbers can be approximately described by the geometrical path enhancement according to the sun's position (see Equation 5.2 and Figure 5.1). In consequence it depends strongly on the SZA. Due to the increased air pressure and the enhanced aerosol load near the surface, multiple scattering plays an important role for the radiative transport in the troposphere. In consequence tropospheric AMFs are smaller than stratospheric AMFs and in particular they depend much less on the SZA than stratospheric ones (Figure 5.12).

Compared to AMFs for stratospheric species the AMFs for tropospheric trace gases can only be calculated with much less accuracy. This is caused by the following reasons:
a) Clouds strongly affect the radiative transport through the troposphere (see also section 5.2.3). On the one hand they (at least partly) hide the view of the satellite down to the atmosphere below the cloud layer. On the other hand they can also enhance the absorption path due to multiple scattering [Erle et al., 1995; Pfeilsticker et al., 1998; Wagner et al., 1998d,e].
b) The influence of the ground albedo on the AMF increases if the measured species are located closer to the Earth's surface.
c) Aerosols can widely vary in the troposphere. This includes both the composition and size distribution.
To investigate these dependencies more quantitatively similar sensitivity studies as for the stratospheric AMFs were performed (Figure 5.13). In contrast to the stratospheric AMFs the AMFs for tropospheric species are much more sensitive to variations in the measurement conditions. Without detailed information about the ground albedo and the aerosol atmospheric load the uncertainties are within a factor 3 to 4.

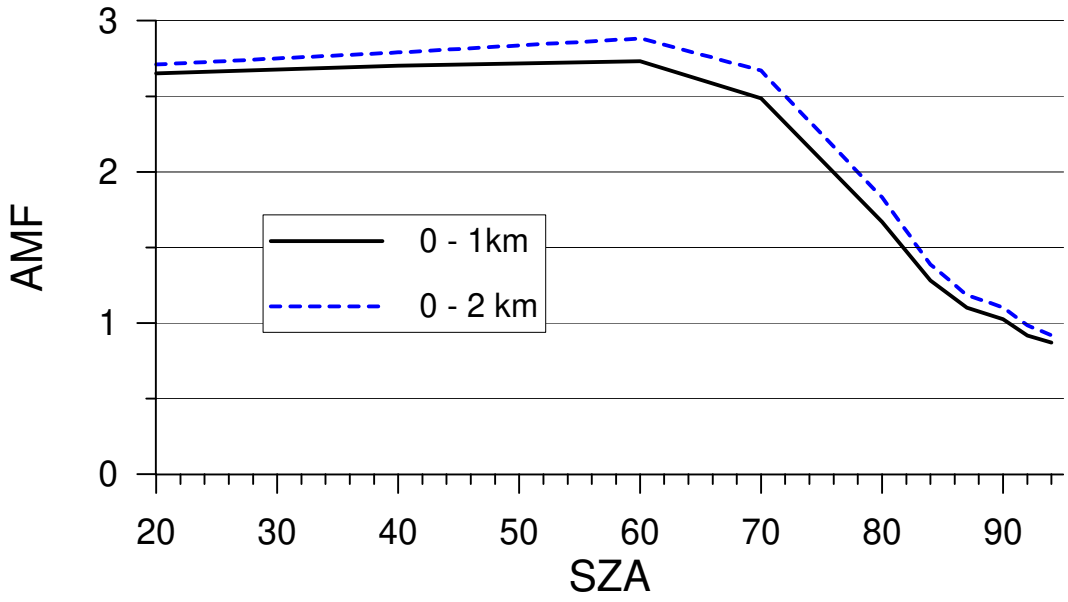


Figure 5.12 AMF for tropospheric profiles (box profiles from the surface to 1 and 2 km). The aerosol extinction profile used for the stratospheric standard BrO AMF (LOWTRAN) was used; the ground albedo was set to 0.8.

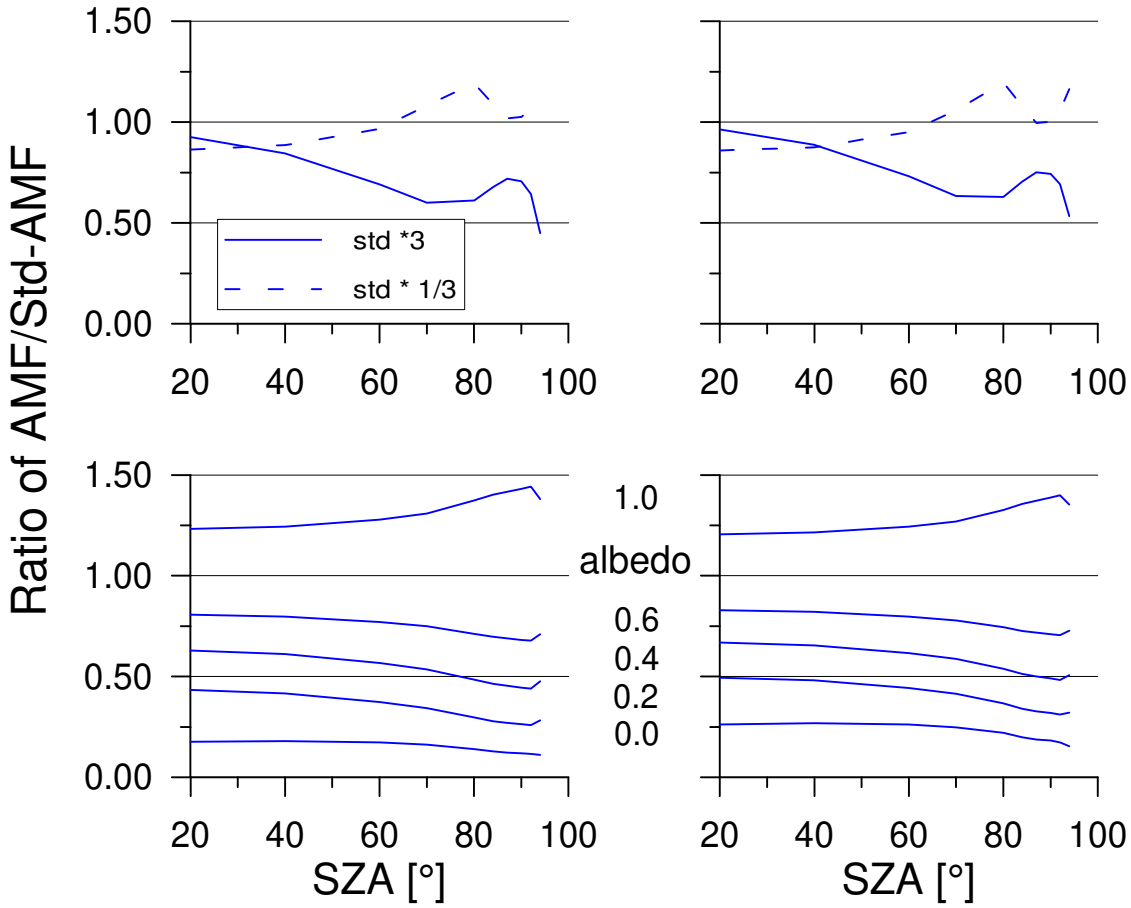


Figure 5.13 Influence of variations in the atmospheric aerosol profile (top) and the ground albedo (bottom) on tropospheric AMFs. Left: AMF for a constant trace gas concentration between the surface and 1 km. Right: AMF for a constant trace gas concentration between the surface and 2 km. Displayed is the ratio of the AMFs calculated for different aerosol profiles and ground albedos with the AMF for the standard conditions (LOWTRAN aerosol profile, ground albedo: 0.8).

5.2.3 Air mass factors for stratospheric OClO

Due to the strong diurnal variation of the stratospheric OClO concentration the conversion of OClO SCDs into VCDs is not appropriate for most applications (see Otten et al., [1998]). However, for comparison studies with OClO profiles from balloons GOME OClO VCDs are required. For that purpose AMFs for stratospheric OClO were calculated (Figure 5.14) assuming a concentration profile with Gaussian shape (height of the maximum: 18 km, full width of half maximum: 8 km).

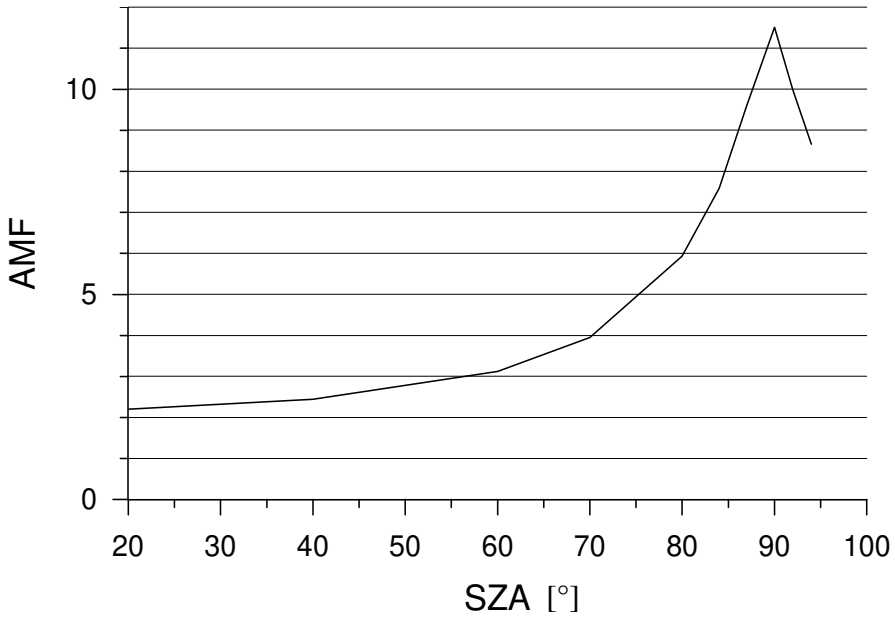


Figure 5.14 AMFs for stratospheric OClO. They are calculated for an OClO concentration profile with Gaussian shape (height of the maximum: 18 km, full width of half maximum: 8 km).

5.3 Influence of clouds on the air mass factors for ground based and satellite measurements

For ground based observations clouds can affect both AMFs for tropospheric and stratospheric absorbers. Tropospheric AMFs can be enhanced due to multiple scattering inside the clouds but can also be decreased by the change of the slant tropospheric absorption path into a vertical one below the cloud (Figure 5.15) [Erle et al., 1995; Wagner et al., 1998e; Pfeilsticker et al., 1998]. For ground based instruments also stratospheric AMFs can be affected because clouds make the instrument more sensitive for scattered light traversing the stratosphere compared to direct sun light [Wagner et al., 1998d].
For satellite observation the situation differs because of two major reasons (see Figure 5.15):
a) First because the observed light is not only scattered by molecules and aerosol particles but also reflected on the earth's surface which can be seen as a Lambertian reflecting surface. Thus for a given SZA a satellite instrument (in contrast to a ground based instrument) is sensitive for light which has penetrated the atmosphere under any arbitrary zenith and azimuth angle.
b) Second the light detected by the instrument has not necessarily penetrated the whole atmosphere, e.g. when a ground pixel is totally covered by clouds.

5.3.1 Influence on satellite air mass factors for stratospheric species

Based on point a) in section 5.3 it follows that the satellite AMF for stratospheric species is expected not to change when clouds appear [Wagner et al., 1998d]. Only for large zenith angles small changes might occur because then the change of the scattering height due to clouds is no more negligible [Pfeilsticker et al., 1998]. However these changes are small, in particular compared to the uncertainties in the AMF calculations caused by the lack of information about the

specific conditions of the measurements (see above). In summary we can conclude that for SZA below 90° the influence of clouds on the satellite AMFs for stratospheric species is negligible.

5.3.2 Influence on satellite air mass factor for tropospheric species

Based on point b) in section 5.3 it follows that (in contrast to ground based measurements) the satellite AMF for tropospheric species can be smaller than unity. In particular for clouds hiding the satellite's view to the atmosphere below the cloud the tropospheric AMF (for species below the cloud) can be close to zero. Although there can also occur a light path enhancement due to multiple scattering inside the clouds. However, this effect is of much less important for reflected light compared to light transmitted through the cloud [Pfeilsticker et al., 1998].

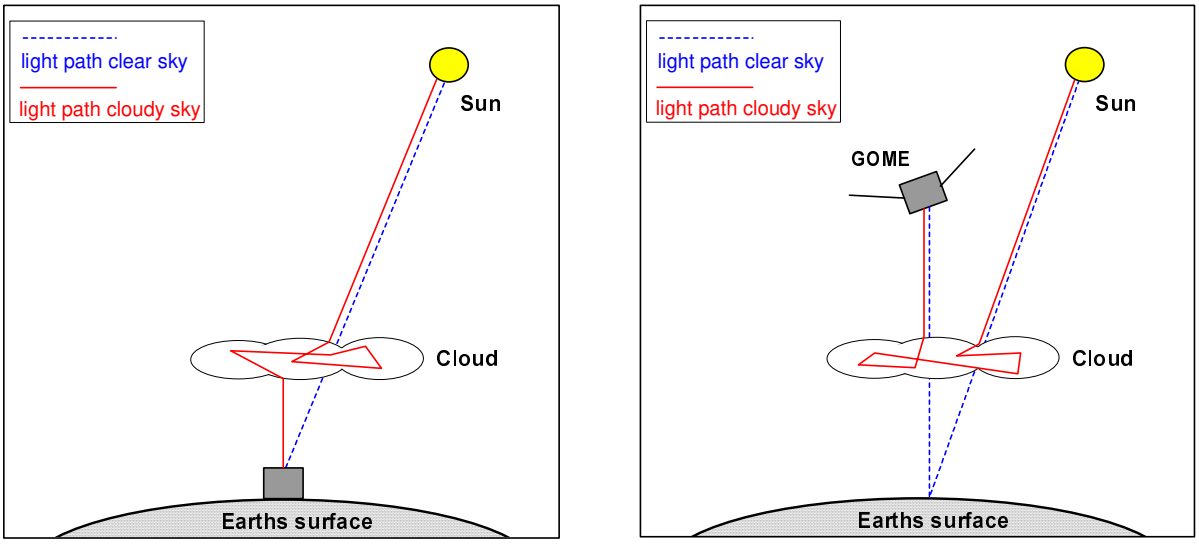


Figure 5.16 Modification of the absorption paths for ground based (left) and satellite (right) geometry in the presence of clouds.

Thus in summary we can conclude that clouds typically decrease the satellite AMF for tropospheric species. While on first sight this cloud influence might be seen as a restriction of the sensitivity of the satellite instrument to tropospheric species there also arise several advantages which will be in particular applied to the interpretation of the results of this study:

a) Determination of cloud properties. Since clouds affect the radiative transport through the atmosphere it is possible to derive information about the properties of clouds from satellite measurements of tropospheric species [Wagner et al., 1998c; Bösch, 1998]. For that purpose in particular the measurement of O_2 or the oxygen dimer O_4 are well suited because their atmospheric concentrations vary only slightly (with air pressure and temperature); thus changes of the measured atmospheric absorptions can almost exclusively be attributed to changes of the radiative transport (e.g. due to clouds). If a homogeneous cloud cover is present it is possible to determine the cloud height from the measured absorption decrease of O_2 and O_4 compared to clear sky conditions. Furthermore, since O_2 and O_4 have different atmospheric concentration profiles the combined measurement of both species can provide additional information, e.g. about a light path

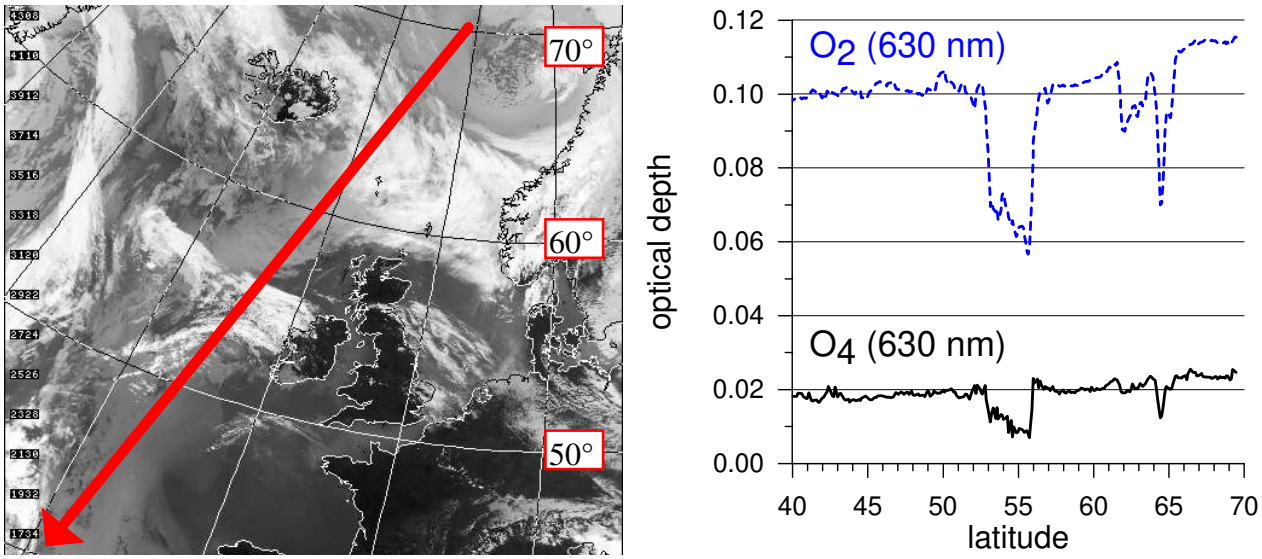
enhancement due to multiple scattering inside the cloud [Wagner et al., 1998e]. However, it should be noted that the typical size of a GOME ground pixel is quite large (320 x 40 km²) and except for very rare cases the cloud cover is not homogeneous across the entire ground pixels. Thus the above considerations could not directly be applied to a GOME measurement without taking into account the horizontal pattern of the cloud cover (see section 5.3.3). But in any case, when e.g. the absorptions of O_2 and O_4 are significantly lower compared to clear sky it can be concluded that the ground pixel is at least partly covered with clouds (see Figure 5.17). This relation can be used to indicate the presence of clouds from the absorption measurements of the GOME instrument itself.

It should be noted that there already exists a variety of algorithms for the detection of clouds from GOME data; most of them are based on the modelling of the measured intensities around the oxygen-A-band at 762 nm (ICFA [Kuze and Chance, 1994]). One fundamental difficulty of these techniques is having to distinguish between areas with high ground albedo and/or the presence of clouds. In Figure 5.18 it is shown that even for a very strong change in the ground albedo from 0.05 to 0.8 (as e.g. found at the edge of Antarctica) the AMF for the O_4 absorption at 630 nm is only weakly affected whereas the measured intensity changes by a factor of about 10.

The use of the O_4 absorption for the detection of clouds has two further advantages:

First, O_4 shows weak broad band absorptions where no saturation effects have to be taken into account (this is unlike e.g. H_2O or O_2 which show very strong, narrow absorption lines which cannot be resolved with the GOME instrument; thus for the measurement of these species saturation effects have to be corrected for.).

Second due to the square dependence of the O_4 concentration from the O_2 concentration the main bulk of atmospheric O_4 is located very low down in the troposphere (with a scale height of about 4 km). Thus even relatively low clouds significantly affect the absorption of O_4.



Satellite picture: 16.07. 1996, 13:40

GOME overpass: 16.07. 1996, 11:50

Figure 5.17 Influence of clouds on the absorption of species which are mainly located in the troposphere like O_2 and the oxygen dimer O_4. On the satellite image [Dundee, 1999] the GOME flight track for which the respective O_2 and O_4 absorptions are shown, is displayed in the right plot. It is obvious that the absorptions of both species are significantly decreased when clouds are in the field of view.

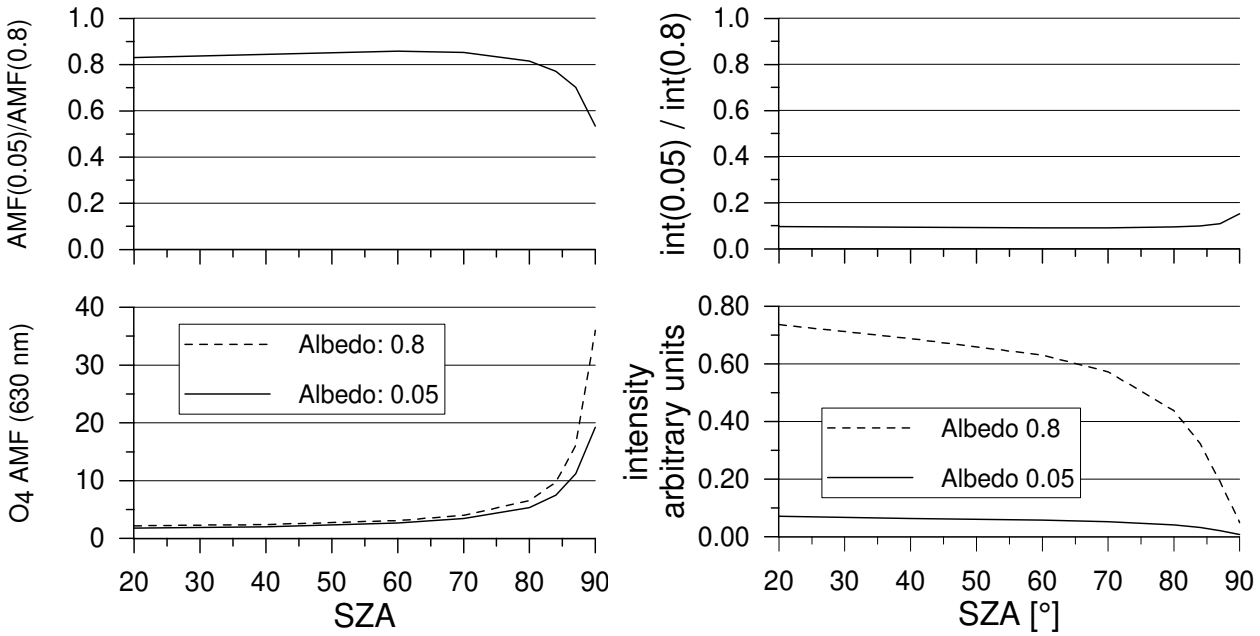


Figure 5.18 Influence of the ground albedo on the O_4 AMF at 630 nm (left) and the intensity (right). The influence on the measured intensity is about a factor of 10 while on the O_4 AMF it is only about 10%.

b) From GOME NADIR observations it has been possible to determine profile information only for ozone which is the dominant absorbing species over a wide range of the UV/vis spectrum [Hoogen et al., 1998, 1999; Eichmann et al., 1998]. For other weaker absorbing species it has not been possible yet (and won't probably be possible in the future) to derive similar highly resolved atmospheric profiles. Nevertheless, for many research aspects it is of major importance to know where the measured absorptions have taken place; especially whether they have occurred in the stratosphere or the troposphere. The influence of clouds on tropopsheric absorber now provides a very convenient tool to decide whether an absorption has taken place in the troposphere. Since clouds hide the absorption of species below the cloud layer, one must expect a decrease of the respective absorption if and only if this species is located in the troposphere. In the previous section it was shown that the absorption of O_4 can be used as a very sensitive indicator for clouds (Figure 5.17). Thus, in order to clarify whether a species is located in the troposphere one can directly study the correlation of the absorptions of O_4 and of the species of interest (see sections 6.3 and 6.4).

5.3.3 Broken cloudiness across one ground pixel, sensitivity of GOME measurements for tropospheric species.

The above considerations are strictly valid for a homogeneous cloud cover across a GOME ground pixel. In contrast, the 'normal' GOME ground pixel which covers a large area (40 x 320 km²) is usually partly covered with clouds. In consequence, the absorptions in almost each GOME measurement have tropospheric contributions. However, it is rather difficult to quantify the sensitivity of GOME to tropospheric absorptions. While this is in principle possible it strongly depends on the quality and the availability of information about clouds. In the following it is

discussed how critically the sensitivity of GOME observations of tropospheric species depends on these parameters.
The light measured almost in all GOME spectra is the sum of different contributions:

a) light reflected from the earth's surface.
b) light scattered back by molecules and aerosols.
c) light scattered back from the clouds within the ground pixel, which can be located at different altitudes and can be of different composition.
In principle, several parameters such as the cloud fraction, the cloud height, and the ground albedo have to be known if the sensitivity of GOME measurements to tropospheric species should be determined.
Several algorithms exist [Kuze and Chance, 1994; Bösch, 1998; Wenig, 1998] for the determination of the cloud fraction of a GOME pixel, that is the ratio of the pixel area covered by clouds and the total area. However, these algorithms are partly based on assumptions on missing atmospheric parameters (as e.g. cloud height or ground albedo) and the derived cloud fractions still have relatively large uncertainties, in particular at large SZA and at situations with changing ground albedo. But even if the actual cloud cover of a GOME observation is known (e.g. from such a cloud algorithm), the sensitivity of this measurement to tropospheric species cannot be derived taking into account only the cloud fraction. At least additional information about the average cloud height and the ground albedo is necessary:

a) Albedo: Information about the average ground albedo for the cloud free area of the ground pixel and the average albedo of the cloud surface is needed because the detected light is the sum of the cloud free and cloudy areas weighted with their respective albedos. In particular the albedo of the surface can vary over a wide range, especially at the border between land and ocean. How strong the sensitivity of a given GOME observation depends on the ground albedo is illustrated by the following example:
I) Assuming that a ground pixel has a cloud fraction of 50% an albedo of the cloud surface of 1 and an albedo of the surface (ocean) of 0.05, the sensitivity of the measurement to species below the cloud cover is only about 5% compared to the cloud free case.
II) If instead an albedo of the surface of 0.8 (snow) is assumed, the sensitivity is about 45%, about ten times higher than in the first example.
It should be noted that this albedo effect is further increased by the dependence of the tropospheric AMF on the ground albedo (see section 5.3).
This strong dependence of the tropospheric sensitivity on the ground albedo in the presence of clouds is a strong restriction for the quantitative measurement of tropospheric species. However, for the observations studied in this thesis (BrO concentrations in the boundary layer of polar regions) the high ground albedo diminishes the influence of clouds on the measurements of tropopsheric species. In fact, as can be seen in sections 6.3 and 6.4, only very seldom can the pattern of clouds be recognised in the maps of tropospheric BrO.

b) Cloud height: For the correct interpretation of a GOME measurement with respect to its tropospheric contributions the average height of the cloud cover and the height profile of the species of interest must also be known. As two extreme examples we can assume that thin clouds (or fog) are either located near the tropopause or near the ground. In the first case almost the complete tropospheric contribution of the tropospheric absorber will be suppressed, in the second case almost all will be measured.

It should be noted that in some rare cases the sensitivity to tropospheric species might also be increased by 'thick' clouds at low altitudes, when multiple Mie scattering inside the clouds enhances the tropospheric absorption path. However, while for ground based measurements this effect often leads to an enhancement of the sensitivity to tropospheric species, for satellite measurements generally the shielding effect dominates [Erle et al., 1995; Wagner et al., 1998c, e; Pfeilsticker et al., 1998].

5.3.4 Conclusions

We calculated AMFs for satellite observations of light which is reflected by the Earth's surface or scattered from the atmosphere. It was found that the accuracy of these calculations is limited by the uncertainty of the atmospheric parameters or the ground albedo rather than the accuracy of the model itself.
The uncertainties of the calculated AMFs are different for the different species and depend also strongly on their location in the atmosphere. In general, the uncertainties for stratospheric AMFs were found to be smaller than for tropospheric AMFs. The uncertainties of the tropospheric AMFs depend mainly on the knowledge about the ground albedo and the cloud cover, those of the stratospheric AMFs mainly on the knowledge of the atmospheric profiles of the measured species and the aerosol extinction. The errors for different scenarios are summarised in Table 5.3.

Species, location	relative uncertainty of the AMF if the atmospheric profile of the species is known within ±1 km and the ground albedo within ±0.05.	relative uncertainty of the AMF if the atmospheric profile of the species is known within ±3 km, but the ground albedo is unknown.	relative uncertainty of the AMF without knowledge about the cloud cover
Stratospheric BrO	10%	up to about 30%	a few %
Stratospheric OClO	10%	up to about 30%	a few %
Boundary layer BrO	≈30%	more than 100%	more than 100%

Table 5.3 Summary of the uncertainties in the AMFs for different measurements conditions.

Concerning the influence of clouds we can state that in principle it can be corrected for if the cloud parameters are known, which is, however, in general not the case. But even with the knowledge of the cloud parameters the interpretation of satellite measurements with respect to tropospheric species is very complex (see section 5.3).
In contrast, as has been proposed in section 5.3 and will be demonstrated in sections 6.3 and 6.4 the measurement of O_4 provides a very simple but powerful method to directly assess the sensitivity of a GOME measurement with respect to tropospheric species.