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Ozone and NO_2 air-mass factors for zenith-sky spectrometers: Intercomparison of calculations with different radiative transfer models

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Abstract. Calculations of air-mass factors (AMFs) for ground-based zenith-sky UV-visible spectrometers are now well developed in laboratories where stratospheric constituents are measured with this technique. An intercomparison between results from the different radiative transfer models used to calculate AMFs at twilight is presented here. The comparison was made for ozone AMFs at 510 nm and for NO_2 AMFs at 440 nm. Vertical profiles were specified. Results are presented firstly for calculations in a pure Rayleigh atmosphere, then including background aerosols. Relative differences between calculated AMFs from different models cause relative errors in vertical columns of ozone and NO_2 measured by zenith-sky spectrometers. For commonly used averages over solar zenith angles, these relative errors are ±2.3% in the vertical column of ozone and ±1.1% in the vertical column of NO_2. Refinements to the calculations, suggested by the intercomparison, should reduce these errors to ±1.0% for ozone and ±0.5% for NO_2.

Introduction

Several stratospheric constituents important in ozone depletion are routinely measured by ground-based zenith-sky UV-visible spectrometers. The line-of-sight amounts observed during twilight by spectrometers are interpreted using air-mass factors (AMFs): the AMF of a constituent is the ratio between the amount of the constituent in the line-of-sight of the observation and the amount in a vertical column. AMFs of ozone and NO_2 in the visible are a maximum at twilight, justifying observation during this time.

AMFs are calculated by radiative transfer models. Although AMFs were calculated in the past [Noxon et al., 1979], the work of Solomon et al. [1987], the recent deployment of UV-visible spectrometers such as SAOZ (Système d'Analyse par Observations Zénithales) [Pommereau and Goutail, 1988] in SCUVS (Stratospheric Climatology Using UV-visible Spectroscopy) and the NDSC (Network for the Detection of Stratospheric Change) have given AMFs and their calculations a high priority. Since 1990, at least 5 laboratories have developed new models, with original schemes of computation. It is important that there are no trends induced in the results of zenith-sky spectrometers because of time- or atmosphere-dependent artefacts in AMFs. Furthermore, computations made by different radiative transfer models should agree as closely as possible to reduce bias between sets of data.

The goal of this paper is to enlarge our knowledge of some of the possible errors in calculated AMFs by making a comparison between existing models. Section 2 presents an overview of existing radiative transfer models developed at several laboratories, using single or multiple scattering schemes. Section 3 presents vertical profiles used for the intercomparison. Section 4 presents the results of the intercomparison which are discussed in section 5.

This paper does not address the question of the absolute accuracy of calculation of AMFs. This can only be done by comparing results of measurements of vertical columns by UV-visible zenith-sky spectrometers with measurements by independent techniques. For the formulation of the AMF and for a wider discussion about sources of errors in calculation (including vertical profiles, absorption and scattering cross-sections), see Sarkissian et al. [1995].

Existing Models and Participants in the Intercomparison

To reproduce zenith-sky observations from the ground, models must make radiative transfer calculations, simulating the source (the Sun) and calculating optical paths in the atmosphere. Sunlight is absorbed and scattered as it traverses the atmosphere. Models have to calculate geometrical paths, absorption, extinction and scattering, and must integrate fluxes coming from different altitudes and directions. Differences between models can arise from (i) the scheme used in the path calculation, (ii) constituents and parameters included in the calcu-lation of optical thickness, and (iii) the scheme used to integrate the field of view if the model is more than two-dimensional.

Although some details differ, the basic scheme used for geometrical path calculation in spherical geometry is the same for all models in the intercomparison, and adopts that of Solomon et al. [1987]. Table 1 lists some laboratories where AMF calculations have been made since 1987 and the computation scheme used by each. Briefly, the different schemes are:

- single scattering model (called standard here) using ray tracing in a spherical 2-D atmosphere [Solomon et al., 1987] ;
- Monte Carlo model, which traces rays backward from a source at the ground and where photons are scattered randomly until they leave the atmosphere or are absorbed;
- Discrete Ordinate, from the radiative transfer equation solved by Chandrasekhar for parallel layers, corrected for a spherical atmosphere;
- Numerical Integration method, which follows the standard

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Table 1. A summary of more recent radiative transfer models used for calculation of air-mass factor.

Laboratory	Model	References	Orders
NOAA (USA)	Standard	Solomon et al. [1987]	1
SA (France)	Standard (SAOZ)	Sarkissian [1992]	1
INTA (Spain)	Standard	Gil and Cacho [1992]	1
UH (Germany)	Standard	Fiedler et al [1993]	1
IASB (Belgium)	Standard	Not published	1
UCAM (UK)	Standard	Not published	1
LOA (France)	Standard	Not published	1
NOAA (USA)	Monte Carlo	Perliski [1992]	All
LOA (France)	Monte Carlo	Lenoble and Chen [1993]	All
NILU (Norway)	Discrete Ordinate	Dahlback et al. [1994]	All
BAS (UK)	Numerical Integration	Sarkissian et al. [1995]	2

scheme with an extension to the 3-D atmosphere and the second order of scattering.

When there is no publication for the model, table 1 includes the nearest reference (results of observations, presentation of the instrument). SA results are supplied to SAOZ users for routine analysis. The list is not exhaustive. Note that model BAS is a significant technical and schematic advance on the SA model from which it grew [Sarkissian, 1992].

Vertical Profiles

A first attempt at an intercomparison of ozone AMFs used different vertical profiles of constituents and air density, reflecting the prejudice of each group. The results were not quite as chaotic as we might now expect with hindsight: the spread was 6% between 86° and 91° SZA and increased at higher SZA to reach 35% at 94°. The conclusion was that the identification of differences between calculations was not easy without specification of vertical profiles.

For the intercomparison proper, input profiles of constituents were specified, chosen from some in frequent use by the community. Figure 1 shows the atmospheric density from Handbook of Geophysics [1965] corresponding to subarctic winter, and the Mie extinction coefficient at 450 nm by background aerosol. The Rayleigh scattering cross-section and phase function were not specified. The Mie background aerosol extinction coefficient comes from the Handbook of Geophysics [1965] in the troposphere and from SAGE II (Stratospheric Aerosol and Gas Experiment on Nimbus 7) satellite observations in April 1988 at 65°N for the stratosphere (low content of aerosol after years without volcanic eruption). The Mie scattering coefficient at 90° is

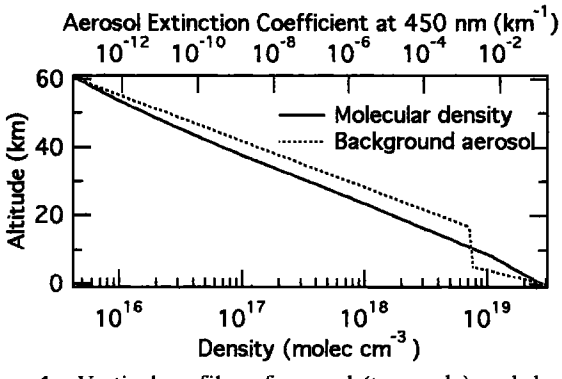

Figure1. Vertical profiles of aerosol (top scale) and density (bottom scale) used for the intercomparison.

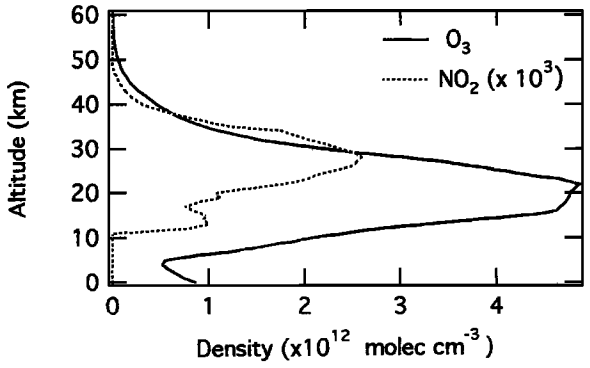

Figure 2. Vertical profiles of O3 and NO2 used for the intercomparison.

specified to be the extinction coefficient divided by 40. This corresponds to a Henyey-Greenstein phase function with an asymmetry factor g = 0.6715. In some models the angular dependence is neglected. The Mie extinction coefficient is specified to be inversely proportional to the wavelength.

Figure 2 shows the specified ozone profile from the Handbook of Geophysics [1965], and specified NO2 profile from balloon-borne solar occultation measurements from 10 to 22 km and from SAGE II above, both at 44° N in September 1986 [Cunnold et al., 1991]. Absorption cross-sections of ozone and NO2 were not specified.

Results of the Intercomparison

Geometrical parameters (thickness of the layers, sphericity of the atmosphere, etc.) were not specified, although all profiles are given from 0 to 60 km at 1 km intervals, limiting the top of the atmosphere to 60 km.

Calculations were requested at solar zenith angles (SZAs) of 86°, 88°, 90°, 92° and 94°, and at single wavelengths of 440

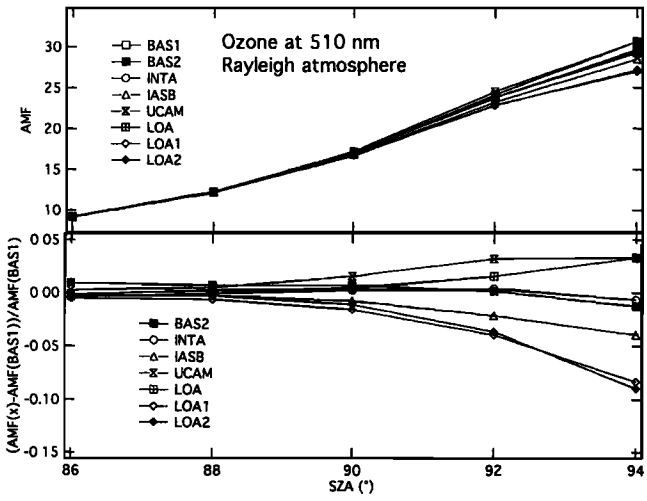

Figure 3. Results of the intercomparison of AMF for O3 at 510 nm in a pure Rayleigh atmosphere with specified profiles of atmospheric, O3 and NO2 densities. Upper figure, the AMFs. Lower figure, their relative differences from BAS1. Calculations with more than one scattering event are shown with full symbols. The numbers at the end of the name of the laboratories indicate that the same model is used for calculations with both a single (1) and more than one (2) scattering event allowed. LOA calculations are made by a standard model. LOA1 calculations are made with Monte-Carlo code but allowing one scattering only.

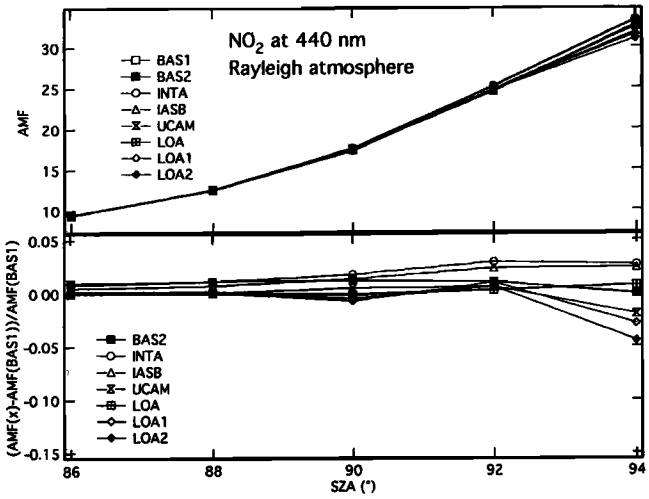

Figure 4. As Fig 3, but for NO2 at 440 nm.

nm for NO_2 and 510 nm for O_3. Separate calculations were requested with a pure Rayleigh atmosphere and with added background aerosol.

AMFs calculated for ozone in an aerosol-free atmosphere are presented in figure 3. The lower panel shows the relative difference from one of the calculations, chosen arbitrarily. The numbers at the end of the name of the laboratories indicate that the same model is used for calculations with both a single (1) and more than one (2) scattering event allowed.

At low SZA (86° to 90°), the maximum spread of the calculations is small, < 4%. At high SZA (92° to 94°), the spread increases to 13%. Differences between BAS1 and BAS2 or between LOA1 and LOA2 are due to including multiple scattering. These differences are small (<1%) for both models. Models IASB, INTA, UCAM, LOA and BAS1 are all standard, with nominally the same scheme, but the spread in the results at 94° is 10%. The difference between LOA1 and BAS1 illustrates the difference between Monte-Carlo and standard schemes, both with single scattering. This difference is small, less than 1% from 86° to 90°, 5% at 92° and 9% at 94° SZA; it is of the same order as the spread between the different standard models.

Figure 4 shows results for NO_2, which are similar in character to those for ozone. The spread is 7% at high SZA. From 86° to 92° SZA, the effect of including multiple scattering is small (<1%) rising to 2% for LOA2 versus LOA1 at 94° SZA. At low SZA (86° to 90°), the spread of standard calculations is small (<1°). At high SZA, spread increases to 5%. The difference between Monte-Carlo single scattering and standard schemes is <1% from 86° to 92° SZA rising to 3% at 94°.

Figure 5 shows the relative difference between calculations of ozone AMF made by the same model with and without background aerosol. AMFs decrease upon introducing background aerosol. They differ in the size of the decrease which can reach 15% at 94° SZA. The spread rises from 3% at 86° to 8% at 94° SZA. The spread due to including multiple scattering is <1% at SZA ≤ 90° and rises to 3% at 94° SZA.

Sensitivity of NO_2 AMFs to background aerosol are shown in figure 6. No systematic effect due to background aerosol can be observed. The amplitude of the spread is similar to the one previously observed in the aerosol-free atmosphere. At low SZA (86° to 90°), the spread is 1%. At high SZA, some (UCAM, BAS1, IASB and LOA) models are barely affected (less than 2%) by background aerosol, INTA increases by 3% at 92° SZA, and LOA1 decreases by 3% at 94° SZA.

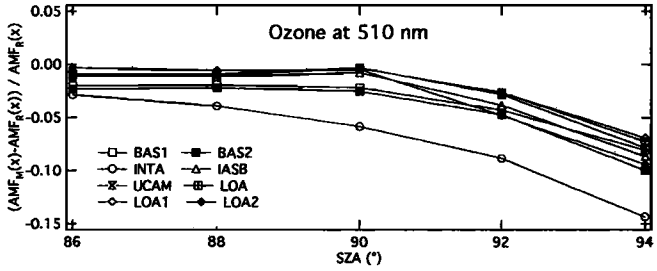

Figure 5. Relative effect of background aerosol on AMF of O3 at 510 nm. The subscript M refers to calculations with both Mie (aerosol) and Rayleigh (molecular) scattering, the subscript R to calculations with Rayleigh scattering only.

Discussion

In the intercomparison of ozone AMF, the spread of the results decreased from 6% to 1% at 86° SZA and from 35% to 13% at 94° SZA when vertical profiles were specified. This emphasises the well-known conclusion [e.g. Syed and Harrison, 1980] that vertical profiles are some of the dominant parameters in AMF calculations (as well as the less obvious point that research groups will not choose identical profiles even when there are standard profiles in the literature).

However, even after specifying profiles, the remaining differences between models show that other parameters in models cannot be neglected. Sarkissian et al. [1995] evaluate the effects of computational parameters on ozone AMF with the BAS1 model. Amongst other influences on AMF, they show that: (i) the common approximation of calculating AMFs by intensity weighting instead of from the ratio of fluxes with and without absorber decreases AMF by 1% at 90° and 4% at 94° SZA; (ii) optical thickness of each atmospheric shell calculated using the value interpolated to the centre instead of the value at the bottom of the shell increases AMF by 2% at 94° SZA; and (iii) a systematic underestimation by x% of the geometrical path decreases the AMF by the same value at all SZA.

BAS1, INTA, IASB, LOA and UCAM are all standard models. The spread of their results is due to differences in calculation parameters: IASB and LOA use the intensity-weighted approximation; LOA, BAS1 and INTA use values of densities at the bottom of the shells; UCAM makes an analytic integration of the optical thickness inside those shells which are not homogeneous. Hence the spread in AMF of 2% at SZA≤90° between the five standard models arises from systematic differences in geometrical path calculations in individual shells.

Amongst other smaller influences on NO_2 AMF, calculations with BAS1 show that: (i) optical thickness of each atmospheric shell calculated using the value interpolated to the centre instead of the value at the bottom of the shell increases AMF by 2% at 94° SZA; and (ii) a systematic

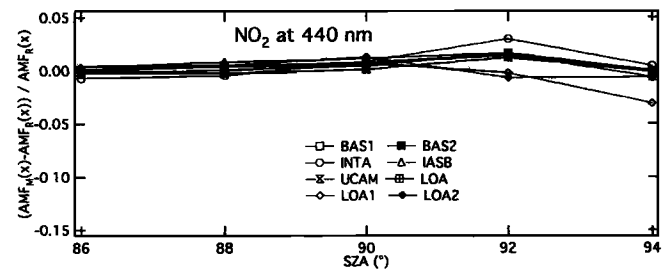

Figure 6. As Fig 5, but for NO2 at 440 nm.

underestimation by x% of the geometrical path decreases the AMF by the same proportion x% at all SZA. Hence the spread of 4% of NO_2 AMF at 94° SZA for the standard models arises from differences in optical path calculations; and the spread of 1% at SZA ≤90° arises from systematic differences in geometrical path calculations in individual shells. Note that removing ozone to calculate NO_2 AMF as done by INTA (only one absorber at a time in the model) does not affect the results.

Introduction of background aerosol affects all computations by a decrease of the ozone AMF at all SZA. The mean change is a decrease of 2% from 86° to 90° and of 10% at 94° SZA. The spread of the results increases from 4% at 86° to 8% at 94° SZA. This is due to differences in optical path calculation in individual shells, because the scale height of background aerosol is 2 to 3 km, very small compared to that of density (7 to 8 km). A value taken at the centre of the shell, instead of the bottom as in BAS1, increases the AMF by 2% at SZA<90° and by 10% at 94° SZA [Sarkissian et al., 1995]. To achieve better accuracy in future calculations, optical paths in individual shells must be integrated.

The effect of background aerosol on NO_2 AMF is small: the mean value is near 0 at all SZA. That is because NO_2 is located at higher altitudes where background aerosols have a smaller extinction and smaller scattering. The spread in results is due to differences in computational parameters as in the case of an aerosol-free atmosphere.

The differences between BAS2 and BAS1, or LOA2 and LOA1 are within the spread of models, pointing to a small influence of multiple scattering both for a molecular atmosphere and for background aerosol.

Conclusion

This intercomparison allowed us to identify the sources of differences between calculations by different models of air-mass factors of ozone and NO_2. When vertical profiles are specified, the spread of the results is 1% at 86° and 13% at 94° SZA for ozone and 1% at 86° and 8% at 94° SZA for NO_2. These differences are due to differences in computational parameters and schemes of radiative transfer model. Some of the lessons for future work are: intensity-weighted AMF and homogeneous shell approximations must be avoided; optical paths have to be integrated in individual shells; background aerosols cannot be neglected ; and including multiple scattering has a small effect on calculations of ozone and NO_2 AMFs, as long as there is no volcanic perturbation or polar stratospheric aerosol [Lenoble and Chen, 1993].

Most workers have calculated vertical amounts of ozone and NO_2 by averaging observations from 85° to 92° SZA [Noxon et al., 1979; Sarkissian, 1992; Fiedler et al., 1993]. Supposing four observations during twilight (86°, 88°, 90° and 92°), the rms scatter from the mean of the values at each angle averaged over the range of angles is the equivalent error due to differences in models, provided they are correlated at different SZA as the figures show them to be. (If they were uncorrelated, they would be divided by the square roots of the number of angles.). The error due to major differences in the type of model is ±1% for ozone and ±0.3% for NO_2. The error due to the computational scheme is ±2% for ozone and ±1% for NO_2. We believe that these computational errors would be reduced by making accurate computations of optical thicknesses in individual shells. The uncertainty due to including multiple scattering or not is ±0.2% for ozone and ±0.4% for NO_2.

Hence total relative errors are ±2.3% for ozone and ±1.1% for NO_2. These errors are comparable with the errors of ±2.4% made when using one set of AMFs for climatological ozone measurements for all seasons and locations varying ozone and air density profiles; these are smaller than the errors due to extreme volcanic aerosol (-14%) or to extreme polar stratospheric clouds (-5.4%) [Sarkissian et al., 1995]. If the problems due to interpolation and other differences in computation scheme can be solved, the remaining relative errors are ±1.0% for ozone and ±0.5% for NO_2. These relative errors are determined without discussion of the absolute accuracy of the AMF.

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