

The manuscript provides an approach to calculate the so called air mass factors (AMFs), quantities that in applications of Differential Optical Absorption Spectroscopy (DOAS) relate slant column densities (SCDs), obtained from fit on measured spectra, with their vertical column densities VCDs. The presented approach accounts for horizontal inhomogeneity of stratospheric trace gases (O_3 , NO_2 , BrO and OCIO) as they are simulated by a photochemical model at polar conditions at high solar zenith angles. The authors also present the calculated AMFs in a systematic way investigating in particular their spectral and temporal variability as function of SZA. Further the simulated SCDs are compared with simulated SCDs to prove the concept.

General comments:

I find the manuscript is generally well written, and especially the systematic investigation of the AMFs makes it recommendable for the publication.

Nevertheless I find the presented two step approach (1 – averaging by a single scattering model, 2 – calculation by a 1D resolved model) to account for the horizontal inhomogeneity as a kind of workaround which I think do not correspond to the state-of-the-art RTM capabilities available today. There are Monte Carlo models generally allowing horizontal variability in their parameter input and/or 2D or 3D box AMFs output. Even analytical models like SCIATRAN have reported to allow for horizontal photochemical correction. Was it too big effort to enable the 2D/3D capabilities of MYSTIC?

Further I find that the treatment of horizontal variability might be presented better. What is the horizontal resolution in AURA and also in the 2D-DISTRORT, how the variability along the light paths while within a single horizontal layer is accounted for?

Last but not least, in the introduction a lot of emphasis is made on discussing whether AMFs of different trace gases have been explicitly published. What is missing before is a presenting that the concept of AMFs is well established (and also) applied for decades (with some important references, e.g. Perliski and Solomon, 1993; Wagner et al., 2007).

Detailed comments:

Abstract, L24-25: "Vertical profile concentrations obtained by this model are averaged over the optical paths and used as an input for the MYSTIC RTM"

You should shortly introduce here the concept of averaging (so the reader don't think here about a simple averaging) and also make clear that you use the 1D version of MYSTIC in your approach.

Introduction, L41: $dSCD = SCD + SCD_{ref}$

Correct is $dSCD = SCD - SCD_{ref}$. Please use Equation formatting (also for other instances in the following text)

L49: During twilight, SCDs provide information on stratospheric trace gases

SCDs contain information on trace gases whose volume where crossed by the light reaching the instrument (not just in the stratosphere but also there and also on other times of the day, not just twilight). Perhaps you can just skip this sentence or reformulate that during twilight zenith sky measurements are mostly sensitive to stratospheric trace gases.

L:49: , SCDs are dependent on the viewing geometry.

SCDs depend on both viewing and Sun geometry

L51: Vertical Columns Densities (VCDs), which only depend on the atmosphere and the geometry of the sun

In contrast to SCDs, VCDs by definition don't depend on the geometry of the Sun, they are just integral of the number density along altitude.

L51: The variable relating both quantities is the Air Mass Factor (AMF = SCD/VCD by definition)

You should provide references here, e.g. Perliski and Solomon, 1993. You should also link the proper optical definition of AMF presented therein, i.e. $AMF = -\ln(I/I_0)/(\sigma \text{ VCD})$ with the effective light path definition you are using. You should also make the reader aware that the application of the last is limited to trace gases with weak absorbers but would e.g. be problematic e.g. for ozone in short wave UV (which you don't cover).

L52: AMFs are computed using...

-> AMFs are usually computed using... (keep in mind that e.g. so called geometrical AMFs exist, where no RTMs are used, there are the Langley plot method)

L54: Since 2012,...

Start a new paragraph.

L77: To our knowledge, the only publication showing OCIO AMFs for SZA up to 95° is Pinardi et al. [2023]

This is in contradiction to the statement in L81-82.

L82: However, the specific OCIO concentration profiles are not shown.

In fact Kühl et al. [2004] do provide the Gaussian profiles they have used by stating their height of maximum and full width at half maximum. As only the shape for weak absorbers is necessary to calculate AMFs, all necessary information is given. Please correct.

L85-L89: As you don't introduce the sections in their natural order, I would suggest to reformulate the sentence "Photochemistry taking place during...", so that it starts with e.g. "Before that...Sect. 2.1..."

Sect.2, L98 (1)...

In this paragraph a reference to Sect. 2.1 is missing mentioning that the stacked model is run on the output of the 3-D CTM simulations

Fig.1.: abbreviations AURA, SS, OP are not introduced; amf -> AMF

L129: $VCD_{\{total_ph\}}$

What is this quantity? It is used, not defined in Eq. (6), so the reference is misleading. Is the difference between VCD_{total} defined in Eq. (3) that VCD_{total_ph} is calculated from the VCDs at the SZA above the station while Eq.3. uses the 'averaged' quantities? Please make it more clear.

L169: AURA

Abbreviation not introduced.

L170: *which means that only one profile for each target species can be introduced in the model for the whole atmosphere*

Better: *which means that only one horizontally homogeneous vertical profile for each target species can be introduced in the model*

L172: *we validate a method*

We introduce a method

L186: Eq. 7 and the description before/after, Fig.3

From the presentation it is not clear how the horizontal variability is accounted for. From Eq. 7 it can be concluded that there 1, 2 or 3 different concentration values are taken when a layer is crossed 1, 2 or 3 times, respectively. It is not described also what concentration is taken (e.g. at SZA which is observed by a beam when it crosses the middle of the layer or something else). If this is so, is it accurate enough? Shouldn't the path be separated in finer horizontal sectors? Close to tangent the horizontal extension through the layer seems significant. Have you performed sensitivity studies regarding this?

L191: $S_{\{b,l\}}$ is not introduced in the text

L199 $S_{\{l\}}$ is not introduced in the text

L215: *In that case, the mean concentration is calculated between the concentration at the top of the layer and at the minimum altitude reached by the beam at that layer.*

This is indeed confusing. At what SZA(s) the concentration is taken for the top and for what at the minimum. It is also not said at all how it is done for the 'regular cases' (see the comment above).

L222-L224 *the scattered intensity at the surface is higher in the visible than in the UV.*

The relative scale of x-axis possibly doesn't allow this conclusion. Or e.g. 0.01 scale to same absolute radiance for UV and VIS?

L224 *more UV radiation is available above the station at those altitudes.*

This cannot be true. Due to the wavelength dependence of Rayleigh scattering there is a higher chance for direct VIS light to reach any point (at any altitude) in the atmosphere than for UV light.

L247 onwards.

I don't quite understand the study done here regarding AURA in 1D and 2D modes. Can you please explain what is the difference between AURA in 1D mode (I get from the text that it is the application of AURA calculating the SCDs with the averaged profiles incl. Eq. 12)? But what is then AURA in 2D mode?

L262 clouds or complex surface topography are out of the scope of this work

Nevertheless you should add to the discussion later and the conclusion the possible importance and systematic consequences of these omissions, especially of the clouds

L263 An assessment of cloud effect can be found in e.g. Pukite et al. (2022)

The assessment in Pukite et al. (2022) was on 2D effects taking into consideration polar stratospheric clouds (PSCs), not the (tropospheric) clouds.

L269 ... aerosols have a low influence.

PSCs are not rare at your observation locations. The introduced sensitivity test in the next lines with the bulk of aerosol in the troposphere (scale height 1km, exponential decay), not stratosphere, doesn't cover possible PSC effects and even so the stratospheric aerosol (Junge) layer.

L272 . The solar spectrum of Kurucz [1992] is set as the solar source in our simulations.

Is this relevant information? Is this in anyway affect the AMF calculation? I suppose this can be skipped.

L293: The presented results and Fig. 7 don't indicate wavelengths of the simulations.

L296 onwards. I think it would be more fair to compare the differences on the basis of a daily to day variability. But even given your study on the 10-day averages if one naively multiplies the provided differences with $10^{0.5}$ one gets large uncertainties not just for OCIO. Obviously this limits the overall application. Can you comment?

L321: OCIO in 345-389 nm [Pinardi et al., 2022].

Perhaps this should be moved before "with updated" in the previous line.

L330: perhaps provide some references from the use of NDACC by the scientific community

L331: data available from the literature

You should cite these data

L332: 2D-DISORT vs DISORT mentioned earlier. What is the difference? Make a clear distinction.

L353: outputs of the photochemical model described in Section 2.1, specific for 2018, considering a region of 2.8° around the station, are used directly

Is horizontal inhomogeneity (just) for the region of 2.8 deg around the station considered? At high SZAs the light paths are crossing a region beyond this interval. At SZA 90 deg the distance of light path between the scattering point at e.g. 15 km and altitude 25 km towards Sun is ~360 km (~3.2 deg), exceeding this interval. At SZA above 90 deg, the light paths are even much longer. How the

concentration at distances beyond this 2.8 deg are treated (set to a constant, set to zero, something else)? And how is the horizontal variability within this interval considered? Linearly? In steps? How large are the resolution of the steps? Or 2.8 deg is rather the model output resolution. But this seems to be rather coarse being of the same order of magnitude than the length of the horizontal paths. But also if the last is the case, how the small scale variability is prescribed in your models (linearly, in steps, or by some other approximation)?

L358: what -> this

L368: *7% for sunrise and 18% for sunset*

Can you say a word why the differences are different between sunrise and sunset? Different profile shapes, different horizontal distribution?

L372: *due in this case to the strong decrease of the BrO concentration beyond 90° SZA.*->

due to the strong decrease of the BrO concentration beyond 90° SZA in this case.

L380: *When photochemistry is not considered, the only factor changing with the SZA is the optical path that increases with the SZA. However, when photochemistry is considered, not only does the optical path change but also the vertical profile of the species.*

I think one should split the impact of the photochemical effect in two aspects (1) the effect on the profile shape as $f(\text{SZA})$: this will affect AMFs as function of SZA even if horizontally homogeneous 1D profiles are used in RTM. (2) the effect of the photochemistry on the horizontal distribution: this will have effect on every RTM simulation at any single SZA.

L388: ...calculated for the SZA over the station... -> calculated assuming horizontally homogeneous concentration profiles for the SZA over the station

L431: 2.55×10^{11} molec/cm² for OCIO

The detection limit for OCIO is 3 orders of magnitude larger...

L434: std -> standard deviation of modelled values`?

Fig.11. Perhaps it would be good to include in the plots also SCDs simulated with the photochemically not-corrected AMFs?

L452: 1.3×10^{13} molec/cm³ in the lower 5 km

Given this concentration $\text{VCD}_{\text{troposph}} = 1.3 \times 10^{13} \times 5 \times 10^5 = 6.5 \times 10^{18}$ molec/cm².

Something is wrong here. Prados-Roman et al. 2025 also presents tropospheric BrO being confined below 2km with VCD of $\sim 6.5 \times 10^{12}$ molec./cm² (Fig. 6 therein) for MAR in September while the offset in SCDs (between with and without tropospheric contribution) for the case of albedo being zero in Fig. 12 is $\sim 3 \times 10^{13}$. Given that you are looking into zenith, this must pretty much match the assumed tropospheric VCD. Please clarify these discrepancies. And perhaps it would be helpful if the BrO profiles (as function of SZA) can be plotted as well.

L460 onwards.

Regarding resolution one should distinguish between 3 resolution factors:

- 1) the chemical model resolution (2.8x2.8)
- 2) the resolution of the 1D chemical model in terms of SZA output which you then apply spatially in AURA
- 3) the horizontal extension and resolution of RTM (both AURA and 2D-DISORT)

L478: *different SZAs encountered*

-> trace gas concentrations encountered at the different SZAs

L491 for photo reactive species as the considered in this work

-> for the photo active species considered in this work

L494 You should mention that the aspect of stratospheric dynamics was not the scope of this study and requires further investigation.

L500: In general, for all four species, a good agreement is found within one sigma standard deviation. This confirms the validity of the method employed and the approximations considered.

This conclusion either implies or prerequisites a good agreement between the chemical model and the actual observations. Is this given?