

REPLY TO RC1

The authors would like to thank the Referee for his/her insightful comments, the constructive evaluation of our manuscript and the time dedicated to reviewing our manuscript. We appreciate the positive feedback regarding the clarity of the writing and the systematic investigation of the Air Mass Factors (AMFs), which the Referee found recommendable for publication.

The Referee's comments have been very helpful in identifying areas where our description of the methodology—specifically regarding the treatment of horizontal inhomogeneity and the integration of the chemical model with the Radiative Transfer Models (RTMs)—needed further clarification or refinement. We have addressed each of the general and detailed comments below (in blue, following the Referee's comments in black).

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 (O₃, NO₂, 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 (GC):

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

GC.1: 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?

We thank the Referee for this observation. It is true that 3D Monte Carlo (MC) models and analytical models like SCIATRAN offer advanced horizontal variability capabilities. However, we chose this two-step approach for the following reasons:

1. While MYSTIC is a powerful tool, our study aimed to perform a systematic investigation of AMF variability across a wide range of SZAs, species, and temporal scales. The cost of running a full 3D model under twilight conditions would have been prohibitive. Using the 1D version of MYSTIC in conjunction with our photochemical averaging allowed us to maintain high vertical resolution while keeping the computational cost manageable for the large number of simulations required for this systematic survey. So the solution we adopted is a trade-off between complexity and efficiency

2. Unlike a standard 3D RTM where horizontal boxes might be coarse, our "Step 1" (AURA) explicitly calculates the concentrations encountered along the actual light paths at high SZAs. By

"pre-averaging" these path-dependent concentrations before they enter the 1D RTM, we effectively "fold" the 2D photochemical morphology into the radiative transfer calculation. This ensures that the AMF reflects the true chemical environment the photons traverse without the geometric complexities and "noise" often associated with high-SZA Monte Carlo simulations in 3D mode.

3. In addition, 3D version of MYSTIC is not publicly available. We tested a MC RTM (1D-MYSTIC) that is freely and thus easily available for all the community (libRadtran free software package).

We have updated the manuscript (L 264) to explicitly state points 1 and 2:

"... Using the 1D-MYSTIC version allowed us to maintain high vertical resolution while keeping the computational cost manageable for the large number of simulations required for this work"

GC.2: 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-DISORT, how the variability along the light paths while within a single horizontal layer is accounted for?

The horizontal resolution in AURA and 2D-DISORT depends on the SZA. The considered atmosphere is divided in layers 1 km thick, with the top of the atmosphere at 65 km (L175 of the original manuscript). The distance that a given solar beam travels in a given layer depends on the "local" SZA. In Fig. 3c, for instance, the referee can see that the partial optical paths, and the corresponding horizontal distance, are different even for the same beam.

The considered concentration of a given layer for a given solar beam, each time the beam crosses this layer, is the mean value between: the concentration at the top of the layer and the "local" SZA at this point (θ_2 for op_1 in Fig. 3c, for instance), and the concentration at the bottom of the layer for the "local" SZA at this point (θ_1 for op_1 in Fig. 3c). This is true except if one beam does not reach the bottom of the layer (as optical path between op_1 and op_2 in Fig. 3c). In that case, the mean is performed for the values at the top of the layer and the minimum altitude reached (SZA=90°).

Finally, to take into account all the partial optical paths for a given layer and a given solar beam, the concentration is calculated as explained in L189-190 and eq. (8). Following the example of Fig. 3c, if c_1 is the mean concentration for op_1 , c_2 is the mean concentration of op_2 and c_3 is the mean concentration for $op_3 = dz$, the concentration c' that we finally consider is:

$$(c_1 * op_1) + (c_2 * op_2) + (c_3 * dz) = c' * (op_1 + op_2 + dz)$$

And c' can be expressed as in eq. 9. Please, see answer for question DT.18.

GC.3: 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).

We thank the referee for this observation. We have now included these important references and introduce the robustness and usefulness of the AMF concept:

“AMFs are a robust and well established metric used for decades in many works (e.g. Perliski and Solomon, 1993; Wagner et al., 2007)”

Detailed comments (DT):

DT.1: *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.

The text has been modified as follows (L25-28):

“Vertical profile concentrations obtained by this model are “averaged” over the optical paths. This means that, for each SZA observed at the station, a vertical concentration equivalent to all the concentrations encountered by the solar beams in different parts of the atmosphere is calculated. This is done by considering the different “local” SZAs and the partial optical paths in each layer. These concentration profiles, representative of a complete two-dimensional atmosphere, are then used as input for the one-dimensional version of MYSTIC RTM.”

DT.2: *Introduction, L41: $dSCD = SCD + SCD_{ref}$*

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

We thank the referee for pointing out this error. It has been corrected.

DT.3: *L49: During twilight, SCDs provide information on stratospheric trace gases*

SCDs contain information on trace gases whose volume were 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.

We reformulated the sentence as follows:

“During twilight, measured SCDs are mostly sensitive to the stratospheric trace gases”

DT.4: *L:49: , SCDs are dependent on the viewing geometry.*

SCDs depend on both viewing and Sun geometry

This has been corrected in the text.

DT.5: *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.

This is correct but for photochemical species the vertical distribution of the number density also changes with the SZA. However, we agree that the way that it was presented in the text could be confusing. We have changed the text as follows:

“...Vertical Columns Densities (VCDs), which only depend on the concentration vertical profile of the considered molecule.”

DT.6: 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. $AMF = -\ln(I/I_0)/(\sigma \cdot VCD)$ 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).

The manuscript has been modified introducing the following text:

“..The variable relating both quantities is the Air Mass Factor (AMF=SCD/VCD by definition). Formally, this relates to the optical definition of the AMF as described by Perliski and Solomon (1993): $AMF = -\ln(I/I_0)/(\sigma \cdot VCD)$, where I and I_0 are the intensities with and without the absorber, respectively, and σ is the absorption cross-section. In this work, we use the “effective light path” definition, where the SCD is the concentration integrated over the optical path. It should be noted that the equivalence between these two definitions is strictly valid for weak absorbers, where the change in intensity due to absorption does not significantly alter the radiation field. While this approximation is appropriate for the species and spectral ranges investigated here, it could be problematic for strong absorbers, such as ozone in the short-wave UV.”

DT.7: 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)

This has been corrected.

DT.8: L54: *Since 2012,...*

Start a new paragraph.

This has been done.

DT.9: 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.

It is true. We have modified the text as follows:

“To our knowledge, the only publication providing explicit OCIO AMFs values for SZA up to 95° obtained from measurements is Pinardi et al. [2022]”

DT.10: 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.

The sentence has been deleted from the text.

DT.11: 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..."

We have re-formulated the paragraph as follows:

"In the present work, the stratospheric AMFs of NO₂, O₃, OCIO and BrO are estimated for Marambio and Belgrano stations, for SZAs up to 94°. Photochemistry taking place during twilight is considered using a photochemical box-model based on the SLIMCAT 3-D CTM (Section 2.1, [Denis et al., 2005; Chipperfield, 2006]). Optical path averages of the concentration profiles are calculated following the method described in Section 2.2. Then, the AMFs are obtained by using the Monte-Carlo MYSTIC Radiative Transfer Model (RTM) [Mayer, 2009; Emde et al., 2010] (Section 2.3)."

DT.12: 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

This has been done.

DT.13: Fig.1.: abbreviations AURA, SS, OP are not introduced; amf -> AMF

This has been done.

DT.14: 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.

$VCD_{\{total_ph\}}$ is the total vertical column obtained directly from the photochemical model, not averaged. It has been explained in the text:

"..for AMF_{total} , we use the $VCD_{(total_ph)}$ (eq. 6) calculated from the vertical profiles obtained with the 1-D photochemical model, i.e. calculated from the vertical profiles not averaged and just above the station."

DT.15: L169: AURA

Abbreviation not introduced.

Averaged concentration estimator Using Ray-tracing Approximation. It has now been introduced in the text.

DT.16: 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*

This has been corrected.

DT.17: L172: *we validate a method*

We introduce a method

This has been corrected.

DT.18: 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?

Following our response to the GC.2, all the partial optical paths, $s_{b,l,i}$, and the corresponding concentrations, $c_{b,l,i}$, for a given layer and a given solar beam have been taken into account. For each beam and layer we use $c_{b,l}'$ that is a weighted average of the "partial" concentrations $c_{b,l,i}$. The weight is the ratio of the partial optical paths, $s_{b,l,i}$, and the total optical path, $s_{b,l}$, for that beam in that layer: $s_{b,l}$ is the summation of all $s_{b,l,i}$.

In the example of Fig. 3c, if c_1 is the mean concentration for op_1 , c_2 is the mean concentration of op_2 and c_3 is the mean concentration for $op_3 = dz$, the concentration c' that we finally consider is:

$$\begin{aligned}c_{b,l,1} &= c_1, \quad c_{b,l,2} = c_2 \text{ and } c_{b,l,3} = c_3 \\s_{b,l,1} &= op_1, \quad s_{b,l,2} = op_2 \text{ and } s_{b,l,3} = dz \\s_{b,l} &= op_1 + op_2 + dz\end{aligned}$$

$$(c_1 * op_1) + (c_2 * op_2) + (c_3 * dz) = c' * (op_1 + op_2 + dz)$$

As explained before, the considered concentration in a given layer for a given solar beam, each time the beam crosses this layer, $c_{b,l,i}$, is the mean value between: the concentration at the top of the layer and the "local" SZA at this point (θ_2 for op_1 in Fig. 3c, for instance), and the concentration at the bottom of the layer for the "local" SZA at this point (θ_1 for op_1 in Fig. 3c). This is true except if one beam does not reach the bottom of the layer (as the optical path between op_1 and op_2 in Fig. 3c). In that case, the mean is performed for the values at the top of the layer and the minimum altitude reached (SZA=90°).

At the beginning of this study we performed some simple tests concerning the thickness of the vertical layers and we concluded that 1 km thickness was a good trade-off between accuracy and computation time. A deeper study concerning the thickness of the layer could indeed be interesting, however it is out of scope for this work. The good agreement with the measurements shows that the applied method is sufficiently accurate.

For better clarity, we have changed the text in this way:

"where subscript b is for each solar beam, l is for each layer, and i is for all the partial optical paths, $s_{b,l,i}$, and the corresponding concentrations, $c_{b,l,i}$, that each beam, b, finds when crossing the same layer, l, (red lines in Fig. 3: $s_{b,l,1} = op_1$, $s_{b,l,2} = op_2$, $s_{b,l,3} = dz$). l_b is the contribution of each beam to the total intensity, I_{tot} , measured at surface [Solomon et al., 1987]. To simplify this, we can consider a concentration, $c_{b,l}'$, that is an average of all the concentrations, $c_{b,l,i}$, that a given beam experiences when crossing each layer, weighted by the ratio between the corresponding

partial optical paths, $s_{b,l,i}$, and the total optical path for that given beam and that given layer, $s_{b,l}$, (in Fig. 3: $s_{b,l} = s_{b,l,1} + s_{b,l,2} + s_{b,l,3} = op_1 + op_2 + dz$):”

DT.19: L191: $S_{\{b,l\}}$ is not introduced in the text

It has been done now. See previous answer.

DT.20: L199 $S_{\{l\}}$ is not introduced in the text

It has been done now: “where $S_l = \sum_b s_{b,l}$ ”

DT.21: 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.*

Not exactly, it is a weighted average of all the partial optical paths found by this beam in this layer, as explained in the previous questions (GC.2 and DT.18).

DT.22: 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).

As explained before (GC.2 and DT.18), the top SZA is the SZA at the top of each partial optical path for this beam and this layer (θ_2 for op_1 in Fig. 3c, for instance), and the SZA at the bottom of the layer for that partial optical path (θ_1 for op_1 in Fig. 3c), except if one beam does not reach the bottom of the layer (as the optical path between op_1 and op_2 in Fig. 3c). In that case, the mean is performed for the values at the top of the layer and the minimum altitude reached (SZA=90°) by the beam.

DT.23: 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?

That sentence has been deleted.

DT.24: 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.

We thank the referee for noticing this. It was a mistake. That sentence has been deleted.

DT.25: 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?

AURA is also able to obtain the SCDs. AURA in 2D mode calculates SCDs considering different vertical profiles for different SZAs. AURA in 1D mode calculates SCDs considering the same (averaged) vertical profile for all SZAs. This has been introduced in the text for better clarity:

“AURA is also able to obtain the SCDs. AURA in 2-D mode calculates SCDs considering different vertical profiles for different SZAs, and AURA in 1-D mode calculates SCDs considering the same vertical profile for all SZAs. To check the validity...”

DT.26: 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

It is now mentioned in the conclusions.

DT.27: 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.

This has been corrected: *“An assessment of polar stratospheric clouds effect can be found in e.g. Pukite et al. (2022)”*

DT.28: 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.

That is correct. As mentioned before, investigating the influence of the PSCs is out of the scope of this work. However, as now stated in the conclusions, it would be interesting to study the influence of polar stratospheric clouds in a future work.

DT.29: 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.

It is not crucial information, but it is an extra data.

DT.30: L293: The presented results and Fig. 7 don't indicate wavelengths of the simulations.

The wavelengths of the simulations are indicated at the beginning of Section 2.

DT.31: 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?

This is true, but, as explained in the text, we limited the study to a 10-day average to avoid a large number calculations.

We have modified the last sentence of the paragraph in the text to explicitly quantify the factor by which the actual variability can be smoothed when you work with 10-days averages instead of a daily sampling ($10^{0.5} \approx 3.2$):

“However, taking into account that for individual measurements these differences are expected to increase by about a factor 3, for the study of specific episodes (a few days), daily sampling is recommended specially for OCIO”.

DT.32: L321: OCIO in 345-389 nm [Pinardi et al., 2022].

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

Updated cross-sections refer only to the BrO analysis. The sentence has been changed as follows:

“..BrO in 346-359 nm [Alliwell et al., 2002, with updated cross-sections: O3: Serdyuchenko et al, 2014; O4: Finkenzeller and Volkamer, 2002, OCIO: Kromminga et al, 2003], OCIO in 345-389 nm [Pinardi et al., 2022]”

DT.33: L330: perhaps provide some references from the use of NDACC by the scientific community

This has been done [e.g. Hendrick et al., 2011, Yela et al., 2017]

DT.34: L331: *data available from the literatura*

You should cite these data

This has been done.

DT.35: L332: 2D-DISORT vs DISORT mentioned earlier. What is the difference? Make a clear distinction.

2D DISORT calculates SCDs considering different vertical profiles for different local SZAs, and 1D DISORT calculates SCDs considering the same vertical profile for all local SZAs in one given observational geometry. The following sentence has been introduced:

“(2D refers to using different vertical profiles for different local SZAs in one given observational geometry)”.

DT.36: 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)?

The model's grid resolution is 2.8 degrees. In our calculations, we assume that the evolution of the vertical profiles of the species with respect to the solar zenith angle (SZA) at the stations is similar in all regions through which the solar rays reaching our stations pass. That is, we assume that the evolution of the profiles with respect to SZA is the same throughout the whole considered atmospheric region. This is, of course, an approximation, but taking into account the actual vertical profiles of each geographical location around our stations would be an enormous task. For a very precise calculation, it would also be necessary to consider changes in orography, albedo, etc., but this is beyond the scope of this work.

DT.37: L358: what -> this

This has been corrected.

DT.38: 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?

The evolution of the concentration profiles of photochemical species can be very different for sunrise and sunset, especially for high SZAs (see Fig. 10). In Pinardi et al. [2022] an empirical averaged (am-pm) value was provided, probably closer to the am profile observed in the present work. But, as was also pointed out in Figs 5 and 6 of Pinardi et al. [2022], variability of the AMFs is high, especially for large SZAs. The following text has been added to the manuscript:

“Note that the evolution of the concentration profiles of photochemical species can be very different for sunrise and sunset, especially for high SZAs (see Fig. 12)”.

DT.39: 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.

This has been corrected.

DT.40: 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.

To avoid disrupting the flow of the discussion, we have simply introduced the following sentence:

“However, when photochemistry is considered, not only does the optical path change but also the vertical profile of the species ((1): different profiles for different SZAs over the station, and (2) for each of these SZAs over the station, different profiles along the optical paths of the Sun beams).”

DT.41: L388: ...calculated for the SZA over the station... -> calculated assuming horizontally homogeneous concentration profiles for the SZA over the station

In fact, it is calculated with the photochemical model. The sentence in the text was confusing. We have changed it as follows:

“Thus, when the SZA increases, the SCD averaged over the optical path is lower than the SCD (obtained with the photochemical model) for the SZA just over the station for NO₂ and OCIO and higher for BrO”

DT.42: L431: 2.55×10^{11} molec/cm² for OCIO

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

Yes, it can be considered as 0: *“ 2.55×10^{11} molec/cm² (well below the detection limit of OCIO, thus it can be considered as null) for OCIO”*

DT.43: L434: std -> standard deviation of modelled values`?

For a given 10-days, the photochemical model provides 2 profiles per SZA per day (am and pm), i.e. 20 profiles for a whole 10-day period. The mean profile and its standard deviation for each 10-day period is calculated. In Fig. 11 the green dots represent the SCD obtained with the mean profiles, and the fine green lines, the SCDs obtained with the mean profile plus/minus the standard deviation of the profiles. We have included this in the caption of Fig. 11.

DT.44: Fig.11. Perhaps it would be good to include in the plots also SCDs simulated with the photochemically not-corrected AMFs?

It would be interesting, but the problem is that we perform the simulations with the concentration profiles provided by the photochemical model that already takes into account photochemistry. Thus, we cannot simulate them without photochemistry. Regardless, the purpose of this figure is to compare our simulations with actual measurements in order to validate our method. The comparison with not-corrected AMFs is already in figures 8 and 9.

DT.45: L452: 1.3×10^{13} molec/cm³ in the lower 5 km

Given this concentration $VCD_{troposph} = 1.3E13 * 5E5 = 6.5E18$ molec/cm².

Something is wrong here. Prados-Roman et al. 2025 also presents tropospheric BrO being confined below 2km with VCD of $\sim 6.5E12$ 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 $\sim 3E13$. 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.

It was a mistake. 1.3×10^{13} are molec./cm² It is the partial column up to 5 km. However, it is true that is a limit value. In order to be clear, we have now split Fig 12 in two figures:

In new Fig. 14, we show the BrO modelled values without tropospheric contribution.

In new Fig 15, we have now used the value shown in Prados-Roman et al. 2025 (Fig. 6; median and Q3 values from 2015 to 2023, SZA < 85°), i.e. $6.5E12$ molec./cm² (median) partial column up to 2 km. Left panel are am values, and right panel pm values. Shaded area corresponds to minimum (No tropospheric BrO) and maximum ($12.0E12$ molec./cm² partial column up to 2 km, Q3) tropospheric BrO observed at Marambio during September.

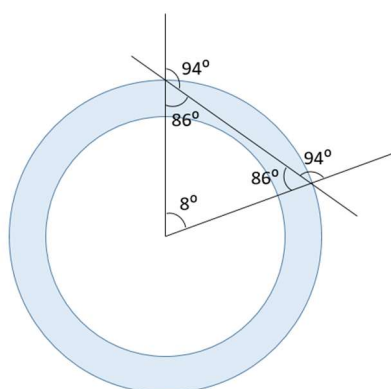
BrO profiles are shown in Fig. 10. The difference between those and the ones with the tropospheric BrO added, is just a layer 2km high, with the mentioned partial column values. We think that another figure will be redundant in part, and to include the tropospheric BrO in Figure 10 will make the figure difficult to understand.

DT.46: L460 onwards.

Regarding resolution one should distinguish between 3 resolution factors:

- 1) the chemical model resolution (2.8×2.8)
- 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)

AURA and 2D-DISORT used the concentration profiles provided by the photochemical model. Those profiles are representative of a region 2.8° width around the stations, but in AURA and DISORT they have been used as if they were representative of all the atmosphere. In our case, the highest SZA considered is 94° . That means that the largest distance from the station considered in our calculations is 8° (6° for SZA= 93° , 4° for SZA= 92° , etc.). Thus, even if most of the photons arriving to the station come from lower distances (less attenuated beams), in some cases, we used the profiles for large distances, representative of a region closer to the station. Thus, there are two limiting factors: the resolution of the photochemical model (2.8°) and the fact of using those profiles as representative of a larger region in AURA and DISORT.



Note: Of course, this figure does not represent reality because the Earth radius is much larger than the atmosphere width.

The text has been modified as follows:

“Additional possible sources of error for all modelled SCDs could be the estimation of the SCD in the reference spectrum. Moreover, we must consider the limited spatial resolution of the SLIMCAT 3-D chemical transport model simulation used ($2.8^\circ \times 2.8^\circ$). During active vortex

periods, this limited model resolution may complicate the comparison with observations, particularly in Marambio, which is highly affected by the dynamics of the polar volar edge. The photochemical model profiles are used as inputs of AURA and DISORT as if they were representative of the whole atmosphere. In the worst case, for SZA = 94°, we are considering regions up to 8° far from the station. Even if the solar beams arriving to the stations coming for such distances are the most attenuated, and so they contribute less to the modelled quantities, it must be kept in mind that this is also an approximation. A further detailed analysis of the differences found herein is beyond the scope of this work and will be subject of future studies.”

DT.47: L478: *different SZAs encountered*

-> trace gas concentrations encountered at the different SZAs

This has been corrected.

DT.48: L491 for photo reactive species as the considered in this work

-> for the photo active species considered in this work

This has been corrected.

DT.49: L494 You should mention that the aspect of stratospheric dynamics was not the scope of this study and requires further investigation.

We have mentioned it in the last paragraph of the conclusions:

“For future work, it would be interesting to also study the influence that clouds and/or orography may have on these kinds of calculation, as well as the stratospheric dynamics.”

DT.50: 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?

For NO₂, BrO and OCIO, the only observables we have are the DSCDs. We do not have direct information on the actual vertical profiles. However, the model has been widely used and validated.

We count with almost 2 decades of ozonesondes from Belgrano, but as it is shown in Fig 13. The agreement between modelled and measured SCD is very good, and the O₃ is the least “problematic” molecule as it stays stable during twilights.

REPLY TO RC2

We would like to thank the reviewer for his/her constructive comments and the time dedicated to reviewing our manuscript. We agree that the suggested changes, particularly regarding the readability of the text and the presentation of the figures, significantly improve the clarity of the study.

Below, we provide a point-by-point response to the specific comments. The reviewer's original comments are shown in black, and our responses are provided in blue:

The paper of Gomez-Martin et al. addresses the calculation of Air Mass Factors (AMFs) for ground-based zenith DOAS observations at twilight for two Antarctic stations. The subject is complicated in particular due to the need to account for the earth sphericity and photochemical variations of several of the measured species. The authors use the models SLIMCAT (CTM) to derive effective concentration profiles along the light path, and MYSTIC (RTM) to calculate corresponding AMFs. They then compare these calculations with DOAS measurements of NO₂, O₃, BrO, and OCIO, finding a good agreement except for BrO, which is explained by tropospheric contributions not considered in the model.

This study is important for the community, the method is new and robust and the results consistent so I have only minor comments on the content. However some work could be useful to improve the presentation before publication.

General Comments (GC):

GC.1: In several sections (2.2 and especially 4.1) the text should be split in paragraphs to make it digestible. For instance, when they introduce a new figure, it is normal to start a new paragraph. Same for a new line of reasoning.

We agree with this suggestion. The text in the aforementioned sections has been restructured into a larger number of paragraphs to improve the flow and logical separation of ideas.

GC.2: Carefully using a LLM could improve the text readability as several sentences are hard to read, with for instance the subject too far away from the verb. Exemples of complicated sentence which could be improved in my opinión:

For a nicer reading we have changed the sentences as follows:

L. 248 'To check the validity of these approximations, SCDs of the four target species obtained using AURA in 2-D mode and considering the photochemical model concentration profiles (different for each SZA), have been compared with the SCDs obtained with AURA in 1-D mode, using a single averaged concentration profile (eq. 12)'

"To check the validity of these approximations, a comparison between two sets of data has been performed: (1) the SCDs of the four target species obtained using AURA in 2-D mode and considering the photochemical model concentration profiles (different for each SZA), (2) SCDs obtained with AURA in 1-D mode, using a single averaged concentration profile (eq. 12) for the whole atmosphere"

L. 165 Thus, the concentration of a given gas in a given atmospheric layer encountered by the sunlight reaching an instrument at the surface, for SZA = θ (c ,), is actually an average of the concentrations corresponding to all values of the SZAs encountered by all the beams passing through this layer along their optical paths (see Fig. 3).

“Let ($c(l, \theta)$) be defined as the concentration of a specific gas observed by a ground-based instrument within an atmospheric layer and for a given SZA = θ . This concentration is represented as an average of the concentrations associated with all SZA values encountered by the various beams as they are passed through the layer along their respective optical paths (see Fig. 3).”

GC.3: Regarding the figures: the texts are often too small, especially in the legend. It's partly due to the fact that they are loaded.

We have increased the font size of all figure legends to ensure better legibility.

GC.4: Some of the figures could be split in two or more, e.g. figure 7 (we don't see the value for ozone AMF relative difference due to the scale defined by OCLO). In Figure 8, some material could go to the supplement. Do we need all the months in the main text?

The size of Figure 7 has been increased for better clarity.

Regarding Figure 8, we believe including all months is valuable as it illustrates the seasonal variations between them. We have noted that Figures 8 and 9 are the only ones displaying the full annual cycle, while others focus on specific months for clarity.

However, to facilitate visualization, we have split the previous Figures 8 and 9 into separate plots for visible and UV absorbing gases. Consequently, the original Figure 8 is now Figures 8 and 9, and the original Figure 9 has become Figures 10 and 11.

GC.5: Figure 5: There is nothing to see for 80° because the average profile perfectly matches the model. So showing 80° is not that useful. It would be interesting on the other hand to plot the ratio of the maximum average concentration with respect to the model, to see at which SZA the averaging starts to matter.

While the average does not change the profile appreciably at SZA = 80° , we agree it is useful to demonstrate at which point the averaging becomes significant. We have updated the figure to include profiles for SZA = 80° , 85° , 90° , and 94° to better illustrate this transition.

GC.6: AMF calculation: it would be useful for readability to have a table for the inputs and algorithms used in p. 15.

We have added Table 1 to the manuscript, which details the inputs and algorithms used in the AMF calculations.

GC.7: L 428 'Figure 10' seems to relate to figure 11. I missed where the true figure 10 was presented in the text.

We thank the reviewer for identifying this error. The numbering has been corrected, and Figure 10 (now Figure 12) is correctly cited in the text.

Specific Comments (SC):

SC.1: L.54 Since 2012, the ground-based DOAS community working on stratospheric research [e.g. Adams et al., 2012]. If it s the DOAS community, there should be one more than one paper to refer to?

We have updated the citations to better reflect the work of the community: [e.g., *Hendrick et al., 2011; Adams et al., 2012; Yela et al., 2017*]

SC.2: L 77 reads contradictory with L 81. Can you please explain or reformulate?

L. 77 'To our knowledge, the only publication showing OCIO AMFs for SZA up to 95° is Pinardi et al. [2023].'... "

L. 81 'Finally, in Kühl et al. [2004], OCIO AMFs are estimated with the AMFTRAN radiative transfer model [Marquard et al., 2000] for different Gaussian vertical profiles and for SZAs between 40 and 95.'

We have reformulated the sentence for clarity: "*To our knowledge, the only publication providing explicit OCIO AMFs values for SZA up to 95° obtained from measurements is Pinardi et al. [2022]*"

SC.3: Figure 1: SLIMCAT should be in the figure?

SLIMCAT has been added to Figure 1.

SC.4: L 130: I think a a_l is the box-AMF? but it s not explained in the text, could you add that in the text?

This is explicitly stated in the revised manuscript (L131): "*For each of those SZA above the station, box-AMFs (a_l) relate the optical path followed by sunlight at each atmospheric layer (ds_l) with the vertical layer thickness (dz_l)*"

SC.5: Equation (2) to (6) Do I understand correctly that this calculation is for one SZA at the station? If so, it would be pedagogical to explicitly state that VCDtotal_ph depends on this SZA.

We have explicitly stated in the text that calculations are performed for each SZA above the station (θ in Fig. 3). We have also modified the description to clarify that VCD_total_ph is calculated from vertical profiles not averaged and just above the station:

“we use the VCD_(total_ph) (eq. 6) calculated from the vertical profiles obtained with the 1-D photochemical model, i.e. calculated from the vertical profiles not averaged and just above the station.”

SC.6: L.151-152: 'In addition to gas phase chemistry ...' -> I assume you do not use this PSC module? If not, please indicate or remove this sentence, if yes, please give more details

Yes, the model uses the PSC module. It is essential for the long-term (decadal) 3-D model simulation that provides the output for the ground-based stations. The module is kept switched on for the 1-D diurnal photochemical sampling to avoid any spurious chemical trends (e.g. if an air parcel within the PSC regime of the 3D model suddenly appears to no longer contain PSCs). A reference for the model scheme and a sentence on the importance of including this chemistry has been added.

SC.7: L.162: 'The concentration ... representative for ... 2.8° -> In Chipperfield (2006), I read that the model grid is variable. So it s the model runs that you have that were calculated at 2.8°, not the model itself. If this it true, can you please reformulate?

The sentence has been reformulated:

“The concentration profiles used in this work and provided by the photochemical model are representative for a horizontal resolution of 2.8°”

SC.8: l.172 takes chemistry into account -> photochemistry would be clearer

This change has been made.

SC.9: L.177: 'single scattering is already a good approximation' -> can you be quantitative on that?

A detailed study is provided in Perliski and Solomon [1993]. While we do not provide a single numerical value, the differences between approximations are visually evident in Figures 2 and 3 of that reference.

SC.10: Figure 4 y label should be 'scattering altitude' for clarity

Since the scattered intensity (x-axis) is a function of altitude (y-axis), we believe that using "scattering altitude" might be redundant or confusing. We have elected to keep the current labelling.

SC.11: L.303 'daily or even more resolved sampling is recommended for OCIO' -> what would it mean, more resolved than daily? Two AMFs for the two twilights a day?

We agree that "more resolved than daily" is unclear in this context. We have revised the sentence to:

"However, taking into account that for individual measurements these differences are expected to increase, for the study of specific episodes (a few days), daily sampling is recommended especially for OCIO"

SC.12: L.460 'source of error for all modelled SCDs could be the estimation of the reference ' -> measured instead of modelled?

This correction has been made.