

# UV/Vis Stratospheric Air Mass Factors considering photochemistry at two Antarctic stations

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**Abstract.** The molecules NO<sub>2</sub>, O<sub>3</sub>, OCIO and BrO play a major role in the photochemistry of stratospheric ozone, notably in the formation of the springtime Antarctic ozone hole. For this reason, these species have been monitored by Differential Optical

15 Absorption Spectroscopy (DOAS) instrumentation for many decades. In order to transform DOAS Slant Column Densities (SCDs) into Vertical Column Densities (VCDs), independent of the viewing geometry, the Air Mass Factors (AMFs) relating these quantities are needed. Ground-based stratospheric trace gas measurements are performed in zenith-viewing geometry at twilight, around and beyond 90° solar zenith angle (SZA). At those solar angles, the Earth's sphericity and the rapid changes in photochemical parameters (e.g., photolysis rate coefficients) affect the calculation of the AMFs, particularly for

20 photochemically active species such as NO<sub>2</sub>, OCIO and BrO. This study presents a methodology to infer AMFs that account for sphericity and photochemical effects. We estimate stratospheric AMFs of NO<sub>2</sub>, O<sub>3</sub>, OCIO and BrO for Belgrano and Marambio Antarctic stations using the MYSTIC [Mayer, 2009; Emde et al., 2010] Radiative Transfer Model (RTM). The photochemical changes taking place during twilight are considered using a photochemical box-model based on the SLIMCAT chemistry transport model [Chipperfield et al., 1999, 2006]. Vertical profile concentrations obtained by this model are

25 "averaged" over the optical paths. That is, 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, taking into account 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. The robustness of the proposed methodology is tested against measurements of NO<sub>2</sub>, O<sub>3</sub>, OCIO and BrO SCDs obtained at Marambio and Belgrano.

30 A good agreement is observed between modelled and measured values of NO<sub>2</sub>, O<sub>3</sub> and OCIO SCDs. For BrO bigger differences are obtained but they have been attributed to the tropospheric BrO contribution that has not been included in the model. Our results show that monthly averaged AMFs can be considered as a good approximation for O<sub>3</sub> and BrO, but more temporally

resolved sampling is recommended for NO<sub>2</sub> and especially OCIO during July. This work shows the large impact of photochemistry for both the magnitude and also the SZA dependency of the evolution of the AMFs during twilight.

## 35 1 Introduction

Although evidence for a progressive recovery of the stratospheric ozone layer has been recently reported [WMO, 2025], the Antarctic ozone hole continues to form every year during austral spring [e.g. Solomon et al., 2014]. Therefore, long-term observations of ozone and related key stratospheric trace gases such as NO<sub>2</sub> [e.g. Crutzen 1979] and halogen compounds [e.g. Solomon et al., 1990; McElroy et al., 1986; Gil et al., 1992, Hendrick et al., 2007; Pinardi et al, 2022; Chong et al, 2024] remain essential. Ground-based observations performed with zenith viewing DOAS instruments [e.g., Yela et al., 2017, Yela et al., 2005] have allowed the accumulation of multi-decadal time-series of O<sub>3</sub>, NO<sub>2</sub>, BrO and OCIO columns. OCIO is formed from the reaction between BrO and ClO and can provide a good proxy for chlorine activation [Sander and Frieds, 1989].

Using the DOAS retrieval technique, differential Slant Column Densities (dSCDs) of gases absorbing in this UV-visible spectral region can be obtained:

$$dSCD = SCD - SCD_{ref}, \quad (1)$$

where  $SCD_{ref}$  refers to the chosen reference spectrum). SCDs represent the concentration of a given molecule integrated over the optical path of the sunlight through the atmosphere to the instrument. INTA has been operating UV-VIS DOAS spectrometers at the Belgrano (77°S) and Marambio (65°S) Antarctic stations since 1994 [Yela et al., 2017]. Since 2016, both stations are part of the Network for the Detection of Atmospheric Composition Change (NDACC, [www.ndacc.org](http://www.ndacc.org)), that aims to monitor the evolution of the atmospheric composition, evaluate the impact of the observed changes, provide valuable data for satellite validation, fill in satellite data gaps and test atmospheric models. Currently, this network is composed of more than 70 stations and 160 ground-based remote sensing instruments.

During twilight, measured SCDs are mostly sensitive to the stratospheric trace gases. However, SCDs are dependent on the viewing and Sun geometry. Thus, to compare measurements performed at different times or places, SCDs are usually transformed into corresponding Vertical Columns Densities (VCDs), which are the integral of the concentration vertical profile of the considered molecule along altitude. 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):

$$AMF = -\ln(I/I_0)/(\sigma \cdot VCD), \quad (2)$$

where  $I$  and  $I_0$  are the intensities with and without the absorber, respectively, and  $\sigma$  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 [Platt & Stutz, 2008]. While this approximation is appropriate

65 for the species and spectral ranges investigated here, it could be problematic for strong absorbers, such as ozone in the short-wave UV [e.g., Rozanov & Rozanov, 2010]. AMFs are a robust and well established magnitude used for decades in many works (e.g. Perliski and Solomon, 1993; Wagner et al., 2007). They are usually computed using Radiative Transfer Models (RTM), which require an a-priori knowledge of the state of the atmosphere, i.e. vertical profiles of the different gases, temperature, pressure, etc.

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Since 2012, the ground-based DOAS community working on stratospheric research [e.g. Hendrick et al., 2011; Adams et al., 2012; Yela et al., 2017], has used O<sub>3</sub> and NO<sub>2</sub> AMFs provided by NDACC [Hendrick et al., 2011]. These NDACC AMFs are provided monthly in latitude bins of 10° between 85°S and 85°N and consider surface albedo equal to 0 and 1 and SZAs extending from 30° to 92° (for NO<sub>2</sub>, AMF for 10° is also included). NDACC O<sub>3</sub> AMFs are computed from 440 nm to 580 nm in steps of 35 nm, and for NO<sub>2</sub> from 350 nm to 550 in steps of 40 nm, using the pseudo-spherical DISORT RTM [Kylling and Mayer, 2003]. Input profiles are based on the Total Ozone Mapping Spectrometer (TOMS) v8.0 [Barthia et al., 2004] climatology for O<sub>3</sub> and on the Lambert et al. [1999, 2000] climatology supplemented by SAOZ balloon soundings for NO<sub>2</sub>. NDACC O<sub>3</sub> AMFs take into account the whole atmosphere from the surface up to the stratosphere, while for NO<sub>2</sub> the AMFs are exclusively stratospheric (from 12 km upward). Twilight photochemistry is neglected in NDACC AMFs.

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With regard to BrO, there is little literature on stratospheric AMFs. In the recent work of Chong et al. [2024], BrO AMFs have been calculated with the *Vector Linearized Discrete Ordinate Radiative Transfer Model* (VLIDORT, [Spurr, 2006, 2008; Spurr and Christi, 2019]) using input from the *Community Atmosphere Model with Chemistry* (CAM-Chem) climatology [Fernandez et al., 2019], to analyse a decade of data obtained by the Ozone Mapping and Profiling Suite Nadir Mapper (OMPS-NM) onboard the Suomi National Polar-orbiting Partnership (Suomi-NPP) satellite [Flynn et al., 2014]. In the work of [Theys et al., 2007], [Hendrick et al., 2007] and [Koenig et al., 2024], BrO AMFs are used to analyse ground-based DOAS measurements from Reunion Island (21°S), Harestua (60°N) and Mauna Loa (19°N) stations, respectively. In [Theys et al., 2007] and [Hendrick et al., 2007], the setup applied for the BrO retrieval includes the DISORT pseudo-spherical RTM coupled with the SLIMCAT 3-D chemical transport model (CTM) and the stacked-box photochemical model PSCBOX [Errera and Fonteyn, 2001; Hendrick et al., 2004]. A similar setup is used in [Koenig et al., 2024] but based on the CAM-Chem model [Lamarque et al, 2012] profiles.

Regarding OCIO, stratospheric AMFs are calculated in Pukite et al. [2022] using the 3-D full spherical RTM McArtim [Deutschmann et al., 2011; Deutschmann, 2014] to analyse data from the *TROPospheric Monitoring Instrument* (TROPOMI) onboard the Copernicus Sentinel-5 Precursor platform. In all of these studies, the AMF calculations are mostly limited to SZAs <= 90° and AMFs values are not explicitly provided. To our knowledge, the only publication showing OCIO AMFs for SZA up to 95° obtained from actual measurements is Pinardi et al. [2022]. In that work, ground-based DOAS instruments at 9 NDACC stations covering polar regions from both hemispheres are used to validate OCIO measurements by the GOME-2

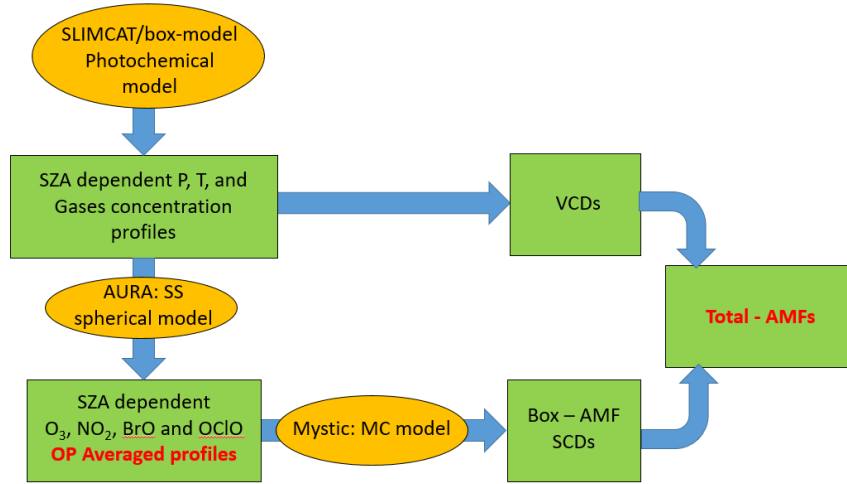
satellite instrument. Ground-based OCIO values are offset corrected using a Langley plots approach making use of empirically-  
100 derived OCIO AMFs. To be more precise the AMF in Pinardi et al. is defined as the ratio of the measured slant column to the  
vertical column estimated at  $70^\circ$  of SZA, assuming that at this solar elevation a simple geometrical AMF can be used. 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  $40^\circ$  and  $95^\circ$ .

105 In the present work, the stratospheric AMFs of  $\text{NO}_2$ ,  $\text{O}_3$ , OCIO and BrO are estimated for Marambio and Belgrano stations for  
SZAs (above the station) up to  $94^\circ$ . 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). Section 3 introduces  
110 the ground-based observations used to validate our approach. The observed AMF results are shown and compared with  
previous work and ground-based observations in Section 4. Our main conclusions are summarised in Section 5.

## 2 AMF Calculation Method

The AMFs presented in this work are calculated in the UV and in the Vis spectral range: at 510 nm for  $\text{O}_3$ , 470 nm for  $\text{NO}_2$ ,  
351 nm for OCIO and 355 nm for BrO at Marambio and Belgrano stations. The wavelengths used for  $\text{O}_3$  and  $\text{NO}_2$  correspond  
115 to those routinely applied in Marambio and Belgrano for NDACC retrievals. The wavelengths selected for BrO and OCIO are  
chosen for being close to the maximum absorption of those species in the spectral range used in our DOAS measurements (see  
Section 3). We follow a four-step approach as depicted in Fig. 1:

- (1) In a first step, a photochemical 1-D stacked box-model coupled to SLIMCAT [Chipperfield, 1999, 2006] (see Section  
2.1) is run with a 5-minute timestep to obtain the daily SZA-dependent vertical profiles (288 SZAs per day) of  $\text{O}_3$ ,  
120 OCIO, BrO,  $\text{NO}_2$ ,  $\text{H}_2\text{O}$ , pressure (P) and temperature (T) for Marambio and for Belgrano for a whole year. These are  
grouped as monthly (sunrise-am and sunset-pm) averaged profiles for SZAs from  $80^\circ$  to  $94^\circ$  in steps of  $1^\circ$ . The values  
of the SZAs at each station depend on the time of the year considered. Whenever possible, AMFs for SZA=  $50^\circ$ ,  $60^\circ$   
and  $70^\circ$  are also calculated. The motivation of grouping the profiles monthly is to reduce data processing. The validity  
of using monthly averages versus 10-day-averaged values is evaluated in Section 2.2.2.
- (2) In a second step, (for each SZA above the station:  $\theta$ ) the concentration profiles obtained with the box model are  
125 averaged over the SZAs encountered along the optical path for each atmospheric layer ( $c_l$ ), taking into account the  
spherical geometry. This is described fully in Section 2.2.
- (3) Then, by using those averaged profiles as input, Box-AMFs ( $a_l$ ) and SCDs are computed using the MYSTIC RTM  
[Mayer, 2009; Emde et al., 2010] for different SZA above the station.
- 130 (4) Finally, total AMFs are calculated as explained in the following paragraph.



**Figure 1: Summary of the AMF retrieval method. AURA (Averaged concentration estimator Using Ray-tracing Approximation) is a single scattering (SS) ray tracing model that estimates atmospheric gases concentrations averaged over the optical path (OP), (See Section 2.2).**

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For each of those SZAs 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 ( $dz_l$ ):

$$a_l = \frac{ds_l}{dz_l}, \quad (3)$$

In this work, atmospheric layers of 1 km thickness have been considered from the surface to an altitude corresponding to 0.13 hPa (55-62 km, depending on the time of the year), treated here as the top of the atmosphere (TOA). From the vertical profiles of the considered gases and these Box-AMFs, the total VCDs, SCDs and the corresponding AMFs can be calculated by integrating concentration over the optical path (slant or vertical) from the surface to the TOA:

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$$vcd_l = c_l dz_l, \quad (4)$$

$$VCD_{total} = \sum_0^{TOA} vcd_l, \quad (5)$$

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$$scd_l = vcd_l a_l dz_l, \quad (6)$$

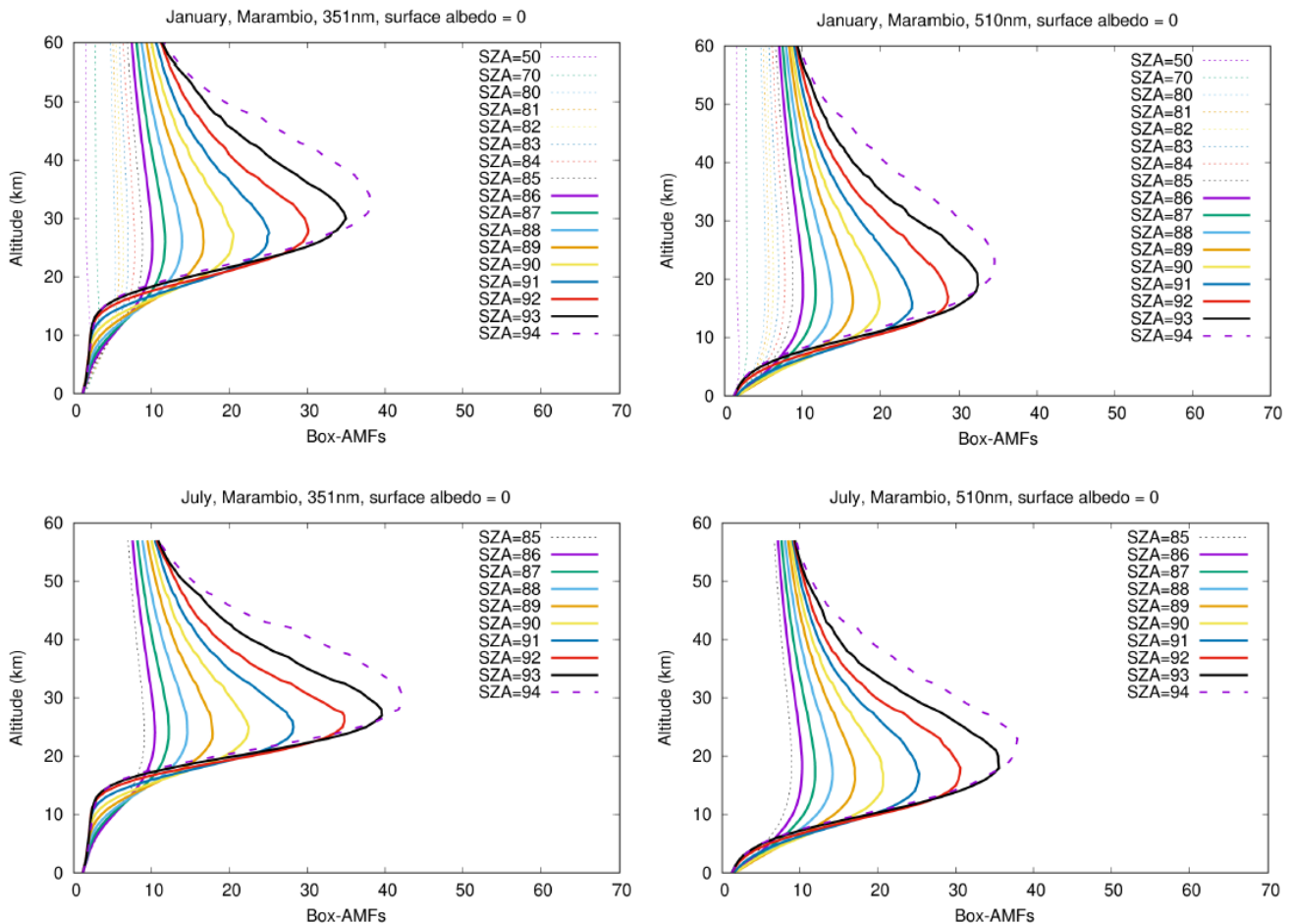
$$SCD_{total} = \sum_0^{TOA} scd_l, \quad (7)$$

$$AMF_{total} = \frac{SCD_{total}}{VCD_{total_{ph}}}, \quad (8)$$

where  $c_l$  is the average concentration of the considered trace gas in each layer  $l$ ,  $vcd_l$  and  $scd_l$  are the partial VCD and SCD in each layer, and  $SCD_{total}$ ,  $VCD_{total}$  and  $AMF_{total}$  are total SCD, VCD and AMF values. Note that in all these equations,

150  $vcd_l$  are calculated using the averaged concentrations, but for  $AMF_{total}$ , we use the  $VCD_{total\_ph}$  (eq. 8) 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.

155 Figure 2 presents some examples of these Box-AMFs for Marambio with a surface albedo = 0 in the UV and in the Vis. Note that, as expected for the higher SZA values, Box-AMFs below 10 km are small, due to the limited contribution of the troposphere to the optical path for this high SZA. Figure 2 shows that Box-AMFs peak at higher altitude at UV than at visible wavelengths, and the maxima of these peaks are also higher. Due to the lower attenuation of visible radiation, visible Box-AMFs extend to lower altitudes.



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**Figure 2: Box-AMFs computed for Marambio, corresponding to January (top) and July (bottom) 2018, for surface albedo=0 and different SZAs (see legend). Left panels are Box-AMFs in the UV (351 nm), right panels are Box-AMFs in the Vis (510 nm).**

## 2.1 TOMCAT/SLIMCAT model simulations

165 Our analysis uses results from the TOMCAT/SLIMCAT (hereafter SLIMCAT) 3-D CTM [Chipperfield 1999, 2006]. First the full 3-D model is used to perform a long-term simulation (see e.g. Dhomse et al. [2022]). The model was run from 1979 to 2024 at a horizontal resolution of  $2.8^\circ \times 2.8^\circ$  and 32 levels from the surface to around 60 km. This simulation was forced using meteorology from ECMWF ERA5 reanalyses [Hersbach et al., 2020]. The model has a detailed stratospheric chemistry scheme including long-lived source gases, such as  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , halocarbons, and the chemical families Ox,  $\text{NO}_y$ , HOx, Cly and Bry. It  
170 also includes selected brominated and chlorinated very short-lived substances (VSLs), including  $\text{CHBr}_3$  and  $\text{CH}_2\text{Br}_2$ . The chemistry is constrained by specified time-dependent monthly global mean surface mixing ratios of the long-lived tracers [WMO, 2022]. The two brominated VSLs both have constant tropospheric mixing ratios of 1 pptv, which together contribute a total 5 pptv to stratospheric bromine. Photochemical data used in the model is taken from NASA/JPL (2019). In addition to gas-phase chemistry, the model includes a detailed treatment of heterogeneous chemistry on liquid sulfuric acid aerosols along  
175 with liquid and solid polar stratospheric clouds (PSCs).

Daily (00 UTC) outputs from the full 3-D simulation are stored for the locations of Marambio and Belgrano. This is then used as an input for daily simulations of a 1-D (column) chemical model based on the same SLIMCAT chemical scheme without transport. The goal of this 1-D chemical model is to obtain the photochemical state of the atmosphere (i.e., concentrations of  
180 the different target gases) at much high temporal resolution than could be obtained directly from the 3-D model. The 1-D model is integrated each day with a 5-minute timestep (meaning SZA step always lower than  $0.6^\circ$ ) and the fields of the target gases are saved for each timestep, providing a dataset of concentrations at varying SZA for every day. The profiles at the SZAs used in our calculations are obtained linearly interpolating the photochemical model SZA values.

## 2.2 Accounting for photochemistry along the light path

185 The concentration profiles used in this work and provided by the photochemical model are representative for a horizontal resolution of  $2.8^\circ$  (the horizontal resolution of the SLIMCAT 3D-CTM). However, for large optical paths, the angle at which the solar beams reach each atmospheric layer (far away from the station) can be very different from the SZA over the station (Fig. 3), and thus the gas concentration can also differ substantially. The larger the SZA over the station, the greater the difference in the angle that each incident solar beam forms with each layer. Let  $(c_{l,\theta})$  be defined as the concentration of a  
190 specific gas observed by a ground-based instrument within an atmospheric layer and for a given  $\text{SZA} = \theta$ . 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). To take this effect into account, we average the

concentrations of the target species over the optical path using a ray-tracing model, AURA (Averaged concentration estimator Using Ray-tracing Approximation), developed for this purpose at INTA. There are two reasons to proceed in this way: (1) the multi-scattering Monte Carlo (MC) MYSTIC model used in this work is a 1-D model, which means that only one horizontally homogeneous vertical profile for each target species can be introduced in the model. Thus, we want to use a concentration profile representative of the whole atmosphere that takes photochemistry into account. (2) By doing this, we introduce a method that simplifies calculations and that can be used for other studies.

To average the concentrations along the light path, we make some approximations. First, we assume that solar rays are scattered only once before reaching the surface, and we divide the atmosphere into layers 1-km thick, with the top of the atmosphere (TOA) at 65 km. Note that, for an absorber above 15 km altitude and wavelengths between 350 and 650 nm, the single scattering is already a good approximation for zenith-sky stratospheric AMFs [see Figs. 2 and 3 of Perliski and Solomon, 1993]. Figure 3 illustrates the geometry of the problem; panel (a) shows the optical path followed by the solar beams before reaching the surface for SZAs up to 90° at the vertical of the station; panel (b) shows the same information for SZAs > 90°. In the first case, solar beams pass through each layer just once. In the second case, a solar beam can pass through a given layer once or twice slantwise and once vertically (see Figure 3 b and c)). In these figures, we have labelled the SZA at which a solar beam crosses a layer as  $\theta_1$  (bottom of the layer) and  $\theta_2$  (top of the layer). Analogously, when the solar beam passes through the layer a second time,  $\theta_3$  and  $\theta_4$  are the SZAs at which the solar beam reaches the bottom and the top of the layer. Note that, when the scattering is produced above the layer considered, this layer is crossed vertically and the concentration at SZA =  $\theta$  is then considered. For each SZA and each layer the partial slant column,  $scd_l$ , can be calculated as follows:

$$scd_l = \sum_b \frac{I_b}{I_{tot}} (\sum_i c_{b,l,i} s_{b,l,i}), \quad (9)$$

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:  $s_{b,l,1} = op_1$ ,  $s_{b,l,2} = op_2$ ,  $s_{b,l,3} = dz$ ). The  $c_{b,l,i}$  is obtained as the mean value between: the concentration at the top of the layer and the “local” SZA at this point ( $\theta_2$  for op1 in Fig. 3c, for instance), and the concentration at the bottom of the layer for the “local” SZA at this point ( $\theta_1$  for op1 in Fig. 3c). This is true except if one beam does not reach the bottom of the layer (as optical path between op1 and op2 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°).  $I_b$  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:  $s_{b,l} = s_{b,l,1} + s_{b,l,2} + s_{b,l,3} = op_1 + op_2 + dz$ ):

$$\sum_i c_{b,l,i} s_{b,l,i} = c'_{b,l} \sum_i s_{b,l,i} = c'_{b,l} s_{b,l}, \quad (10)$$

$$c'_{b,l} = \sum_i \frac{s_{b,l,i}}{s_{b,l}} c_{b,l,i}, \quad (11)$$

Introducing (9) in (7):

$$scd_l = \sum_b \frac{I_b}{I_{tot}} c'_{b,l} S_{b,l}, \quad (12)$$

230 Analogously, we now calculate the final averaged concentration for each layer,  $c_{ave,l}$ , as follows:

$$\sum_b \frac{I_b}{I_{tot}} c'_{b,l} S_{b,l} = c_{ave,l} S_l, \quad (13)$$

$$c_{ave,l} = \sum_b \frac{I_b}{I_{tot}} \frac{S_{b,l}}{S_l} c'_{b,l}, \quad (14)$$

where  $S_l = \sum_b S_{b,l}$ . If we now introduce (12) into (10), we have:

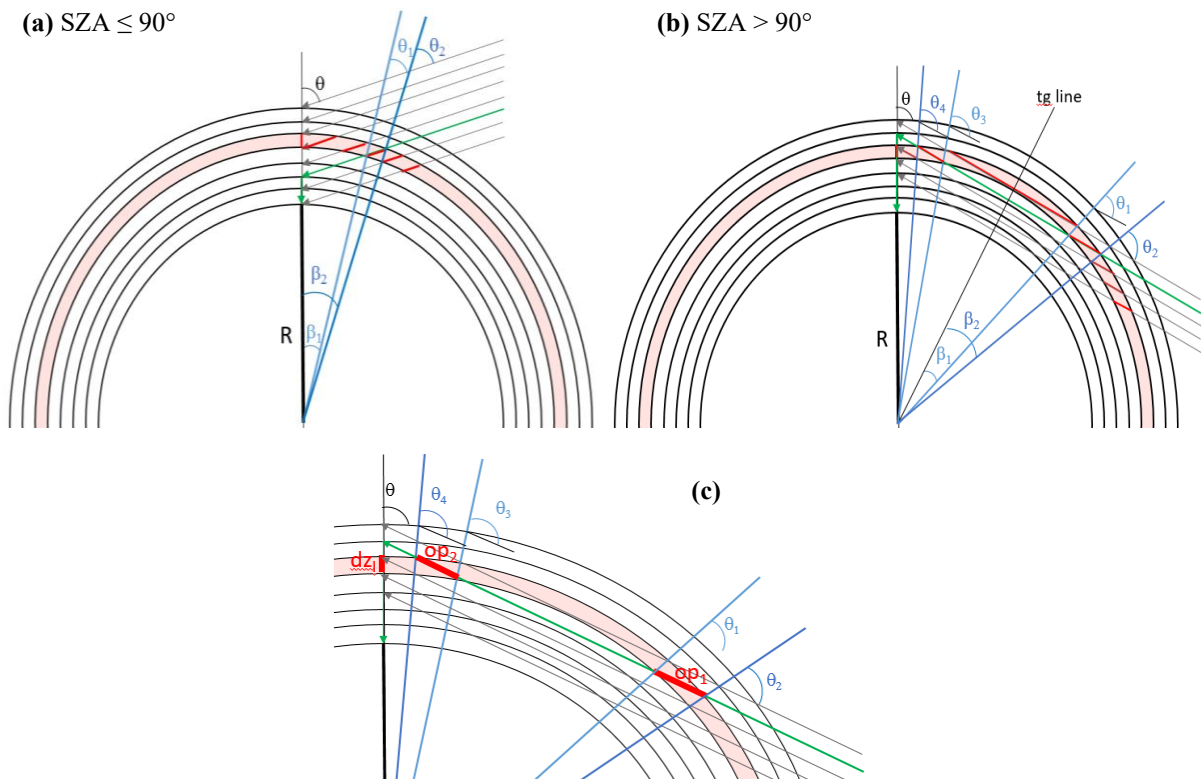
235  $scd_l = c_{ave,l} S_l, \quad (15)$

By doing this, we now have an averaged concentration for each SZA and each layer that represents all the concentrations found by all beams that pass through this layer.

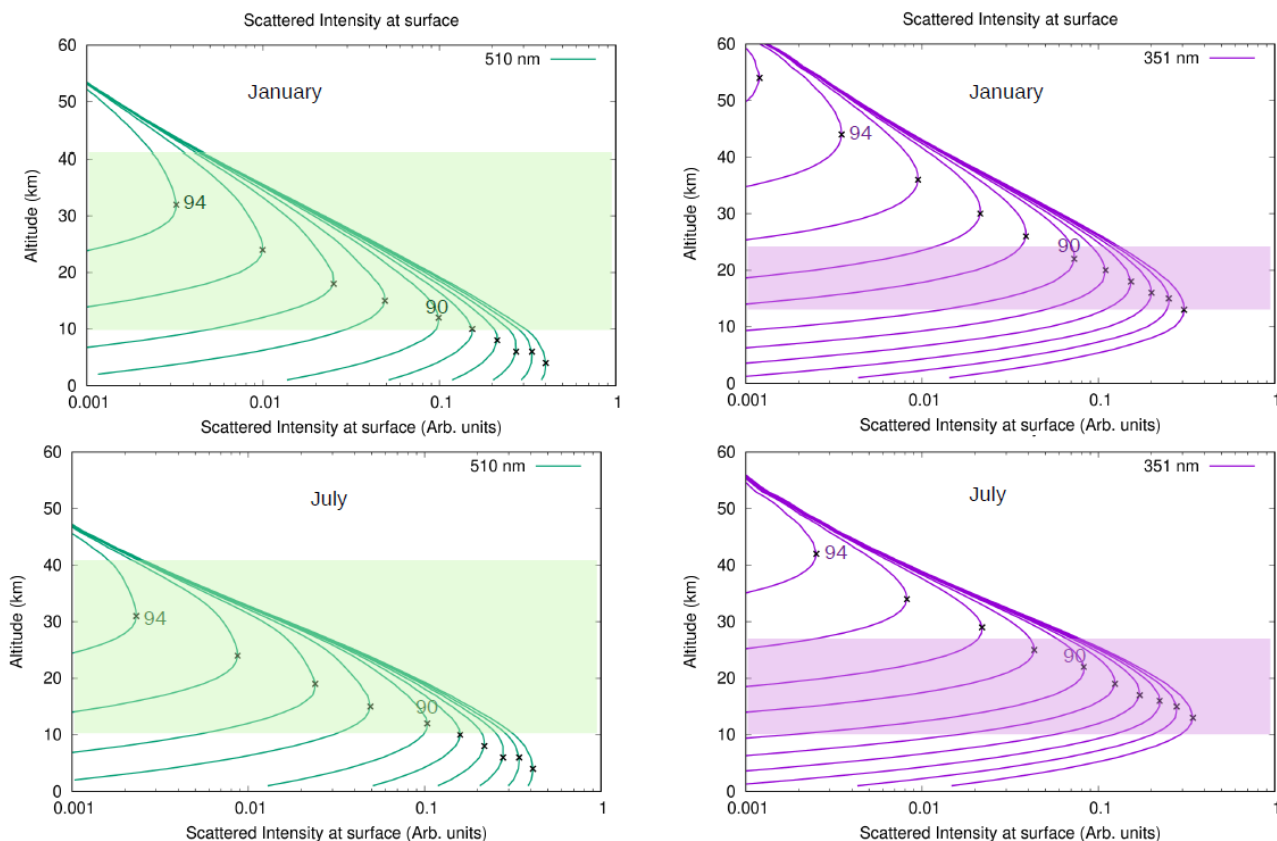
240 In some cases, the solar beam does not touch the bottom of the layer, for example see lower solar beam (grey arrows) in Figure 3b, and the lower layer. In that case, the mean concentration is calculated between the concentration at the top of the layer and at the minimum altitude reached by the beam at that layer.

As has been indicated in the equations, the contribution of each beam to the SCD is weighted by its contribution to the total intensity observed at the surface,  $I_b/I_{tot}$ , [Solomon et al., 1987]. In Figure 4, the contribution of the intensity observed at the surface by an instrument looking at zenith as a function of the scattering altitude is represented for different SZAs, (the scattering altitude being the vertical distance from the instrument at which sunlight beams are scattered towards the instrument). UV solar beams are scattered towards the surface at higher altitudes compared to visible ones.

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255 **Figure 3: Schematic showing how spherical geometry is taken into account in the calculation of the averaged trace gas concentrations. Panel (a) shows the case for  $SZA \leq 90^\circ$  is shown. Panel (b) represents the case for  $SZA > 90^\circ$ . In panel (c) the partial optical paths for one beam and one layer are shown.**



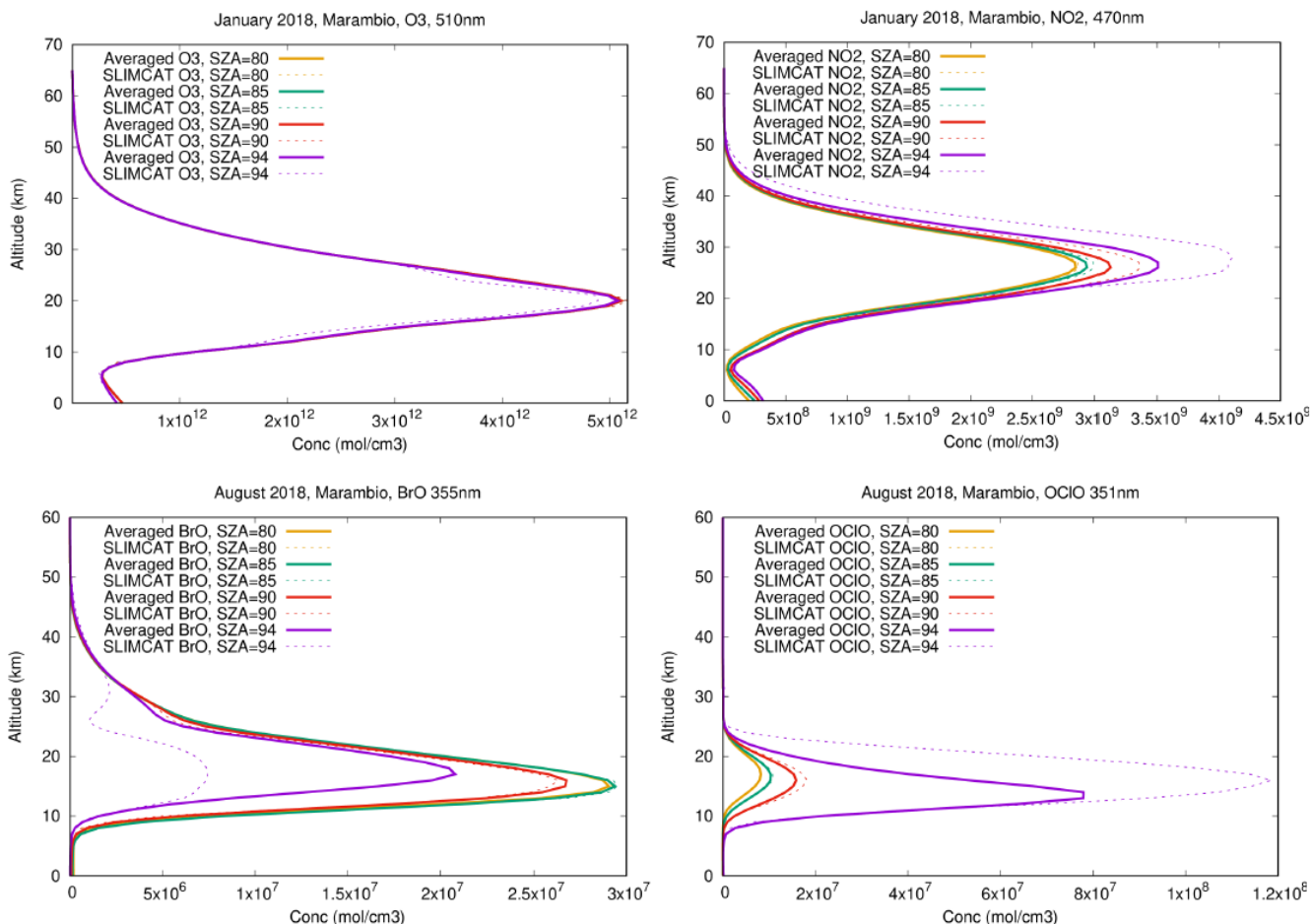
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**Figure 4: Scattered intensity reaching the surface for a zenith-looking instrument, as a function of the scattering altitude. Green lines (left) are the corresponding curves for the visible (510 nm) spectral range, and violet lines (right) correspond to the UV (351 nm) spectral range. Values for SZA from 85° to 94° (510nm) and to 95° (351 nm) in steps of 1° are represented. The corresponding maxima of each of these curves (maximum scattering altitude) are represented by black crosses. Shaded regions correspond to the altitudes where most of the O<sub>3</sub> or NO<sub>2</sub> (green) and BrO or OCIO (violet) are found (from chemical model profiles used in this work). Calculations are performed for January (top panels) and July (bottom panels) 2018 at Marambio.**

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Figure 5 shows some examples of how the concentration profiles change after averaging their values as described above. For species such as O<sub>3</sub>, or for low SZA for which solar beam optical paths stay close to the station, the concentration profiles do not change appreciably after averaging. However, for photochemically active species such NO<sub>2</sub>, BrO or OCIO, this can have a big impact on the profiles, especially for high SZAs. The impact of considering these averages in the final results is discussed in Section 3.

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**Figure 5: Comparison of vertical concentration profiles for Marambio as they are output by the 1-D chemical model above the station (dashed lines) and after averaging (solid lines) over the optical path as described in the text. Profiles for SZA=80° (above the station) are represented in yellow, for SZA=85° in green, for SZA=90° in red and for SZA=94° in violet. Top left: O<sub>3</sub> profiles calculated at 510 nm for January; Top right: NO<sub>2</sub> profiles calculated at 470 nm for January; Bottom left: BrO profiles calculated at 355 nm for August; Bottom right: OCIO profiles calculated at 351 nm for August.**

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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 of these approximations, a comparison between 2 set 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. 14) for the whole atmosphere. Results are almost identical (See Figures S1 – S4 of the Supplementary Material), meaning that the calculated averaged profiles reproduce well SCDs obtained from the SZA-dependent profiles. In addition, SCDs obtained with AURA have been compared

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290 with a ray tracing model developed at BIRA that has been validated against other codes [Hendrick et al., 2006], showing in general similar results as AURA (See Figures S1 – S2 of the Supplementary Material).

### 2.3 MYSTIC radiative transfer simulations

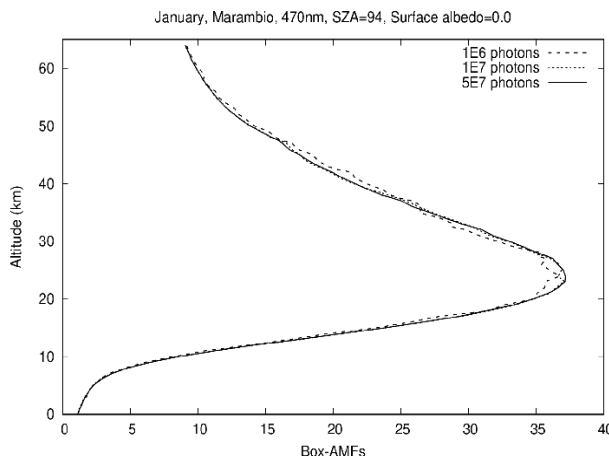
MYSTIC [Mayer, 2009; Emde et al., 2010] is a fully spherical Monte Carlo (MC) radiative transfer code. Simulations performed with this code have been compared to different benchmark results [Emde et al., 2010] and other RTMs [Zawada et al., 2021] showing consistently good agreement. In MYSTIC, individual photons are traced on their random paths through the atmosphere in order to obtain solar-radiation-related magnitudes as radiances, irradiances, actinic fluxes, optical paths and Box-AMFs, for given viewing and solar geometries. Even though MYSTIC was originally conceived as a 3-D model to consider complex cloud shape [Mayer, 2009] and/or topography [Mayer et al., 2010; Schwaerzd et al., 2021], for the purpose of this work the standard Box-AMF output of 1D-MYSTIC provided in version 2.0.4 of libRadtran software package [Emde et al., 2016; Mayer and Kylling, 2005] have been used, since it is the only version available in libradtran and clouds or complex surface topography are out of the scope of this work. An assessment of polar stratospheric clouds effect can be found in e.g. Pukite et al. (2022). The method used in this work does not intend to replace the powerful and straightforward 2D/3D RTM, but to provide a simplified and computationally less expensive approach accounting for photochemical changes along long twilight light paths while still working with a 1D box-AMF calculations. Note that this study is aimed to systematically investigate the variability of AMFs across a wide range of solar zenith angles (SZAs), species, and timescales. Using the 1D (open-source) 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 study.

#### 310 2.3.1 RTM settings

As explained above, O<sub>3</sub>, OCIO, BrO, NO<sub>2</sub>, H<sub>2</sub>O, P and T vertical profiles in our calculations are taken from the 1-D photochemical box-model and averaged along the light path as explained in Section 2.2. Except in very rare cases when aerosols reach the stratosphere (i.e. volcanic or fire ashes), aerosols have a low influence. Thus, no aerosols are considered in our calculations. Sensitivity tests have been performed (not shown here) introducing aerosol with AOD=0.1, exponentially decreasing profile with a scale height = 1 km, asymmetry parameter = 0.6, and single scattering albedo = 0.9. Differences in Box-AMFs with and without aerosols are less than 1%. The solar spectrum of Kurucz [1992] is set as the solar source in our simulations. Two extreme cases of surface albedo (SA) are considered: SA=0 and SA=1. AMFs for intermediate values of SA can be estimated by interpolating between these two.

320 An important parameter to take into account in the MC RTM is the number of photons used in the simulations. To avoid statistical instabilities in our results, we performed several calculations changing the number of photons for the different SZAs

(see Fig. 6). The higher the SZA, the lower the probability of a photon reaching the ground-based instrument. Thus, the number of photons that need to be considered increases with the SZA. In our calculations, we have set the number of photons to  $10^6$  for SZAs between  $50^\circ$  and  $90^\circ$ ,  $10^7$  for SZAs between  $91^\circ$  and  $93^\circ$ , and  $5 \times 10^7$  for  $SZA = 94^\circ$ . By using these numbers we  
 325 observe a smooth profile of the Box-AMFs in all cases (Fig. 6).

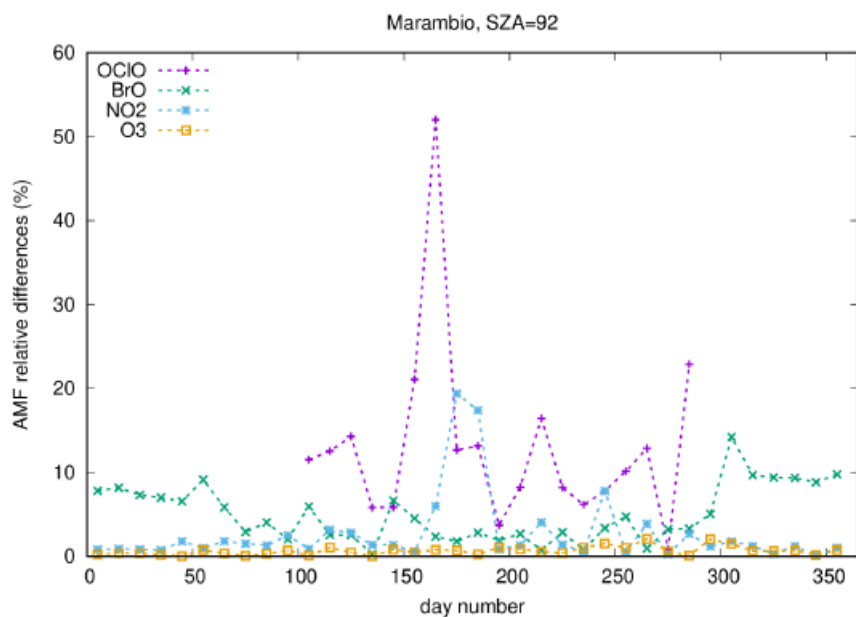
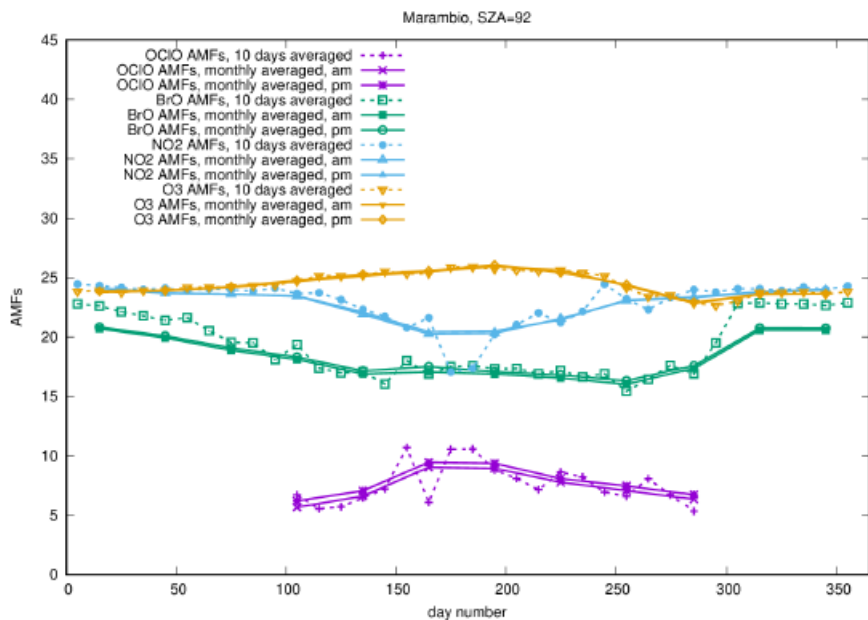


**Figure 6: Box-AMFs computed for Marambio, January 2018, for  $SZA=94^\circ$ , surface albedo=0, a wavelength of 470nm and different number of photons:  $1 \times 10^6$  (dashed line),  $1 \times 10^7$  (dotted line),  $5 \times 10^7$  (solid line).**

### 330 2.3.2 Temporal sampling of the AMFs

In order to evaluate if the use of monthly averaged AMFs is a good approximation, we have compared monthly averaged AMFs with 10-day averaged AMFs for  $O_3$ , OClO, BrO and  $NO_2$  and for  $SA = 0$ . Note that an even shorter period of time could have been chosen, daily averages for instance, however, to perform these calculations for 2 stations, 4 spectral ranges, 2 surface albedos and 36 time periods (10-days intervals in a year) means that the number of calculations is  $2 \times 4 \times 2 \times 36 = 576$   
 335 calculations with AURA and 576 with MYSTIC. Performing daily averages would mean that  $2 \times 4 \times 2 \times 365 = 5840$  calculations should be performed with AURA and then with MYSTIC, which is prohibitive. In addition, by performing 10-day averages, outlier values, not representative of the “normal” variability, are smoothed. Figure 7 (left) shows results for Marambio where, compared to Belgrano, a higher number of twilights (SZAs from  $90^\circ$  to  $95^\circ$ ) are available. In the right panel of Figure 7, relative differences between 10-day averages and interpolated monthly values for  $SZA=92^\circ$  are shown. Similar  
 340 results are obtained for  $SZA=93^\circ$  and  $94^\circ$ , and for  $SA = 1$ . The figure shows that  $O_3$  relative differences are always under 2%. Thus, since AMFs follow a smooth temporal variability, using monthly values can be considered as a good approximation. Maximum relative differences for BrO are below 7% most of the year, except during summer where these differences increase up to 14%. We conclude that monthly values are still a reasonable approximation. Also, for  $NO_2$ , relative differences are below

8% except during the month of June (minimum in NO<sub>2</sub>) when the differences reach 19%. In contrast, OCIO shows a high  
345 temporal variability during the chlorine activation period. Thus, if the goal of using the AMFs is to reveal annual or inter-  
annual variability, the use of monthly averages is justified. 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  
specially for OCIO.



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Figure 7: Top panel: OCIO (violet), BrO (green), NO<sub>2</sub> (blue) and O<sub>3</sub> (yellow) stratospheric AMFs computed for Marambio, for SZA=92°, and surface albedo=0. Continuous lines correspond to monthly averaged values; dashed lines correspond to 10-day averaged values. Bottom panel: Relative difference between monthly and 10-day averaged AMFs: OCIO (violet), BrO (green), NO<sub>2</sub> (blue) and O<sub>3</sub> (yellow). Note that for OCIO only the period in which it is observed is shown in the figure.

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### 3 Ground-based DOAS observations

The measurements used for the validation of our AMF calculation approach rely on ground-based MAX-DOAS instruments [Platt and Stutz, 2008] operated at the Antarctic stations of Marambio (64° 13' S, 56° 37' W) and Belgrano II (77° 52' S, 34° 7' W). At each of these sites, INTA has deployed MAX-DOAS systems operating in the visible and UV spectral ranges (for O<sub>3</sub>/NO<sub>2</sub> and BrO/OCIO, respectively). At SZA < 85°, these instruments perform vertical scans of the atmosphere with small telescopes moving from the horizon to the zenith, capturing scattered skylight. During morning and evening twilights, the telescopes are fixed in zenith-viewing geometry to focus on the measurement of stratospheric gases such as O<sub>3</sub>, NO<sub>2</sub>, BrO and OCIO. Details on the design of the instruments can be found in Prados-Roman et al. [2018] and Gomez-Martin et al. [2021]. Spectral radiance data are analysed using INTA's analysis software LANA [Gil et al., 2008; Peters et al., 2017]. NO<sub>2</sub> is processed in the spectral range 425-490 nm [Kreher et al., 2020], O<sub>3</sub> in 450-534 nm [Hendrick et al., 2011], BrO in 346-359 nm [Alliwell et al., 2002, with updated cross-sections: O<sub>3</sub>: Serdyuchenko et al, 2014; O<sub>4</sub>: Finkenzeller and Volkamer, 2002, OCIO: Kromminga et al, 2003], OCIO in 345-389 nm [Pinardi et al., 2022]. Measurements used in this work refer to observations performed in 2018.

### 4 Results

#### 4.1 AMF calculations for O<sub>3</sub>, NO<sub>2</sub>, BrO and OCIO

Applying the method described in Section 2, stratospheric AMFs were calculated for the four target species O<sub>3</sub>, NO<sub>2</sub>, OCIO and BrO. Results for surface albedo = 0 are shown in Figures 8 and 9 for Marambio and Figures 10 and 11 for Belgrano. Differences between AMFs calculated for albedo = 0 and albedo = 1 are very small (i.e., for 90°SZA, less than 0.8% for O<sub>3</sub> and NO<sub>2</sub>, up to 2% for BrO and 3% for OCIO for September). The values of the AMFs calculated in this work are provided in the Supplementary Material. The validity of our calculations in the Vis spectral range is tested by comparing our O<sub>3</sub> and NO<sub>2</sub> AMFs with those from NDACC which have been used since 2012 as a reference for the DOAS scientific community [e.g. Hendrick et al., 2011, Yela et al., 2017]. The validity of our UV results is evaluated by comparing them with data available from the literature [Theys et al, 2007; Pinardi et al., 2022]. For SZAs up to 93°, our results are also compared to AMFs obtained with the pseudo-spherical 2D-DISORT [Hendrick et al., 2004] (2D refers to using different vertical profiles for different SZAs). This comparison, which addresses both UV and visible AMFs, is restricted to albedo = 0, since large differences are not observed in the AMFs for other albedo values. All the data used in figures 8 to 11 are included in Table 1.

In Figure 8, for O<sub>3</sub> and NO<sub>2</sub> our results have been cross-checked with the February and September O<sub>3</sub> and NO<sub>2</sub> AMFs used for NDACC (red dot symbols in the figures), for the same surface albedos and wavelengths and for a latitude of 65°S (close to the latitude of Marambio) [Hendrick et al., 2011]. In Figure 10, our O<sub>3</sub> and NO<sub>2</sub> results for Belgrano have been also cross-checked with the February and September O<sub>3</sub> and NO<sub>2</sub> AMFs used for NDACC (red dot symbols), for the same surface albedos and wavelengths, and for a latitude of 75°S (close to the latitude of Belgrano). In the same figures, 2D-DISORT AMFs for the

same example months (February: violet dots; September: black dots) are also shown. As  $SZA=90^\circ$  is the value used to report VCDs within NDACC, we discuss results using the AMF values at this SZA as reference.

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Molecule	Reference	Vertical concentration profiles	RTM - Approximation
O <sub>3</sub>	This work	Averaged Concentrations	MYSTIC - Spherical
	2D-DISORT	Photochemical model profiles	DISORT - Pseudospherical
	NDACC	TOMS v8.0 climatology	DISORT - Pseudospherical
NO <sub>2</sub>	This work	Averaged Concentrations	MYSTIC - Spherical
	2D-DISORT	Photochemical model profiles	DISORT - Pseudospherical
	NDACC	Lambert et al. 1999, climatology	DISORT - Pseudospherical
BrO	This work	Averaged Concentrations	MYSTIC - Spherical
	2D-DISORT	Photochemical model profiles	DISORT - Pseudospherical
	Theys et al, 2007.	photochemical box model PSCBOX	DISORT - Pseudospherical
OCIO	This work	Averaged Concentrations	MYSTIC - Spherical
	This work relative to $SZA=70^\circ$ (Marambio)	Averaged Concentrations	MYSTIC - Spherical
	2D-DISORT	Photochemical model profiles	DISORT - Pseudospherical
	Pinardi et al, 2022	photochemical box model PSCBOX / Empirical	DISORT – Pseudospherical / Langley plot

**Table 1: Models and concentration profiles referred in this work and used in figures 8 to 11.**

For O<sub>3</sub> at Marambio, our results are similar to NDACC as well as 2D-DISORT values, showing maximum relative differences of 1.8% (NDACC) and 0.6% (2D-DISORT) larger AMFs for September with even smaller differences for February. However, these differences increase up to +26% when comparing NO<sub>2</sub> AMFs from this study with NDACC data, while the difference with 2D-DISORT simulations remains low (1.2%). Regarding Belgrano, our results for O<sub>3</sub> show differences with NDACC always below 3.5% and the same with 2D-DISORT values. For NO<sub>2</sub> these differences increase with SZA up to 29.0% for NDACC and remain below 1.0% for 2D-DISORT. To better understand the origin of these deviations, we consider the differences between the methods used to obtain these different data sets. First pseudo-spherical RTM have been used for NDACC and 2D-DISORT AMFs in contrast with the fully spherical RTM used in this work. However, given that DISORT and MYSTIC are providing similar results (see Figures 8-11 and S3.1), this geometrical difference cannot explain the observed differences. Concerning vertical profiles, NDACC AMFs use the TOMS v8.0 [Barthia et al., 2004] climatology for O<sub>3</sub>, and Lambert et al. (1999, 2000) climatology in combination with SAOZ balloon soundings for NO<sub>2</sub> as vertical profiles of these molecules, provided for latitudes from 85°S to 85°N in steps of 10°. Twilight photochemistry and optical path averages taken into account in this work are not considered in the NDACC AMF calculation. In the case of 2D-DISORT and MYSTIC, outputs

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of the photochemical model described in Section 2.1, specific for 2018, considering a region of  $2.8^\circ$  around the station, are used directly (DISORT) or averaged to obtain equivalent concentration profiles that take into account photochemistry (MYSTIC). That means that the geographical region considered in this work is significantly smaller than the latitude belt ( $10^\circ$ ) considered for NDACC. In addition, the concentration profiles used in this work are specific for the year 2018, while NDACC  
410 AMFs use climatological data published 25 years ago. Therefore, this seems to be the most probable factor causing the observed differences is the different concentration profiles considered in each set of data.

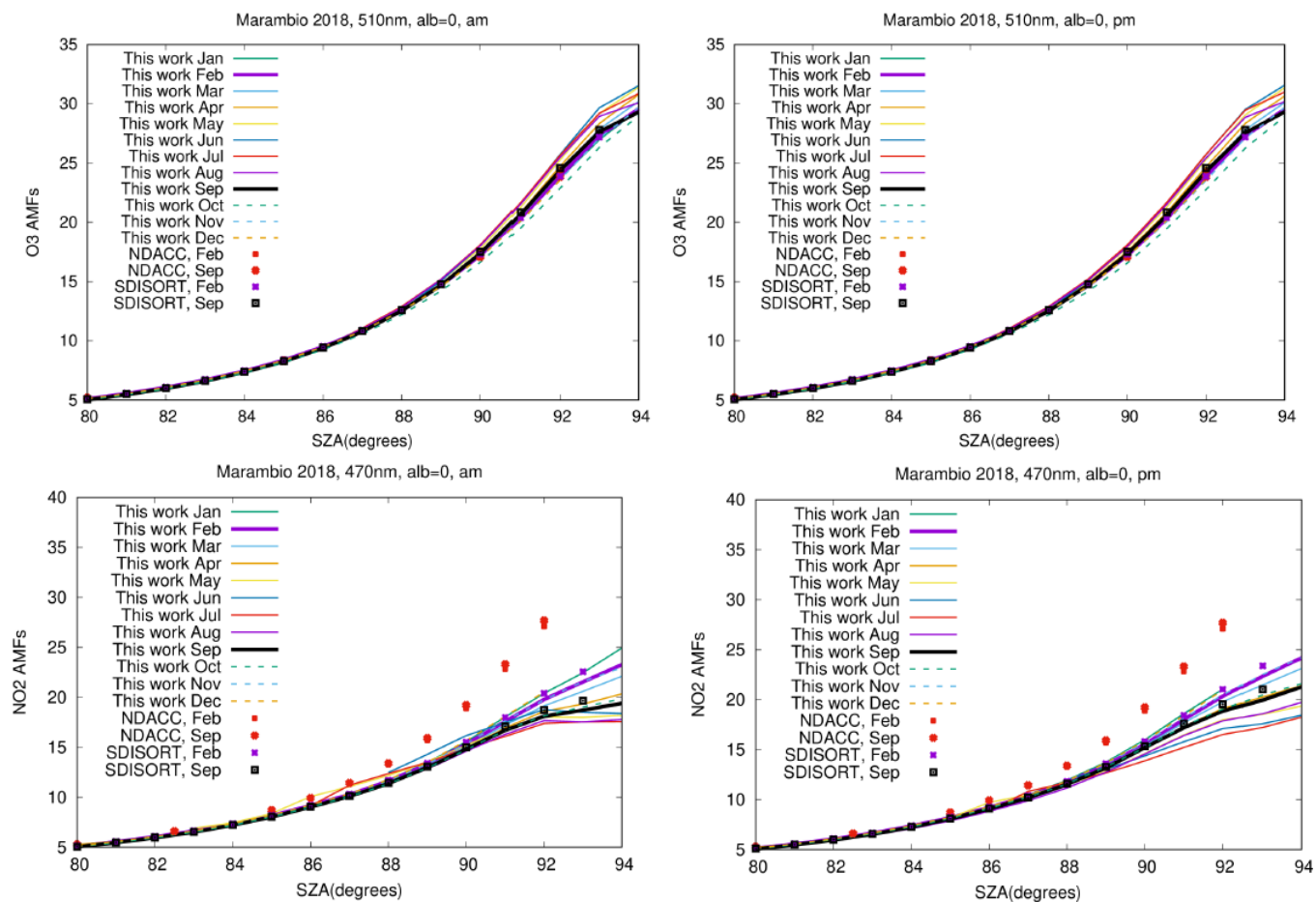
For species like  $O_3$ , whose composition and distribution with altitude do not suffer large variation during twilights, these differences do not have a big impact on the results as can be seen in Figure 8. For other species with larger variations in their  
415 vertical profiles during twilight (e.g.,  $NO_2$ ), the differences in AMFs are more important. This fact is of special relevance for the short-lived molecules BrO or OCIO. In this case, there are very few AMF values available in the literature for comparison. In Figures 9 and 11, we compare our results with those of Pinardi et al., (2022) for OCIO, and Theys et al., (2007) for BrO. Note that for BrO, we have not found any published reference of the AMFs for SZA higher than  $90^\circ$ . In both cases, we have also compared MYSTIC with 2D-DISORT calculations. In the work of Pinardi et al. (2022), AMFs are obtained as the ratio  
420 between SCDs for different SZAs and the VCD at  $SZA=70^\circ$ . To properly compare our results with those of Pinardi et al. (2022), AMFs referred to  $VCD=70^\circ$  for September have also been included in Figure 9 as blue dots. Differences in both sets of data are of 7% for sunrise and 18% for sunset (both at  $SZA=90^\circ$ ). 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). However, in Fig. 9 the [Pinardi et al., 2022] AMFs are empirical averaged (am-pm) values, corresponding to the AMFs provided to the several  
425 groups participating in that work. In contrast to other species, for which AMFs increase with SZA, the stratospheric OCIO AMFs obtained in this work show a local minimum close to  $SZA=93^\circ$  for most of the year, also observed in [Kühl et al, 2004]. This results from the strong increase of the OCIO concentrations beyond  $90^\circ$  SZA. Comparisons with 2D-DISORT simulations show absolute differences lower than 0.5 for Marambio, and 0.3 for Belgrano. For BrO, both 2D-DISORT and MYSTIC present an important increase of the AMFs with SZA, due to the strong decrease of the BrO concentration beyond  $90^\circ$  SZA in  
430 this case. Note that in the visible spectral range, the maximum scattering altitude ranges between 12 and 42 km for SZA between  $90^\circ$  and  $95^\circ$  (see Fig. 4). This coincides with the bulk altitude of both  $O_3$  and  $NO_2$  concentrations (see Figs. 4 and 5). In the UV spectral range, the maximum scattering altitude ranges between 22 to 54 km for SZA (see Fig. 4), while the bulk of the OCIO and BrO concentrations is located between 10 and 25 km (see Figs. 4 and 5), i.e., mostly below the scattering altitude. However, while OCIO increases at low sun and essentially remains in the same altitude range, BrO decreases and its maximum  
435 concentration moves towards higher altitudes, where the main scattering takes place (see Fig. 12). This fact was already observed in the work of [Perliski and Solomon, 1993].

There is also another factor contributing to these different behaviours between the different species AMFs. When photochemistry is not considered, the only factor changing with the SZA is the optical path that increases with the SZA.

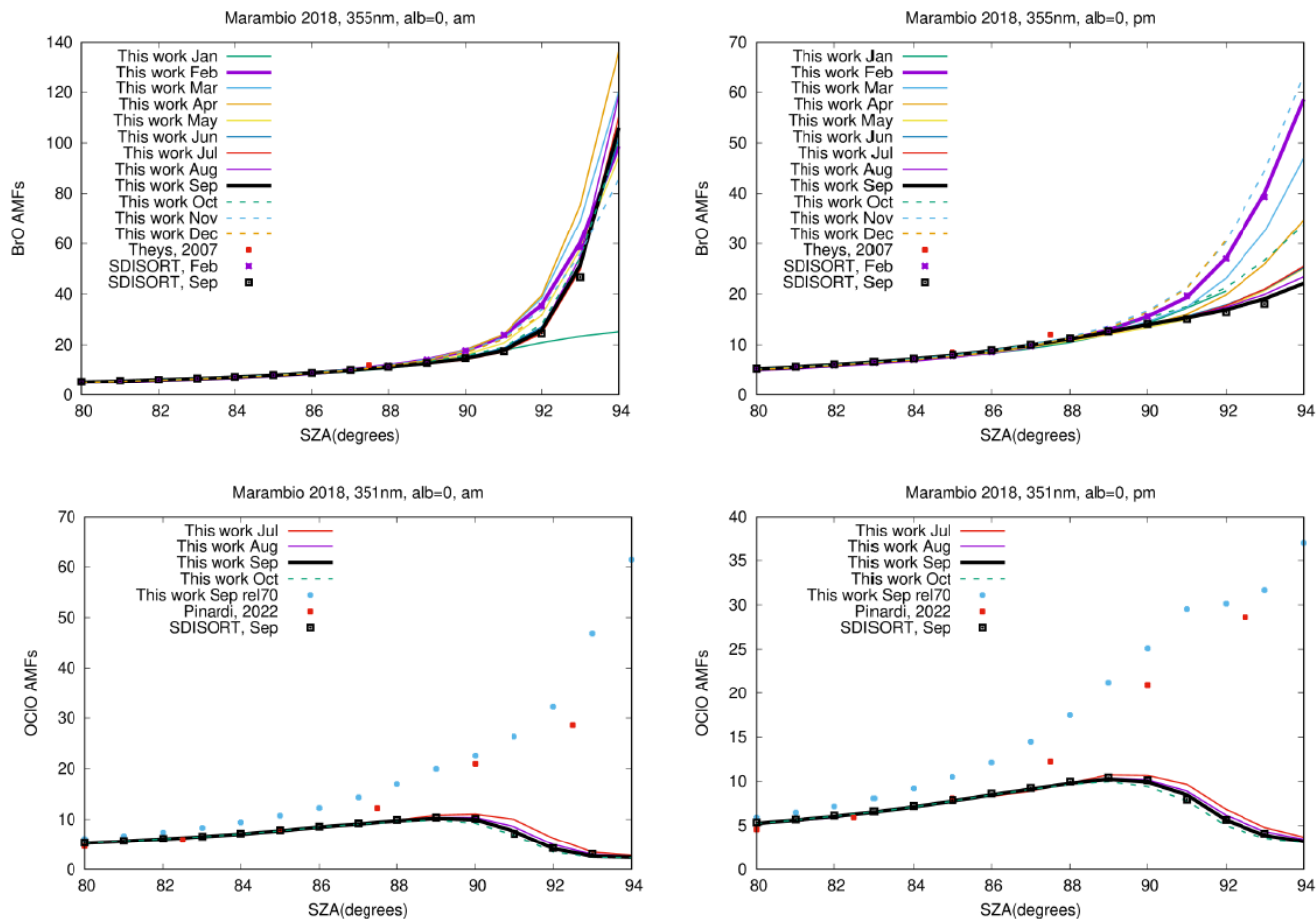
440 However, when photochemistry is considered, not only does the optical path change but also the vertical profile of the species  
(1): different profiles occur for different SZAs over the station, and (2) for each of these SZAs over the station, different  
profiles along the optical paths of the Sun beams). As the AMFs is the ratio between the SCD and the VCD, the value of the  
AMFs depends on the evolutions of the VCD and SCD, which are affected not only by the optical path but also by the changing  
profile concentration. Note that, when calculating the optical path SCD average, we consider the concentration vertical profiles  
445 observed across the optical path, with SZA increasing up to the SZA above the station (see Fig. 4). These paths experienced  
lower SZA, corresponding to lower concentrations of NO<sub>2</sub> and OCIO but higher concentrations of BrO (see Fig. 5). 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 NO<sub>2</sub> and OCIO and higher for BrO. As already noted, this also contributes to the  
evolution observed in the twilight AMFs of these molecules.

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All of the features explained above are also applicable to the Belgrano station (see Fig. 10 and 11). In this case, the number of  
months for which the sunlight reaches our instrument is smaller than for Marambio, thus the number of AMFs is also smaller.  
However, the behaviour of the AMFs calculated for all of the molecules is similar to that observed at Marambio.

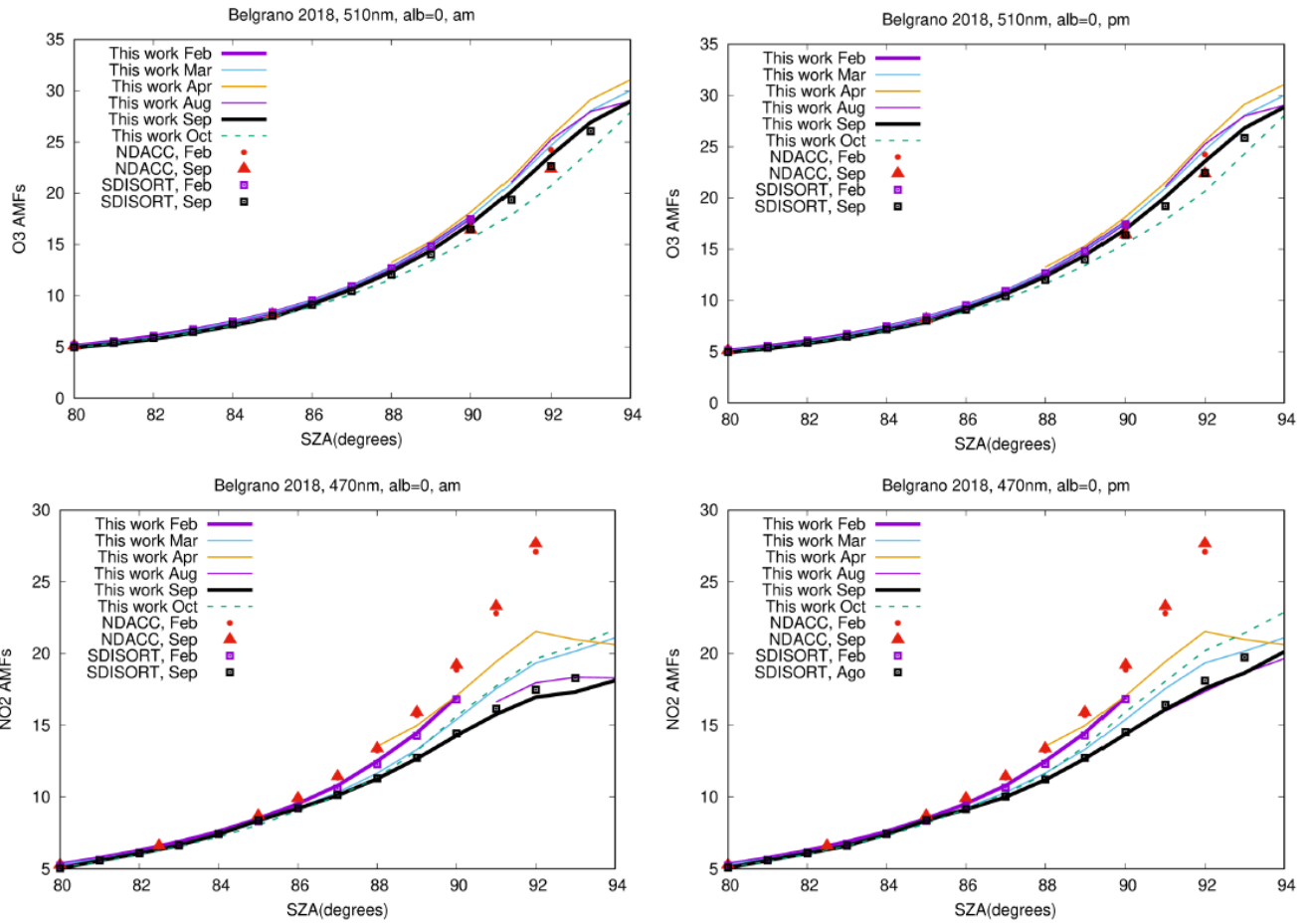


**Figure 8: Total Visible AMFs: O<sub>3</sub> (first row), NO<sub>2</sub> (second row) computed for Marambio 2018, for surface albedo=0: Sunrise values at left and sunset values at right. Red symbols correspond to NDACC AMFs for O<sub>3</sub> and NO<sub>2</sub> [Hendrick et al, 2011]. 2D-DISORT AMFs for February (violet crosses) and September (black squares) are also shown.**



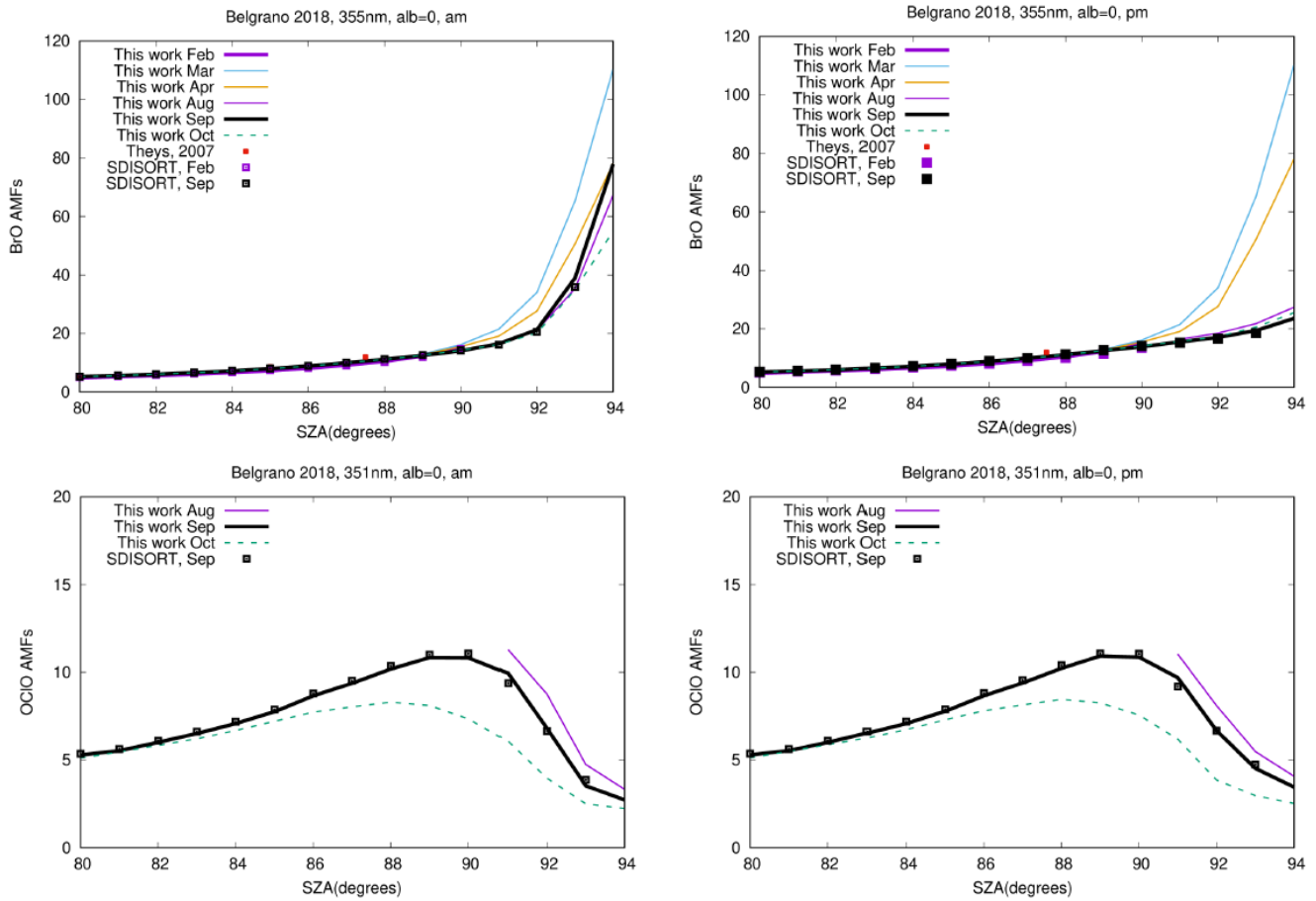
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**Figure 9: Total UV AMFs: of OCIO (first row), BrO (second row) computed for Marambio 2018, for surface albedo=0: Sunrise values at left and sunset values at right. OCIO AMFs from Pinardi et al., 2022 and BrO AMFs from Fig. 2 of Theys et al., 2007. 2D-DISORT AMFs for February (violet crosses) and September (black squares) are also shown.**



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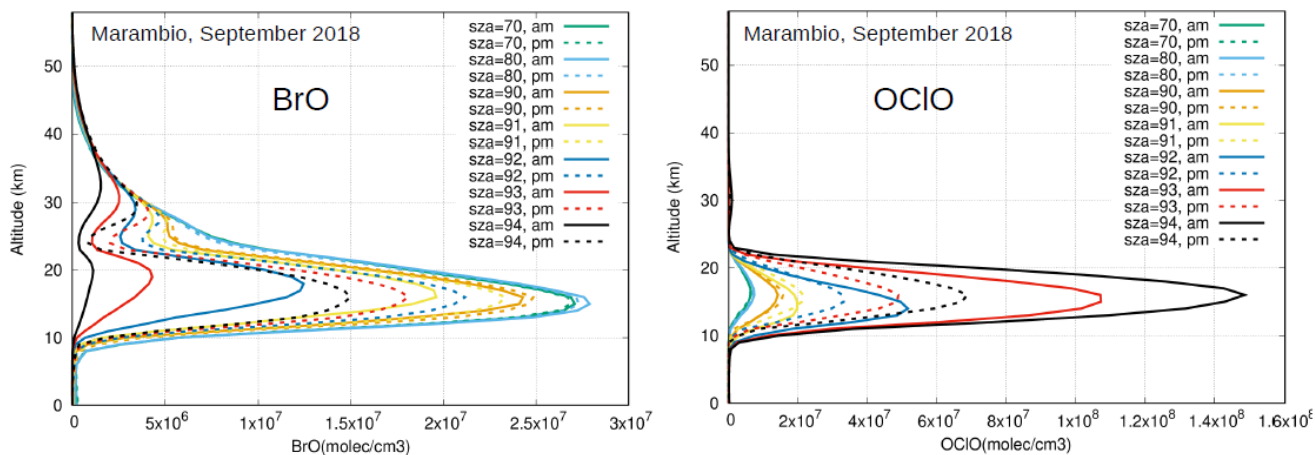
**Figure 10: Total Visible AMFs:  $O_3$  (first row),  $NO_2$  (second row) computed for Belgrano 2018, for surface albedo=0: Sunrise values at left and sunset values at right. Red symbols correspond to NDACC AMFs for  $O_3$  and  $NO_2$  [Hendrick et al, 2011]. 2D-DISORT AMFs for February (violet crosses) and September (black squares) are also shown.**



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**Figure 11: Total UV AMFs: of OCIO (first row), BrO (second row) computed for Marambio 2018, for surface albedo=0: Sunrise values at left and sunset values at right. OCIO AMFs from Pinardi et al., 2022 and BrO AMFs from Fig. 2 of Theys et al., 2007. 2D-DISORT AMFs for February (violet crosses) and September (black squares) are also shown.**

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**Figure 12: Evolution with SZA of the concentration of BrO (left) and OCIO (right) over Marambio during September 2018. Concentration profiles have been obtained with the photochemical model based on SLIMCAT.**

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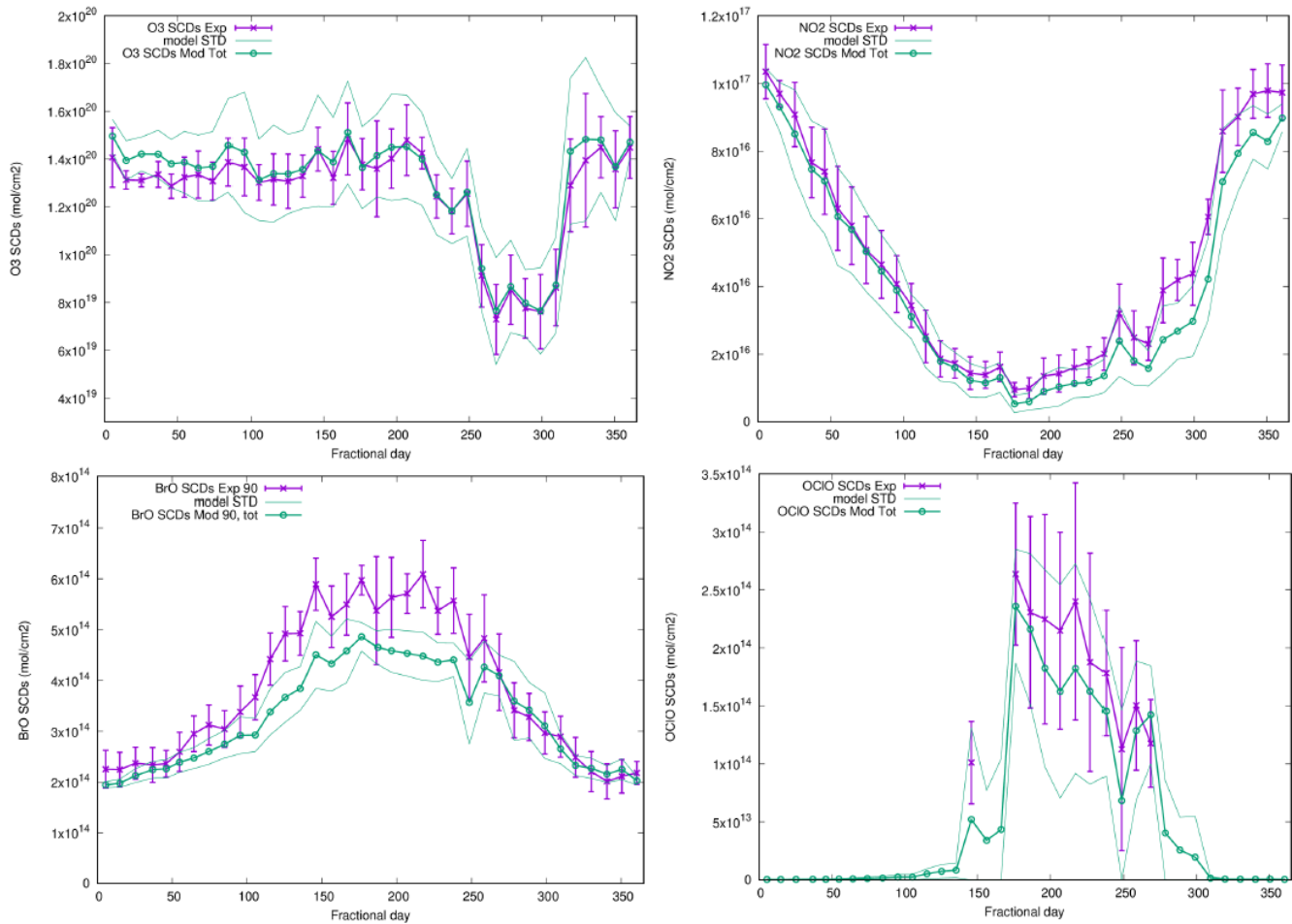
#### 4.2 Comparison with measurements

To further verify the validity of our results, experimental SCDs obtained in 2018 using our ground-based DOAS instrument in Marambio have been compared with modelled SCDs (see Fig. 13). Note that for OCIO, the detection limit is about  $1.0 \times 10^{14}$  molecules/cm<sup>2</sup>, thus measurements below this detection limit have not been included in the figure. We have compared SCDs calculated and measured at SZA=90° since that SZA is a good compromise in terms of instrumental signal-to-noise ratio for twilight observations. Similar results (not shown) have been found for SZA=92°. For comparison, experimental and modelled SCDs have been averaged in a 10-day period and represented in the middle of the period considered. Error bars of experimental data represent the standard deviation of all the points used in the average. Modelled SCDs are obtained from the calculated Box-AMFs, considering photochemistry, Earth sphericity and the optical path averages described in previous sections. In practice, the analysis of measured spectra provides differential SCDs (dSCDs) against a given reference (see Section 3). This reference is usually selected for conditions at which the contribution of the SCD of the target trace gas is a minimum. When studying stratospheric SCDs, the reference is also chosen to minimise the possible contribution from tropospheric absorbers. For the case of interest in this work, these conditions are met at the beginning or at the end of the calendar year. In Figure 13, the modelled reference SCD have been added to the experimental dSCDs to estimate the experimental SCDs. To do so, the exact experimental conditions (fractional day, SZA) of the reference have been used in the reference content calculation, obtaining a value of  $1.34 \times 10^{19}$  molec/cm<sup>2</sup> for O<sub>3</sub>,  $5.76 \times 10^{15}$  molec/cm<sup>2</sup> for NO<sub>2</sub>,  $6.51 \times 10^{13}$  molec/cm<sup>2</sup> for BrO and  $2.55 \times 10^{11}$  molec/cm<sup>2</sup> for OCIO.

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All year round, measured O<sub>3</sub> SCDs are very well captured by mean and std modelled values (less than 7.7% difference), which  
 500 give us confidence in the methodology used in this work. Regarding NO<sub>2</sub>, measured and modelled SCDs agree within the one  
 one sigma std of the measurements accumulated in 10-day periods. Regarding BrO, modelled SCDs are smaller than observations,  
 particularly for winter, with a maximum relative difference of ~20%. Similar differences can be seen for mean measured-  
 modelled OCIO, although in this case values fall within the once sigma variability of the measurements. Regarding BrO,  
 frequent tropospheric bromine explosions have been reported at Marambio [[Prados-Roman et al., 2025](#)], which could lead to  
 505 a contamination of the observed SCD by tropospheric BrO even at high SZA.



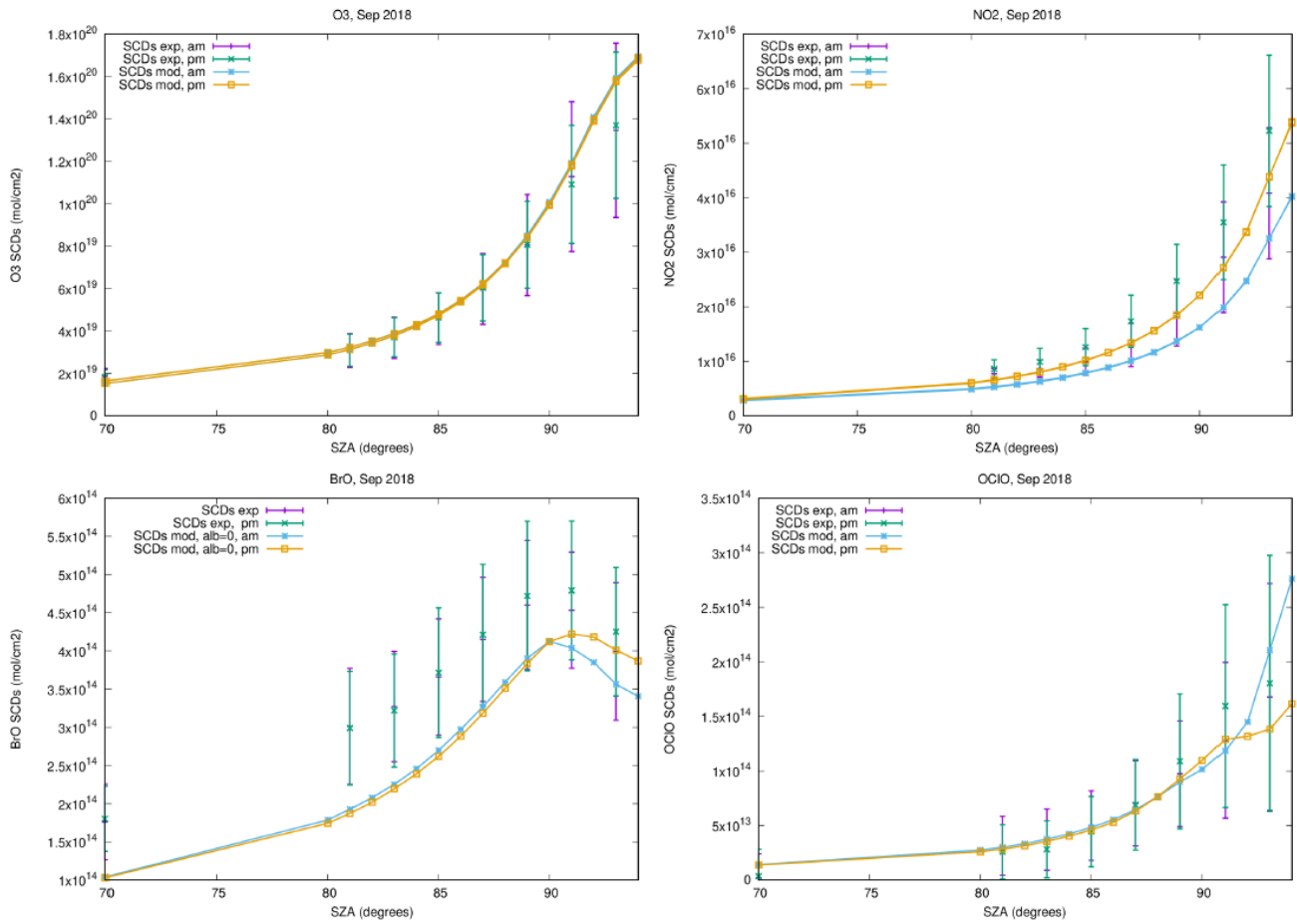
**Figure 13: Measured (violet) and modelled (green) O<sub>3</sub> (top, left), NO<sub>2</sub> (top, right), BrO (bottom, left) and OCIO (bottom, right) SCDs for Marambio 2018, and SZA=90°. For a given 10-days, the photochemical model provide 2 profiles per SZA per day (am and pm), i.e. 20 profiles for a whole 10-days period. The mean profile and its standard deviation for**  
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each 10-days period are calculated. In this figure, 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.

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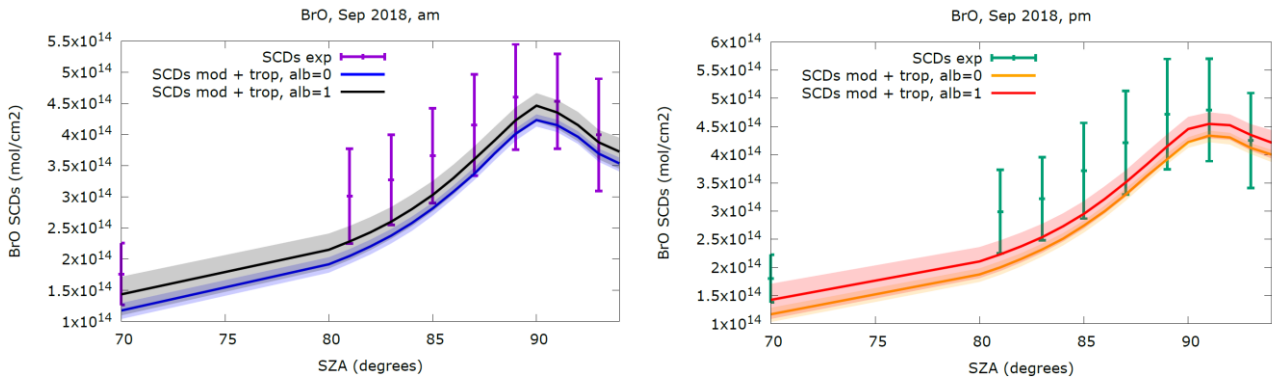
In Figure 14, the evolution of the measured SCDs with the SZA (violet for am and green for pm) and the corresponding modelled values (yellow for am and blue for pm) have been represented for Marambio in September. In addition, to consider the possible impact of tropospheric BrO emissions, SCDs simulated with an added tropospheric contribution representative of what is observed at Marambio at this time of the year ( $6.5 \times 10^{12}$  molec/cm<sup>2</sup> in the lower 2 km of the atmosphere Marambio [Prados-Roman et al., 2025]), are also plotted in Figure 15. Left panel of Figure 15 corresponds to sunrise (am) values and right panel to sunset (pm) values. Blue and orange lines correspond to surface albedo = 0 and black and red lines to albedo = 1. Shaded areas correspond to the range of values between the maximum tropospheric BrO observed at Marambio during September ( $12.0 \times 10^{12}$  molec/cm<sup>2</sup>: median value from 2015 to 2023, [Prados-Roman et al., 2025]) and minimum (No BrO). While the surface albedo has a small influence in the “pure” stratospheric SCDs, when considering an extra BrO tropospheric contribution, the role of the albedo becomes important. As can be seen, when considering this tropospheric BrO contribution, modelled BrO SCDs fall within the error bars of the measured SCDs. This strengthens support for the hypothesis of tropospheric BrO as being the main cause of the observed differences between measured and modelled BrO SCDs shown in Figure 13.

530 Additional possible sources of error for all measured SCDs represented in Figure 13 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 =  $94^\circ$ , we are considering regions up to  $8^\circ$  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. The further detailed analysis of the differences found herein is beyond the scope of this work and will be the subject of future studies.



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**Figure 14: Solar zenith angle evolution of the monthly SCDs of O<sub>3</sub> (top left), NO<sub>2</sub> (top right), BrO (bottom left) and OCIO (bottom right) over Marambio during September 2018. Violet and green lines are measured values (am and pm respectively). Blue and yellow lines are modelled values (am and pm respectively).**



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550 **Figure 15: Solar zenith angle evolution of the monthly SCDs BrO over Marambio during September 2018. Violet and green lines are measured values (am and pm respectively). Left panel: Blue and black lines are am modelled values (surface albedo = 0 and = 1 respectively). To take into account possible tropospheric BrO explosions, these simulated SCD values consider a tropospheric BrO contribution representative of the BrO values observed at Marambio during September ( $6.5 \times 10^{12}$  mol/cm<sup>2</sup> in the first 2 km [Prados-Roman et al., 2025]). Shaded areas correspond to minimum (no tropospheric BrO) and maximum ( $12.0 \times 10^{12}$  mol/cm<sup>2</sup> in the first 2 km [Prados-Roman et al., 2025]) tropospheric values observed at Marambio during September. Right panel: Orange and red lines are pm modelled values (surface albedo = 0 and = 1 respectively). Shaded areas correspond to the same minimum and maximum tropospheric values as the left panel.**

555

## 5 Conclusions

Stratospheric AMFs for O<sub>3</sub>, NO<sub>2</sub>, BrO and OCIO at Marambio and Belgrano Antarctic stations have been calculated for the year 2018. They have been obtained by using a spherical Monte-Carlo RTM. Temperature, pressure and optical path averaged concentration vertical profiles obtained from a photochemical box-model have been used as input in the RTM. These optical path averages have been calculated taking into account the trace gas concentrations encountered at the different SZAs during twilight. To our knowledge, BrO and OCIO stratospheric AMFs are reported for the first time for SZAs up to 94° taking into account photochemistry and optical path averages of the concentrations.

560 In order to simplify the complex calculations, monthly averaged AMFs have been calculated (see values in Supplementary Material). The impact of the temporal sampling in the calculation of these quantities has been studied, concluding that for NO<sub>2</sub> and OCIO shorter temporal sampling is recommended especially during the months of June and July.

Comparing the obtained O<sub>3</sub> and NO<sub>2</sub> AMFs with those provided by 2D-DISORT, a good agreement is found. However, when comparing with NDACC AMFs, while all sets of data show similar results for O<sub>3</sub>, for NO<sub>2</sub> larger differences are observed. 570 Considering that 2D-DISORT and MYSTIC simulations produce similar results, these differences are attributed to the different concentration profiles used as input in NDACC as compared to the photochemical concentration profiles used in this work.

Our results show that, for the photo active species considered in this work, the evolution of the AMFs and SCDs with the SZA mainly relies on their photochemical variations (total concentration and its vertical distribution), the optical path followed by the sunlight beams, i.e. the geometry of the problem (observation view, Earth sphericity, Sun position, etc), and the effective scattering altitude. 575

To validate our results, simulated SCDs of the four considered compounds have been compared to measurements performed in Marambio. A general good agreement is found for O<sub>3</sub>, NO<sub>2</sub> and OCIO. Although some discrepancies are found at winter for BrO, they can be attributed (mostly) to the contribution of the tropospheric BrO that is not taken into account in the 580

photochemical profiles, but that have a significant influence on the total BrO SCDs even for zenith measurements. In that case (of large tropospheric contribution) surface albedo significantly influences the results. In general, for all four species, a good agreement is found within one sigma standard deviation. Assuming that the photochemical model is accurate; this confirms the validity of the method employed and the approximations considered.

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

### **Author contributions**

LGM: Conceptualization, data curation, formal analysis, investigation, methodology, software, project administration, supervision, validation, visualization and writing; CPR: Conceptualization, data curation, formal analysis, investigation, validation, writing and funding acquisition; MPC: data curation, formal analysis, investigation and validation; MvR: 590 conceptualization, formal analysis, investigation, methodology, software, and validation; OP: resources, MNC: data curation, software; HO: resources; MY: conceptualization, data curation, formal analysis, funding acquisition, investigation, validation and resources.

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