March 24, 2018

Response letter to Referee #4 on the manuscript "Monte Carlo method for determining uncertainty of total ozone derived from direct solar irradiance spectra: Application to Izaña results"

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Article reference: amt-2017-403

Authors: We thank Anonymous Referee #4 for the valuable comments that helped us in improving the manuscript. We have included below our detailed responses to all comments.

Abstract

"**P1, L1** replace "calculate" with "estimate"."

> ***Authors:*** Corrected according to reviewer's suggestion. The new sentence is: "We demonstrate a Monte Carlo model to estimate the uncertainties of total ozone column (TOC), derived from ground-based direct solar spectral irradiance measurements."

Introduction

"P1, L13-14 At this point the authors should make clear that they are talking for correlations in spectral measurements. According to the authors this is the main problem solved when the new methodology is applied. I also suggest adding more information here to help the reader understand what they mean when they refer to "correlations"."

> ***Authors:*** We revise the text about spectral correlations in the introduction and include a new paragraph with some examples about where they might arise:
>
> "TOC can be determined from spectral measurements of direct solar UV irradiance (Huber *et al.* (1995)). We have developed a Monte Carlo (MC) based model to estimate the uncertainties of the derived TOC values. One frequently overlooked problem with uncertainty evaluation is that the spectral data may hide systematic wavelength dependent errors due to unknown correlations (Kärhä *et al.* (2017b, 2018); Gardiner *et al.* (1993)). Omitting possible correlations may lead into underestimated uncertainties for derived quantities, since spectrally varying systematic errors typically produce larger deviations than uncorrelated noise-like variations that traditional uncertainty estimations predict. Complete uncertainty budgets for quantities measured are necessary to understand long term environmental trends, such as changes in the stratospheric ozone concentration (e.g. Molina and Rowland (1974)) and solar UV radiation (e.g. Kerr and McElroy (1993); McKenzie *et al.* (2007)).
>
> Physically, correlations may originate, e.g., from lamps or other light sources used in calibrations. If their temperatures change e.g. due to ageing or current setting, a spectral change in the form of Planck's radiation law is introduced. Non-linearity in the responsivity of a detector causes systematic differences between high and low measured values. The introduced spectrally systematic but unknown changes in irradiance may change the derived TOC values significantly, exceeding the uncertainties calculated assuming that the uncertainty

in irradiance behaves like noise. The presence of correlations in measurements can be seen in many ways. For example, problems have occurred when new ozone absorption cross-sections have been taken into use (Redondas *et al.* (2014); Fragkos *et al.* (2015)). Derived ozone values may change significantly because different systematic errors are included in the different cross-sections. Also, TOC estimated from a measured spectrum often depends on the wavelength region chosen, although the measurement region should not affect the result much."

Regarding these paragraphs, a new reference is included in the manuscript and one reference is updated:

Redondas A., Evans R., Stuebi R., Köhler U., and Weber M.: Evaluation of the use of five laboratory-determined ozone absorption cross sections in Brewer and Dobson retrieval algorithms, Atmos. Chem. Phys., 14, 1635–1648, 2014.

Kärhä P., Vaskuri A., Pulli T., and Ikonen E.: Key comparison CCPR-K1.a as an interlaboratory comparison of correlated color temperature, J. Phys.: Conf. Ser., 972, 012012, 2018. doi:10.1088/1742-6596/972/1/012012

"P2, L4-5 Do you mean here that the field of view of the spectroradiometers is equal to exactly one solar diameter? If not, then some scattered irradiance also enters the spectrometer."

Authors: The field of view of each spectroradiometer was limited. We revise the sentence as: "The field of view of the spectroradiometers has been limited so that they measure direct spectral irradiance of the Sun, excluding most of the indirect radiation from the remainder of the sky."

We also rename Section 2 as "ATMOZ field measurement campaign and instrument description" and included the field of view of each spectroradiometer in Section 2. The field of view with a full opening angle is 2.5° for QASUME (Gröbner *et al.* (2017)), 2.8° for BTS (Zuber *et al.* (2017b)), and 1.5° for AVODOR according to the manual of the collimator tube used, J1004-SMA by CMS Ing.Dr.Schreder GmbH.

Section 2

"The tables 1, 2 and 3 are presented here without any discussion regarding the presented quantities. I suggest that they should be moved to the uncertainty estimation section (section 4). Furthermore, some discussion (e.g. explaining the presented correlation types, description of how the different uncertainty types were estimated) would be useful."

Authors: We admit these tables are better suited in Section 4, after the spectral correlation types have been introduced. We move measurement uncertainty tables for QASUME, BTS, and AVODOR (old Tables 1, 2 and 3) to Section 4. We also include more discussion about the uncertainty components:

"The uncertainties due to radiometric calibration include factors such as the uncertainty of the standard lamp used, and the additional uncertainty due to noise and alignment. QASUME has been validated using various methods, thus the uncertainty due to calibration is low (Hülsen *et al.* 2016). For QASUME and BTS, we assume the correlations to be equally distributed between full correlation, unfavourable correlation, and random correlation (Kärhä *et al.* 2018). Spectra measured with AVODOR are significantly noisier, thus half of the uncertainty is associated to the random component. Values for instability of the calibration lamp are based on long-term monitoring. The lamp irradiances have been noted to gradually drop with no significant wavelength structure within the wavelength region concerned. Nonlinearity values are estimations of the operators of the devices. Nonlinearity is typically manifested so that the responsivity of the device changes gradually from high readings to low readings. This can cause significant change in the TOC values, thus we assume the correlation type to be unfavourable. Uncertainties due to device stability and temperature dependence are based on long-term monitoring. The changes have been found to be independent on wavelength in the region concerned, thus full correlation is assumed. Noise is the average standard deviation of typical measurements at noon over the wavelength region concerned. The wavelength scales of the devices have been checked using emission lines of gas discharge lamps. The uncertainty values given are the estimated standard deviations of the possible remaining errors after corrections. Wavelength error can introduce a significant change in TOC, because it introduces an error in the form of the derivative of the spectral irradiance. Thus, unfavourable correlation is assumed. Most of the uncertainty components are slightly wavelength dependent but to simplify simulations, average uncertainty values are used over the wavelength range between 300 nm and 340 nm."

Section 3

"P7, L2 Gröbner and Kerr (2001) did not assume that the air mass factors for aerosols and Rayleigh scattering are equal."

Authors: Indeed, Gröbner and Kerr (2001) did not deal with aerosols. The assumption was taken from the paper by Gröbner *et al.* (2017). We revise the sentence as: "As the ozone and other molecules creating scattering are distributed at different altitudes, we calculate the relative air mass factor m_{R} for Rayleigh scattering at the altitude of 5 km (Gröbner and Kerr (2001)) and approximate the effective altitude of aerosols so that $m_{\mathrm{AOD}} \approx m_{\mathrm{R}}$ (Gröbner *et al.* (2017))."

References:

Gröbner J. and Kerr J. B.: Ground-based determination of the spectral ultraviolet extraterrestrial solar irradiance: Providing a link between space-based and ground-based solar UV measurements, J. Geophys. Res., 106, 7211–7217, 2001.

Gröbner J., Kröger I., Egli L., Hülsen G., Riechelmann S., and Sperfeld P.: The high resolution extra-terrestrial solar spectrum determined from ground-based solar irradiance measurements, Atmos. Meas. Tech., 10, 3375–3383, 2017.

Section 4

"P14, L5 Again, the reference of Gröbner and Kerr (2001) is not correct here."

Authors: We change the reference and revise the sentence as: "Rayleigh scattering and aerosols are set at the altitude of 5 km ± 0.5 km, which influences the relative air mass $m_{\mathrm{R}} \approx m_{\mathrm{AOD}}$ (Gröbner *et al.* (2017))."

Section 5

"P17 Please add more information regarding the linear model used for AOD. E.g., why using the particular model for AOD? Are a and b the same with those of Ångström (1964)? If not, how they are estimated? What happens if the TOC is derived by QASUME and BTS using this linear AOD model?"

Authors: For example, Huber *et al.* (1995) use such a linear model for AOD. The aerosol model by Ångström (1964) can be approximated with a line when a narrow spectral range is modelled. In the linearized AOD model, parameters a and b do not have exact physical meanings, they are just coefficients. Mostly, because of this, we choose to use the model by Ångström (1964), as it is more physical, but we also compare some of our results with results obtained using the linear equation.

In response to the comments by Anonymous Referee #2, we include an offset factor c to the atmospheric model of Eq. (3) of our AMT Discussion manuscript to compensate for full spectral correlations as:

$$E_{\mathrm{s}}(\lambda) = c \cdot E_{\mathrm{ext}}(\lambda) \cdot \exp\big[-\alpha_{\mathrm{O_3}}(\lambda, T_{\mathrm{eff}}) \cdot \mathrm{TOC} \cdot m_{\mathrm{TOC}} - \tau_{\mathrm{R}}(\lambda, P_0, z_0, \phi) \cdot m_{\mathrm{R}} \\ -\tau_{\mathrm{AOD}}(\lambda) \cdot m_{\mathrm{AOD}}\big]. \quad (1R)$$

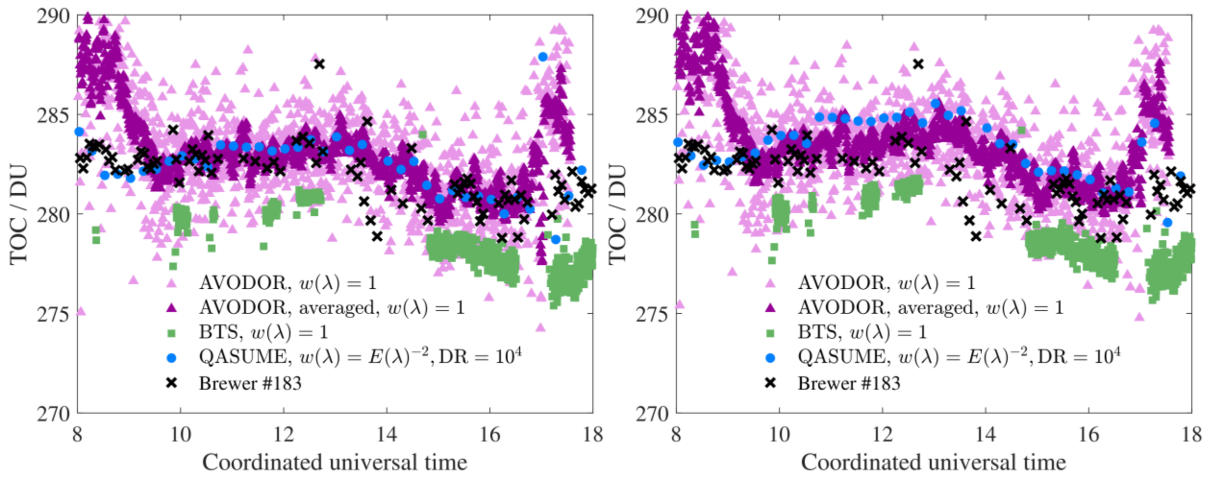
After this change, the atmospheric model has three free fitting parameters: TOC, $\beta \geq 0$, and c, and the TOC estimated for AVODOR at local noon agrees quite well with other instruments. There is still the inverse U-shape in the BTS and AVODOR results, but it diminishes when the relative least squares fitting

$$S = \sum_{i=0}^{N} w_i \left[E_s(\lambda_i) - E(\lambda_i)\right]^2 \quad (2R)$$

with $w(\lambda) = E(\lambda)^{-2}$ is replaced with the least squares fitting of absolute residuals by setting $w(\lambda) = 1$.

To justify our approach, we compare in Fig. 1R the results obtained using Eq. (1R) with the Ångström AOD model of Eq. (7), to those obtained using Eq. (1R) with the linear AOD model of Eq. (13). When we used linear AOD model, we kept all parameters a, b and TOC as free fitting parameters without bound constraints. In addition, we set $c = 1$, because b produces an almost similar offset factor ($e^{-b \cdot m_{\mathrm{AOD}}}$) as c. Parameter a compensates for slope-like spectral deviations.

According to the new simulations presented in Fig. 1R, the TOC values obtained using the linear AOD model are practically the same for BTS and AVODOR as those obtained using the Ångström model and an offset factor c. With QASUME, the results deviate by 2 DU due to the unconstrained slope factor a of the linear AOD model.



(a) TOC estimated using Eq. (1R) with Ångström AOD model

(b) TOC estimated using Eq. (1R) with linear AOD model

Figure 1R. Absolute TOC values estimated for the spectroradiometers studied. Average of 10 neighbouring values has been included for AVODOR to show the spectral shape behind the noise. Abbreviation DR refers to the dynamic range of QASUME data used in the least squares fitting.

Conclusions

"P18, L27 The results from AVODOR deviate up to 10 DU (and not 10 DU) depending on the SZA. Is the stray light effect enough to explain these discrepancies?"

Authors: There is a spectrally constant offset in the spectral irradiance measured by AVODOR that our model in the AMT Discussion manuscript could not handle. We did not take into account how easily full correlations appear in solar UV irradiance measurements, e.g., due to geometrical factors. Thus, we improved our atmospheric model by including an offset factor c as a free parameter in Eq. (1R). Stray light is mostly responsible for the inverse U-shape of TOC (Herman *et al.* (2015)), but using absolute least squares fitting, i.e., by setting the weight to $w(\lambda) = 1$ in Eq. (2R), we get rid of the solar zenith angle dependence. The TOC estimated from the spectra of all the instruments with the improved atmospheric model are presented in Fig. 1R.

We include a new reference in the manuscript:

Herman J., Evans R., Cede A., Abuhassan N., Petropavlovskikh I., and McConville G., "Comparison of ozone retrievals from the Pandora spectrometer system and Dobson spectrophotometer in Boulder, Colorado," Atmos. Meas. Tech., 8, 3407–3418, 2015.

"The last paragraph of the conclusions section is now written leads to the conclusion that the main outcome of the study is that the AVODOR is not suitable for TOC measurements, while QASUME and BTS are. In my opinion the main outcome of this study is that the presented method provides more accurate estimations of the uncertainty budget compared to the traditionally used methods. However, it is not adequate for properly estimating uncertainties if the instruments are not characterized for systematic measurement errors. I suggest re-writing the conclusions section in a way that the main conclusions of the study are highlighted."

Authors: It is true that the conclusions in its present form give too much weight to the comparison of the devices. We will rewrite the conclusions to give more emphasis to the correlation issues. It is worth noting that in response to Referee #2, we revise the algorithm for obtaining TOC from spectra (Please, see separate response letter addressed to Referee #2 for full details). The least squares fitting is modified so that the low irradiance values distorted by stray light with BTS and AVODOR get less weight, and the offset of AVODOR gets corrected. After this change, the results are in better agreement, and the daily variation of TOC seen with BTS and AVODOR diminishes (Please, see new results in Fig. 1R). AVODOR seems to work better than first expected. The results are just noisy but quite well in agreement with other devices. We will write the new conclusions after going through all Referee comments. We need to include some discussion about the model change into the conclusions as well, but we try to keep the emphasis on the uncertainty issue.

Additional notes by the authors

As we modified the retrieval algorithm by including a new offset factor c to compensate for full spectral deviations, the results compared to the AMT Discussion paper will change. We will replace Fig. 5 in the AMT Discussion manuscript with Fig. 1R shown in this document.