

Response to Christoph Kern - RC2

Interactive Comment from Review #2

The author thanks Dr. Kern for reading and providing useful comments on the discussion paper.

Specific Issues

Paragraph 1 It is my experience that imperfect representation of the differential ozone absorption in the 300 to 340 nm region in the DOAS model can lead to errors in retrieved SO₂ column densities. These effects are not captured by the authors' experiments because they did not assess the effect of a varying solar zenith angle (SZA) and hence a change in the ozone SCD on their results. My worry is that these might affect the recommendations for wavelength fit window, possibly leading the authors to consider broadening the window to allow for better discrimination between SO₂ and O₃. To address this issue, the experiments could be repeated for a time early in the morning or late in the evening when the O₃ SCD is changing rapidly with time...

- Response:

Assessment of the impact of differential ozone absorption under varying solar zenith angle conditions are beyond the scope and has been added as a study limitation on Page 10 Lines 28-31. Recommendations that future work repeats the experiments under different solar geometry to address this issue are included on Page 10 Lines 31-32.

“A limitation of this study is the lack of measurements at high solar zenith angles (near dawn and dusk) when the SCDs of O₃ are larger and change rapidly with time. In such cases, fit accuracy may benefit from extending the upper limit of the fit window to allow better discrimination between the differential absorption features in the O₃ and SO₂ cross-sections.”

Paragraph 2 I recommend the authors review the literature with regards to state-of-the-art Ring correction, in particular focusing on an additional dependency of the Ring effect on wavelength (Vountas et al., 1998 Langford et al., 2007), the potential impact of vibrational Raman scattering (Lampel et al., 2015), and the effect of the broad-band shape of the solar spectrum as it reaches the Earth's surface (Lampel et al., 2017).

- Response to Dependency of the Ring on wavelength in Langford et al. (2007):

The inclusion of an adjustable parameter to the non-linear fitting steps of the DOAS analysis to compute the pseudo-absorption Ring cross-section in Langford et al. (2007) is mathematically non-trivial. It requires altering the DOASIS software algorithm or developing one's own algorithm, which is beyond the scope of this study. This study aims to provide information on some fitting parameters available in the widely used DOASIS software. The possibility of adding this correction to the analysis in a future study has been added on Page 10 lines 25-27.

“The DOAS analysis could also be expanded to include a correction to reduce impacts of wavelength dependence of the Ring effect in the near UV due to aerosol and multiple Rayleigh scattering as described in Langford et al. (2007).”

- Response to Potential Impact of vibrational Raman scattering in Lampel et al. (2015):

After becoming familiar with the potential impacts of vibrational Raman scattering (VRS) on DOAS fits and communicating with Dr. Johannes Lampel, it was determined that the VRS effect should be negligible in this deeper UV range. This is due to lack of strong Fraunhofer lines at wavelengths less than the fitting window to produce non-trivial N₂ and O₂ VRS components, the lack of light at these lower wavelengths present below the O₃ layer to be

scattered by VRS into the higher wavelengths of the fit window, and given the size of the fit residuals due to noise etc. In Lampel et al. (2015), the effect in the blue wavelength range was already small. Also, most of the added intensity due to VRS can be compensated by the offset polynomial in the absence of larger Fraunhofer or terrestrial absorption lines in the original intensity.

Response to the effect of the broad-band shape of the solar spectrum as it reaches the Earth's surface in Lampel et al. (2017):

Shift and squeeze terms were included in the fits not only for the absorption cross sections but also the FRS/Ring spectra, which should compensate for the tilt effect (Lampel, 2017). This information and a short description of the tilt effect is now included in the Methods section on Page 5 lines 10-19.

“The shift and squeeze terms were allowed for the fit components with the Ring spectrum terms linked to the FRS terms and the O₃ spectra terms linked to the SO₂ terms (shift limited to -0.2 to 0.2 nm). The shift and squeeze terms are included in DOAS analyses to compensate for wavelength shifts due to instrumental instabilities, such as temperature changes during measurements altering the pixel-to-wavelength calibration (Lampel et al., 2017; Stutz and Platt, 1996). In the case of the FRS, the shift and squeeze terms also compensate for the “tilt effect” that increases fit residuals by artificially shifting the spectral positions of Fraunhofer and molecular absorptions lines between the measurement and reference spectra that have different viewing elevation angles (Lampel et al., 2017). The tilt effect arises because atmospheric modification of the spectral structures in the spectrum occurs before convolution with the instrument slit function and are non-commutative but are applied in the reverse order by the analysis procedure (Lampel et al., 2017).”

Paragraph 3 Finally, it's a bit unclear to me how representative the results are for MAX-DOAS instruments in general. The authors use an Ocean Optics USB2000 spectrometer for their measurements. This instrument is very common and therefore represents a good choice for such a study. However, it is my experience that these relatively economical instruments suffer from a relatively poor stray-light rejection. Therefore, it is no surprise that suppression of stray light using an optical filter and/or accounting for it in the DOAS fit improves the results of the retrieval. At the same time, these results and recommendations may not apply to other, higher quality instruments. It would be of great value if the authors were able to compare their results with those obtained using a higher-grade spectrometer. If this is not possible, the authors should consider explicitly narrowing the scope of their manuscript to reflect the fact that the experiments were all made using this one type of instrument. For example, the authors might include the terms 'low-cost' or 'miniature' in the title and mention the make and model of the spectrometer in the abstract and prominently throughout the manuscript.

- Response:

This is a good point, and the scope of the manuscript has been clarified by specifying that the measurements were conducted using a mini-MAX-DOAS instrument with a compact OceanOptics USB2000 spectrometer. The term 'miniature' (as 'mini') was added to the title. The spectrometer type and 'miniature' MAX-DOAS type was added to the abstract (Page 1 Line 10) and the Summary & Recommendations section (Page 9 lines 32-33). It is now noted that the OceanOptics USB2000 spectrograph is a relatively low-cost spectrometer in the Methods section (Page 4 line 15) and Summary & Recommendation Section (Page 11 Lines 16-18). It is also mentioned that these compact spectrometers tend to suffer from stray light impacts on Page 2 line 17.

Page 4 Line 15: “The MAX-DOAS instrument used a **relatively low-cost and commonly employed compact spectrometer**, an OceanOptics USB2000 spectrograph.”

Page 11 lines 16-18 “Ultimately, the use of higher quality spectrometers with reduced stray light and improved spectral resolution for MAX-DOAS measurements is desirable, but a greater expense **compared to the low-cost spectrometer used in this study.**”

Minor Issues and Corrections

1) P1L11 – I recommend rewording “the dSCDs also exhibited an inverse relationship with the DEPTH OF THE DIFFERENTIAL FEATURES IN THE SO₂ absorption crosssection :”

Response: This sentence was reworded according to the recommendation (Page 1 lines 11).

2) P1L15 – “: : dependence on the SO₂ absorption features SUGGESTING THAT THE RADIANCE AT SHORTER WAVELENGTHS WAS increased by stray light: :”

Response: This sentence was amended according to the recommendation (Page 1 line 17).

3) P1L18 and P7L25 – The uncertainty reported by the fit is not necessarily expected to be an accurate measure of the errors of the results. This is discussed by Stutz and Platt (1996). Please incorporate this information into your discussion.

Response: This is a good point and the information was incorporated into the discussion on Page 9 Lines 7-14 . A set of figures showing the proportion of the fit uncertainty to the fit error for the 2^o spectra of both cell concentrations was added to the supplemental (Fig. S2 on Supplement Page 2) for the reader to be able to interpret the percentage degree of deviation between the values. This figure is referred to in the manuscript on Page 9 on lines 22, 25 and 28. The percentage deviation is also referred to in the abstract on Page 1 line 20.

Page 9 Lines 7-14: “While the fit uncertainty reported by the retrieval is commonly used as the error on the retrieved dSCD, this uncertainty is not always expected to accurately represent the true error due to factors including assumptions about the independence of errors, the presence of noise in the spectrum and structures in the fit residual (Stutz and Platt, 1996). Tests of modelled spectra with noise added found that when noise becomes large, the true errors of the retrieved trace-gas coefficient were >10% larger than the retrieved error and the difference was proportional to the noise level. Also, the inclusion of random residual structures in the spectra caused the fit uncertainty to underestimate the true error by a factor of 3 (Stutz and Platt, 1996). It is useful to examine which fitting windows exhibited the greatest difference between the fit uncertainty and error, shown in the right columns of Figs. 9 and 10.”

4) P2L6 – I suggest adding “typically” before “uses the SO₂ B band: :”

Response: “Commonly” was added (Page 2 Line 7).

5) P2L15 – In my experience, it can be beneficial to include wavelengths with weak or negligible SO₂ absorption in the fit if the extended wavelength range allows for better discrimination between SO₂ and other aspects of the DOAS model (Ozone absorption, Ring effect).

Response: Agreed, the reviewer makes a good point. This clarification was included as “Inclusion of upper wavelengths with weak SO₂ in the fit can improve the fit results by allowing a better distinction between SO₂ absorption features and other fit components (e.g., O₃ absorption features, Ring spectrum).” (Page 2 line 26-29).

6) P3L6 – “: : : may NOT BE IDEAL for smaller: :”

Response: Amended accordingly (Page 3 Line 32).

7) P3L23 – please remove the superscript formatting on the “C”.

Response: Removed on Page 4 Line 19.

8) P3L30 – Please clarify how the 87 ppb were arrived at. I think this is assuming that the 30 degree spectra were evaluated relative to a reference recorded looking towards the zenith through the same atmospheric boundary layer, correct?

Response: The calculations had an error and have now been updated to the correct values of 41 and 4 ppb on Page 4 Line 26. These values were determined by calculating the SO₂ VCD using Eq. (2) in Davis et al. (2019) since the FRS was measured without the cell and should have negligible SO₂, similar to the Davis et al. (2019) mobile-MAX-DOAS measurements using Eq. (2) where the measurement spectrum observed within a polluted mass but the FRS observed in a clean region within a short time period. The method was clarified and reference to this equation was added on Page 4 Lines 27-28. The mixing ratio was then calculated assuming a boundary layer height of 1000 m contained all the SO₂ in the VCD and the density of air given standard temperature and pressure conditions.

9) P3L31 – Please include the time at which the measurements were made. This will allow the readers to deduce the solar zenith angle. How far apart in time where the 2-degree and 90-degree measurements made?

Response: The measurements were conducted on September 23 between 12:53 and 13:26 (local time). The time between the 2° and 90° measurements in the same sequence (both containing the SO₂ cell) was less than 13 minutes. The zenith spectra without a cell used as the FRS were obtained less than 35 minutes after the respective cell measurements. This information was added on page 3 lines 29-33.

10) P4L2 – In the future, you might consider using a Hoya U330 filter. I believe this has better rejection of NIR radiation which can cause stray light in the spectrometer.

Response: Thanks for the suggestion. We will try this filter in future.

11) P5L23 – Wavelengths longer than 324 nm are commonly used in volcanic gas measurements. While they admittedly often encounter larger SO₂ SCDs, it's not clear to me that these wavelengths can be discounted across the board for MAX-DOAS measurements simply based on the increased DOF. See comment above on improved discrimination between SO₂, ozone and Ring features.

Response: Agreed. The sentence referring to DOF was removed (Page 7 lines 2-3). The potential benefit of extending the upper limit to longer wavelengths has been added to Introduction on Page 2 lines 26-29.

“However, an overly narrow fit window can lead to cross-correlation between the reference absorption cross-sections (Vogel et al., 2013). Inclusion of upper wavelengths with weak SO₂ in the fit can improve the fit results by allowing a better distinction between SO₂ absorption features and other fit components (e.g., O₃ absorption features, Ring spectrum).”

12) P5L29 – It's not clear to me how increased Rayleigh scattering due to higher air pressure would preferentially remove shorter UV wavelengths. Is there a citation that you could provide for this? Couldn't one just as easily argue that increased Rayleigh scattering of previously unscattered sunlight would increase the measured radiance at shorter wavelengths? I suspect that another effect or combination of effects is responsible, possibly having to do with radiation being removed from the atmospheric half-sphere by absorption on the ground. In this case, it might be the wavelength dependence of the ground albedo that is responsible.

Response: Since the cause(s) are uncertain for the relatively smaller UV signal in lower compared to higher elevation angle measured spectra this sentence was removed, it being not essential to the manuscript (Page 6 lines 7-9).

13) P7L3 – I suspect you meant to write “ $\lambda > 307 \text{ nm}$ ” here?

Response: Correct, thanks for catching that. Corrected on Page 8 line 16.

14) P7L5 – Again, I suggest rewording to “an inverse relationship with the DEPTH OF DIFFERENTIAL SO₂ ABSORPTION FEATURES: : :”

Response: Reworded accordingly on Page 8 Line 18.

15) P7L14 – “: : : absorption minimum and STRAY light: : :”

Response: Typo corrected on Page 9 line 29.

16) P7L20 – “due TO the increasing: : :”

Response: Typo corrected on Page 9 line 1.

17) P7L20 and P8L18 – You mention “absorption non-linearity effects” here. In my opinion, this is a bit misleading because the DOAS model does not actually require the absorption to be linearly related to the dSCD. Instead, the optical depth (= logarithm of I/I₀) is considered proportional to the SCD, as is described by the Beer-Lambert-Bouguer Law. The issue is actually more complex and has to do with the non-commutative nature of the convolution of absorption cross-sections and the application of the Beer- Lambert Law. Details can be found in Platt and Stutz (2008).

Response: Agreed, the comments on “non-linearity” effects were unclear. The non-linearity phenomenon is now explained in greater detail in the Introduction on Page 2 line 33 to Page 3 line 13. The effect also was better clarified in the results and summary sections on Page 6 lines 25-31 and Page 10 line 11-13, respectively.

Page 2 line 33 – Page 3 line 13: “A further complication is that for measurements of very large column densities of SO₂ (e.g., from volcanic studies), the optimal wavelength window may be present at higher wavelengths where SO₂ absorption features are weaker (Bobrowski et al., 2010). High optical densities below 320 nm from large column densities can cause non-linearities in the relationship between the column density and measured optical density in the fit. This phenomenon occurs for large (actual) optical densities if the cross-section in the fit was not recorded with the same spectrometer as the measurements, which is common, and the instrument’s spectral resolution is too low to completely resolve the absorption bands (Kern, 2009; Platt and Stutz, 2008). Large column densities of SO₂ result in optical densities in the B band that can exceed unity, violating the assumption in the standard DOAS retrieval of weak absorption with optical depths of less than ~0.1 (Bobrowski et al., 2010; Bobrowski and Platt, 2007; Fickel and Delgado Granados, 2017; Kern, 2009; Platt and Stutz, 2008). Compact spectrometers typically have an insufficient spectral resolution for the optical density of the SO₂ absorption bands to be proportional after convolution for large column densities (Bobrowski et al., 2010; Platt and Stutz, 2008). Consequently, the true column density can be underestimated because the differential absorption line depths from the standard DOAS convolution approximation can be greater than mathematically correct convolution (Bobrowski et al., 2010; Kern, 2009; Yang et al., 2007). Underestimation has been shown to increase with decreasing wavelength from 320-300 nm and increasing column density of SO₂ (Kern, 2009).”

18) P7L34 – “fit error was $> 1.1 \times 10^{-6}$: : :” (remove two instances of “greater”/“greater than”)

Response: First instance of “greater” removed on Page 9 line 25.

19) P8L11 – I did not understand this sentence. Can you clarify what you mean by “could be overestimated by the same windows for low concentration measurements.”?

Response: The sentence is referring to the “direction” of the error in SO₂ dSCD being inconsistent for windows with lower limit <307 nm between the higher and lower concentration cells. That is, the higher cell retrievals from these windows generally overestimated dSCD but the lower cell retrievals often underestimated. The sentence was edited and is, hopefully, now clear on Page 10 Lines 4-6.

20) P8L13 – suggest adding “known” before “fit error for many windows”.

Response: “Known” added on Page 10 line 7.

21) **P8L18** – Whether or not strong absorption effects related to the convolution contributed to the errors here might be assessed by comparing two synthetic spectra calculated for a known SCD: $\text{conv}(\exp(-\sigma_{\text{HiRes}} \cdot \text{SCD}))$ compared with $\exp(-\text{conv}(\sigma_{\text{HiRes}}) \cdot \text{SCD})$

Response: This sentence has been removed as now superfluous based on the greater clarification and discussion of non-linearity effects in Section 3.1 on Page 6 lines 25-31. This includes referring the reader a figure in Kern (2009) showing the percentage underestimation of the SO₂ column density under varying actual column densities that include the levels tested here using a similar spectral resolution (Page 6 lines 29-31).

22) P8L20 – “DEPTH OF features: : :”

Response: Amended accordingly on Page 10 line 17.

23) P12L3 – “<10% less OR >10% more: : :”

Response: Corrected on Page 15 line 1.

24) P14Figure4 – Please provide units for the y axis.

Response: Units added to Y-axis of Figure 4 on Page 16.

25) **P17Figure7** – It could be worth pointing out that using starting wavelengths of 304 vs 308.5 nm changes the results by an order of magnitude (!) for the base case.

Response: This observation has been added on Page 8 lines 22-24.

Citations Mentioned

Bobrowski, N., Kern, C., Platt, U., Hoermann, C. and Wagner, T.: Novel SO₂ spectral evaluation scheme using the 360-390 nm wavelength range, *Atmospheric Meas. Tech.*, 3(4), 879–891, doi:10.5194/amt-3-879-2010, 2010.

Davis, Z. Y. W., Baray, S., McLinden, C. A., Khanbabakhani, A., Fujs, W., Csukat, C., Debosz, J. and McLaren, R.: Estimation of NO_x and SO₂ emissions from Sarnia, Ontario, using a mobile MAX-DOAS (Multi-AXis Differential Optical Absorption Spectroscopy) and a NO_x analyzer, *Atmospheric Chem. Phys.*, 19(22), 13871–13889, doi:10.5194/acp-19-13871-2019, 2019.

Fickel, M. and Delgado Granados, H.: On the use of different spectral windows in DOAS evaluations: Effects on the estimation of SO₂ emission rate and mixing ratios during strong emission of Popocatepetl volcano, *Chem. Geol.*, 462, 67–73, doi:10.1016/j.chemgeo.2017.05.001, 2017.

Kern, C.: Spectroscopic measurements of volcanic gas emissions in the ultra-violet wavelength region, Ph.D. Thesis, University of Heidelberg, Germany, 318 pp., <https://doi.org/10.11588/heidok.00009574>, 2009.

Lampel, J., Frieß, U. and Platt, U.: The impact of vibrational Raman scattering of air on DOAS measurements of atmospheric trace gases, *Atmospheric Meas. Tech.*, 8(9), 3767–3787, doi:<https://doi.org/10.5194/amt-8-3767-2015>, 2015.

Lampel, J., Wang, Y., Hilboll, A., Beirle, S., Sihler, H., Pukite, J., Platt, U. and Wagner, T.: The tilt effect in DOAS observations, *Atmospheric Meas. Tech.*, 10(12), 4819–4831, doi:<https://doi.org/10.5194/amt-10-4819-2017>, 2017.

Langford, A. O., Schofield, R., Daniel, J. S., Portmann, R. W., Melamed, M. L., Miller, H. L., Dutton, E. G. and Solomon, S.: On the variability of the Ring effect in the near ultraviolet: understanding the role of aerosols and multiple scattering, *Atmospheric Chem. Phys.*, 7(3), 575–586, doi:<https://doi.org/10.5194/acp-7-575-2007>, 2007.

Platt, U. and Stutz, J.: *Differential optical absorption spectroscopy : principles and applications*, Springer Verlag, Berlin., 2008.

Pukite, J., Kuehl, S., Deutschmann, T., Platt, U. and Wagner, T.: Extending differential optical absorption spectroscopy for limb measurements in the UV, *Atmospheric Meas. Tech.*, 3(3), 631–653, doi:[10.5194/amt-3-631-2010](https://doi.org/10.5194/amt-3-631-2010), 2010.

Theys, N., De Smedt, I., van Gent, J., Danckaert, T., Wang, T., Hendrick, F., Stavrakou, T., Bauduin, S., Clarisse, L., Li, C., Krotkov, N., Yu, H., Brenot, H. and Van Roozendael, M.: Sulfur dioxide vertical column DOAS retrievals from the Ozone Monitoring Instrument: Global observations and comparison to ground-based and satellite data, *J. Geophys. Res.-Atmospheres*, 120(6), 2470–2491, doi:[10.1002/2014JD022657](https://doi.org/10.1002/2014JD022657), 2015.

Theys, N., De Smedt, I., Yu, H., Danckaert, T., van Gent, J., Hoermann, C., Wagner, T., Hedelt, P., Bauer, H., Romahn, F., Pedernana, M., Loyola, D. and Van Roozendael, M.: Sulfur dioxide retrievals from TROPOMI onboard Sentinel-5 Precursor: algorithm theoretical basis, *Atmospheric Meas. Tech.*, 10(1), 119–153, doi:[10.5194/amt-10-119-2017](https://doi.org/10.5194/amt-10-119-2017), 2017.

Theys, N., Hedelt, P., De Smedt, I., Lerot, C., Yu, H., Vlietinck, J., Pedernana, M., Arellano, S., Galle, B., Fernandez, D., Carlito, C. J. M., Barrington, C., Taisne, B., Delgado-Granados, H., Loyola, D. and Van Roozendael, M.: Global monitoring of volcanic SO₂ degassing with unprecedented resolution from TROPOMI onboard Sentinel-5 Precursor, *Sci. Rep.*, 9(1), 1–10, doi:[10.1038/s41598-019-39279-y](https://doi.org/10.1038/s41598-019-39279-y), 2019.