Recommendations for Spectral Fitting of SO_2 from mini-MAX-DOAS Measurements

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Response to RC1

Interactive Comment from Review #1

The author thanks referee #1 for reading and providing useful comments on the discussion paper.

General Considerations

1) How would you use the recommendations discussed in the article with satellite comparisons?

Response: The recommendations are not applicable for satellite measurements since the spectrometers used in satellites are typically much higher quality, and the radiative transfer can be much different. The recommendations in the current study are intended to be representative of low-cost, compact spectrometers such as the OceanOptics USB2000, which is commonly used in mini-MAX-DOAS measurements. For comparison, the TROPOMI satellite spectrometer has a signal-to-noise ratio of 1000:1 and spectral resolution of 0.54 nm in the SO_2 fitting region compared to 250:1 and 0.72 nm for this MAX-DOAS spectrometer. The scope of the recommendations has been greater clarified by including the term 'miniature' (as 'mini') in the title. The spectrometer type and 'miniature' MAX-DOAS type was also added to the abstract (Page 1 Line 10) and the Summary & Recommendations section (Page 9 lines 32-33). It is also 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 Line 16-18).

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

If this comment was referring to the utility of comparing MAX-DOAS and satellite measurements of SO_2: MAX-DOAS measurements are well suited to help validate satellite retrievals as satellite measurements gain increasingly better horizontal pixel resolution that becomes closer to the spatial resolution of MAX-DOAS instruments (i.e., a few kilometres). For example, MAX-DOAS VCDs could provide important validation for satellite retrievals of trace-gases, which depend on modelled a-priori profiles of the gases that may not resolve small areas.

2) Have you tried the 315-325 nm window fit?

Response: Yes, the results of the 315-325 nm window fit are shown in Figs. 2 and 5 for the higher and lower concentration cells, respectively. This window overestimates the true SO_2 dSCD by >10% and >50% for the higher and lower concentration cells, respectively, for all fit scenarios and both the 2° and 30° measurement spectra (Figs. 2 and 5).

3) Have you thought in a comparison, using the window fit recommend, with satellite? OMI? TROPOMI?

Response: The recommended fit window is not intended for use with satellite measurements because spectrometers in satellites are typically much higher quality with higher resolution and reduced stray light (see response to General Consideration Comment #1). Also, satellite measurements can have additional fitting issues affecting the optimal fitting window, and they often observe much greater SCDs (e.g., over volcanoes) than in urban areas.

The recommended window is not appropriate for satellites since satellite retrievals (e.g., GOME, OMI) use the 310-326 nm range. This range is used because increased Rayleigh scattering and O_3 absorption results in a small SO_2

signal relative to O_3 absorption in the spectrum at lower wavelengths (Theys et al., 2017). For example, TROPOMI retrievals use the 312-326 nm window as a baseline for SCDs $\leq 4 \times 10^{17}$ molec. cm^{-2} (15 DU) (Theys et al., 2017). Changing the window to 310.5-326 nm to include an additional SO_2 band reduced sensitivity to lower troposphere absorption by SO_2 and only a small improvement in data scatter from OMI satellite measurements of SO_2, attributed to decreased intensity and signal-to-noise ratio in the short UV due to strong absorption by O_3 (Theys et al., 2015). Additional fitting issues specific to satellite retrievals of SO_2 compared to MAX-DOAS include much longer light path lengths requiring added corrections for wavelength dependence of the light path and absorption by trace-gases, such as O_3, (Pukite et al. 2010) that are used in the TROPOMI retrievals (Theys et al., 2017).

Note that for TROPOMI retrievals of SO_2 SCDs $>4 \times 10^{17}$ molec. cm^{-2} (15 DU), an alternate window of 325-335 nm is used. If the first alternate window retrieves an SCD >250 DU, the second alternate fitting window of 360-390 nm is used to avoid signal saturation (Theys et al., 2017; Theys et al., 2019). The need for fitting windows at higher wavelengths for very large SO_2 column densities is more fully discussed in the Introduction (Page 2 lines 33 to Page 3 line 13). Therefore, using the recommended fit window for satellite measurements would likely result in under-estimated SO_2 for moderate to large SCDs values.

Page 2 line 33 – Page 3 line 13: "A further complication is that for measurements of very large column densities of SO_2 (e.g., from volcanic studies), the optimal wavelength window may be present at higher wavelengths where SO_2 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 SO_2 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 SO_2 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 SO_2 (Kern, 2009)."

4) Is it necessary to correct the ring effect if active DOAS is used?

Response: It is not necessary to correct for the Ring effect if using active DOAS. For cavity enhanced active DOAS (CE-DOAS), the Ring effect is not an issue because the light source is artificial, and the light path is inside a closed cavity. For long path DOAS (LP-DOAS), the instrumental set-up (e.g., path length and retroreflector properties) ensures that the lamp signal is strong enough for the contribution of scattered light to the measured spectrum to be trivial enough not to require correction.

5) It would be very useful to include in the article measurement of calibration cells with high SO_2 concentrations ($\sim 10^{19}$), applying the recommendations presented in the article and discussing the results.

Response: Measurements of such high concentrations are outside of the scope of this study since the aim was to represent a range of SO_2 expected in urban settings, as stated on Page 4 Line 9. Other studies have addressed retrieving SO_2 using DOAS at such higher column densities, including Bobrowski et al. (2010) and Fickel and Delgado Granados (2017), and the readers are referred to these works in the Summary and Recommendations section (Page 9 Line 34 to Page 10 Line 1). The Bobrowski et al. (2010) may be of interest here as it provides examples of using different fitting windows for SO_2 from both MAX-DOAS and GOME-2 satellite measurements.

Future MAX-DOAS studies could repeat the current study with such higher concentrations (3 cells) for applications where both anthropogenic ambient/megacity and volcano emissions are to be observed.

Specific Consideration

1/ Introduction Line 34: Rix et al., 2012, spectral range fit between 315 and 326 nm.

Response: Upper range value corrected on Page 2 Line 13.

2/ Introduction Line 43: verify reference "Wang and Christopher, 2003", is it correct?

Response: The reference was incorrect, thanks for catching the mistake. The reference was replaced by the correct reference, Tan et al. (2018) on Page 3 Line 25.

3/ Methods Line 55: Instrument resolution (FWHM) are calculated or is the information provided by the company (in this case, Ocean Optics)? The company provides an average resolution of the entire spectral range of the insturment and not in the specific absorption range of a given compound (e.g. SO2, NO2, etc..).

Response: The FWHM was measured using a Hg lamp and Gauss fitting the Hg emission line at 334 nm. The value of 0.7 nm on Page 4 Line 18.is the measured value, rather than the provided value.

4/ Methods Line 58: "using the DOASIS software package". Why using DOASIS? In my opinion, QDOAS is currently the best and most widely used software for the fitting of contaminating compounds in the atmosphere with ground-based techniques.

Response: DOASIS is commonly used software for MAX-DOAS applications and has been used for all DOAS measurements in our research group. For future measurements, we can try the recommended QDOAS software.

5/ Line 61-62: Be careful to use high and low concentration referring to the calibration cells. I disagree in considering a concentration of 1e17 as "high". This is relative. What are you talking about? Contaminated areas? industrial areas? volcanic areas? Megacities? The SO_2 concentrations of 1e17 molec/cm2 (occasionally 1e18) are "high" considering anthropogenic contaminated areas, such as megacities or/and industrial areas. Volcanic SO_2 concentrations can reach 1e19 molec/cm2. Using instruments such as UV camera, very concentrated calibration cells are needed (1e19 molec/cm2), to be able to calibrate the instrument for SO2 concentrated plumes. I suggest specifying the "high concentrations" in the atmosphere of polluted areas, like megacities.

Response: This is a good point. For greater clarity, the "high" and "low" concentration cell measurements are now referred to as "higher" and "lower" throughout the manuscript and supplemental. It is specified that the calibration cells are intended to be representative of polluted urban conditions in the introduction on Page 4 Line 9.
This point and the presence of greater SCDs in volcanic or major industrial areas are included in the Summary & Recommendations section on Page 10 Lines 33-34. This includes references to studies relevant to fitting such SO_2 greater SCDs.

Page 10 Lines 33-34 "Greater SO_2 column densities (>$1x10^{18}$ molec. cm^{-2}) can be observed in volcanic areas and close to major industrial sources; discussions of retrieving such greater SO_2 column densities can be found in Bobrowski et al. (2010) and Fickel and Delgado Granados (2017)."

6/ Introduction Line 63: "These SCDs would be equivalent to an air mass with SO_2 mixing ratios of 87 and 8.7 ppb: : :". Is the calculation correct? How did you calculate these values?

Response: The calculations had an error and have now been corrected to the values of 41 and 4 ppb. These values were determined by calculating the SO_2 VCD using Eq. (2) in Davis et al. (2019) since the FRS was measured without the cell and should have negligible SO_2, similar to the conditions of 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 reference to this equation was added on Page 4 Lines 25-28. The mixing ratio was then calculated, assuming a boundary layer height of 1000 m contained all the SO_2 in the VCD and the density of air given standard temperature and pressure conditions.

Final Consideration

Personally, I tried to apply the recommendations, discussed in the article, on the best SO2 fitting windows. I compared, using MAX-DOAS and Direct Sun techniques, the 307.5-319 nm window fit with other windows fit used in the literature. The 307.5-319 nm window fit work well in anthropogenic contaminated areas, I was able to recover more spectra and obtaining a lower RMS than other windows fit. On the other hand, the results obtained by testing the recommended window fit with very concentrated calibration cells (_1e19), greatly underestimate the real concentration inside the cells.

Response: See the responses to comments General Considerations #5 and Specific Considerations #5.