Response to Jochen Stutz, Editor

Thanks for your efforts in editing this paper. The two reviewers provided very insightful comments. We have responded to all those comments and suggestions, and feel the manuscript has been significantly improved as a result. You will find numbered responses to each reviewer below, followed by a Track Changes version of the paper. Thanks again. ZD & RM

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 $\leq 4x10^{17}$ 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 $>4x10^{17}$ 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 (~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.

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 O_3 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 O_3 and SO_2 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 N_2 and O_2 VRS components, the lack of light at these lower wavelengths present below the O_3 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 O_3 spectra terms linked to the SO_2 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° 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 SO_2 in the fit can improve the fit results by allowing a better distinction between SO_2 absorption features and other fit components (e.g., O_3 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 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 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 SO_2 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 SO_2 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 SO_2 in the fit can improve the fit results by allowing a better distinction between SO_2 absorption features and other fit components (e.g., O_3 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 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 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)."

18)   P7L34 – "fit error was > 1.1e16: : :" (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 SO_2 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: conv(exp(-sigmaHiRes*SCD)) compared with exp(-conv(sigmaHiRes)*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 SO_2 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

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Recommendations for Spectral Fitting of SO$_2$ from <u>mini-</u>MAX-DOAS Measurements

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Abstract. Fitting SO$_2$ dSCDs from MAX-DOAS measurements of scattered sunlight is challenging because actinic light intensity is low in wavelength regions where the SO$_2$ absorption features are strongest. SO$_2$ dSCDs were fit with different wavelength windows (λ_{low} to λ_{high}) from ambient measurements with calibration cells of 2.2×10^{17} and 2.2×10^{16} molec cm^{-2} inserted in the light path at different viewing elevation angles <u>using an OceanOptics USB2000 spectrometer in a miniature-MAX-DOAS instrument</u>. SO$_2$ dSCDs were the least accurate and fit errors were the largest for fitting windows with $\lambda_{low} < 307$ nm or $\lambda_{low} > 312$ nm. The SO$_2$ dSCDs also exhibited an inverse relationship with the <u>depth of the differential features in the</u> SO$_2$ absorption cross-section for fitting windows with $\lambda_{low} < 307$ nm. Spectra measured at low viewing elevation angles (i.e., $\alpha = 2^o$) exhibited less accurate SO$_2$ dSCDs for the same fitting windows compared to higher angles. The use of a 400 nm short-pass filter or a polynomial to account for stray light (the offset function), increased the accuracy of the SO$_2$ dSCDs for many different fitting windows, decreased fit errors, and decreased the dSCDs' dependence on the <u>depth of the</u> SO$_2$ <u>differential</u> absorption features. <u>These results suggest that the radiance at shorter wavelengths was increased by stray light</u>. The inaccuracies at lower fitting wavelengths were increased by stray light originating from light with $\lambda > 400$ nm. Deviation of the SO$_2$ dSCD from the true value depended on the SO$_2$ concentration for some fitting windows rather than exhibiting a consistent bias. Uncertainties of the SO$_2$ dSCD reported by the fit algorithm were <u>>50%</u> less than the true error for many windows, particularly for the measurements without the filter or offset function. For retrievals with the filter or offset function, increasing $\lambda_{high} > 320$ nm tended to decrease the reported fit uncertainty but did not increase the accuracy. Based on the results of this study, a short-pass filter and a fitting window of $307.5 < \lambda < 319$ nm are recommended <u>for retrieval of SO$_2$ SCDs from mini-MAX-DOAS measurements</u>. If a filter is not available or conflicts with other species to be determined (NO$_2$, HCHO, etc.), the offset function should be enabled, and a fit window $307.5 < \lambda < 319$ nm is still recommended.

1 Introduction

The Differential Optical Absorption Spectroscopy (DOAS) technique has been used since its introduction by Brewer et al. (1973), Noxon (1975), Perner et al. (1976), and Platt et al. (1979) to measure atmospheric species with narrow-band structures of absorption in the visible and near UV wavelength region. A major challenge for the successful determination of trace-gas of Slant Column Densities (SCDs) using the DOAS method is the optimization of the retrieval parameters (Platt and Stutz,

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2008; Vogel et al., 2013). These parameters depend on the atmospheric composition, measurement conditions, and which DOAS instrument is used. The wavelength range of the retrieval ("fitting window") is a key parameter that depends on the differential absorption features of the trace-gas (Vogel et al., 2013). Retrieval of differential SCDs (dSCDs) of SO_2 from Multi-Axis-DOAS (MAX-DOAS) measurements is challenging in a number of ways, including because the SO_2 absorption features are strongest in the wavelength region where the intensity of solar light becomes relatively small. There are three major regions of photo-absorption by SO_2 in the UV range: the very weak absorption in the A band from 340-390 nm, the moderately strong B band from 260-340 nm, and the strongest C band from 180-240 nm. MAX-DOAS spectroscopy commonly uses the SO_2 B band in the near UV, which has absorption peaks of increasing strength with decreasing wavelength (Hermans et al., 2009; Xie et al., 2013). Retrievals of SO_2 dSCDs in the 300-325 nm range are complicated by the low intensity of scattered sunlight that results in high photon shot noise (Bobrowski et al., 2010). Actinic flux at the surface level of the earth decreases by several orders of magnitude in the 320-290 nm region due to a steep increase in O_3 absorption with decreasing wavelengths (Kreuter and Blumthaler, 2009). O_3 differential absorption features can also cause interference in the fit because of the similarity to the SO_2 differential absorption features between 315 and 326 nm (Rix et al., 2012). An additional challenge due to the low UV intensity is that stray light in spectrometers can be a significant proportion of the measured signal, causing underestimation of the true optical density (and dSCD) and reducing fit accuracy (Bobrowski et al., 2010; Kreuter and Blumthaler, 2009). Stray light impacts tend to be severe for the widely used compact spectrometers, such as from OceanOptics (Bobrowski et al., 2010). The optimal fitting window for retrieval of SO_2 column densities from MAX-DOAS spectra must have a lower wavelength (λ_{low}) small enough to include strong features of SO_2 absorption but large enough to ensure enough solar signal and prevent significant stray light effects. The upper wavelength of the fit range (λ_{high}) should ensure that the fitting window includes multiple SO_2 absorption structures while excluding wavelengths where SO_2 absorption features are so weak that degrees of freedom (DOF) are unnecessarily increased, increasing fitting uncertainty. MAX-DOAS fit windows must be relatively narrow compared to direct sun viewing applications because the air mass factors used to convert SCDs to vertical column densities (VCD) differ with wavelength due to scattering (Fioletov et al., 2016). An overly broad fit window also risks the inclusion of strong absorption features from other gases (Vogel et al., 2013) and increased errors due to insufficient correction of the broad-band terms (Marquard et al., 2000; Pukite et al., 2010). 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 SO_2 in the fit can improve the fit results by allowing a better distinction between SO_2 absorption features and other fit components (e.g., O_3 absorption features, Ring spectrum).

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

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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). This effect is important for volcanic plume studies and in the most polluted urban and industrial environments.

Despite the importance of using an optimal fitting window, various windows have been used to retrieve MAX-DOAS SO_2 SCDs in the literature, and few studies attempted to assess the impact of the window's wavelength range on the SO_2 SCDs (Vogel et al., 2013). Fitting windows in previous MAX-DOAS studies include 305-317.5 nm (Tan et al., 2018), 307.5-328 (Schreier et al., 2015), 307.6-325 nm (Jin et al., 2016), 307.8-330 nm (Wang et al., 2017), 310-320 nm (Irie et al., 2011), and 307.5 to 315.0 nm (Bobrowski and Platt, 2007). Salerno et al. (2009) examined the sensitivity of SO_2 SCD to the fitting window in the 300-320 nm region using calibration cells of SO_2 of $3.2x10^{17}$ and $8.5x10^{17}$ molec. cm^{-2}. An optimal fitting window of 306.7-314.7 nm was determined based on the smallest SCD errors by varying the wavelengths of the fit window. However, the variations of the lower and upper window limits were only conducted for a single fixed upper limit and lower limit, respectively. Also, since the column densities were relatively large, more representative of volcanic plumes, the determined fitting window may not be ideal for smaller SO_2 column densities often observed in urban studies. Fickel and Delgado Granados (2017) observed a high dependence of SO_2 SCDs from measurements of a volcano plume on the fitting window, particularly for large column densities. The authors suggested using different fitting windows for different column densities: 310-322 nm for SO_2 column densities $<10^{17}$ molec. cm^{-2}, 322-334 nm for column densities $>10^{18}$ molec. cm^{-2}, and 314.7-326.7 nm for intermediate column densities. A modelling study by Bobrowski et al. (2010) suggested using fitting windows in the higher 360-390 nm range for column densities on the order of 10^{19} molec. cm^{-2} because the SO_2 absorption features are much weaker. Therefore, DOAS retrievals of SO_2 from instruments that observe a wide range of column densities can switch fitting windows depending on the magnitude of the retrieved SCDs. For example, TROPOMI satellite retrievals of SO_2 uses 312-326 nm as a baseline window but uses the alternates 325-335 nm for SO_2 SCDs $>4x10^{17}$ molec. cm^{-2} and 360-390 nm for SCDs $> 6.7x10^{18}$ molec. cm^{-2} (Theys et al., 2017).

In this study, MAX-DOAS measurements of two different calibration gas cells with column densities of SO_2 representative of polluted urban conditions were conducted to examine the variation in the retrieved SO_2 dSCDs with 1) different fitting windows, 2) different viewing elevation angles (α), 3) the use of a 400 nm short-pass filter, and 4) the offset function enabled.

2 Methods

The mini-MAX-DOAS instrument (Hoffmann Messtechnik GmbH model #16127) consisted of a sealed metal box with a UV fibre-coupled spectrometer and all electronics inside. Incident scattered sunlight received by the cylindrical black telescope in

front of the entrance optics is focused into the quartz fibre by a cylindrical quartz lens with a focal length of 40 mm. The MAX-DOAS instrument used a relatively low-cost and commonly employed compact spectrometer, an OceanOptics USB2000 spectrograph. The spectrometer has a 50 μm wide entrance slit and a Sony ILX511 linear silicon Charge-Coupled Device (CCD) array detector (2048 pixels, pixel size 14x200 microns, signal-to-noise ratio at full signal 250:1). The spectral range of

5 the spectrometer is 290-433 nm, with a resolution of ~0.7 nm FWHM in the fitting range used. A Peltier stage cooled the spectrograph to maintain the chosen temperature of 5^oC. A stepper motor mounted underneath allows the instrument to point at different α above the horizon. The instrument was connected to a laptop via USB to transfer spectrometer data and allow automated measurements by Jscript programs using the DOASIS software package.

MAX-DOAS spectra of scattered solar light were recorded with an SO_2 calibration gas cell (Resonance Ltd.) inserted in the

10 light path (in the telescope tube). The two cylindrical gas cells with a 22 mm diameter and 14.13 mm thickness had calibrated slant column densities (SCDs) of 2.2×10^{17} molec cm^{-2} (higher) and 2.2×10^{16} (lower) (+/- 10%) molec cm^{-2}. Active-DOAS measurements of the SO_2 gas cells confirmed the SCDs. These SCDs would be equivalent to an air mass with SO_2 mixing ratios of 41 and 4 ppb, respectively, for a α=30° measurement within a homogeneous boundary layer of 1 km, assuming the measurement was fit against a zenith pointing reference spectrum observing outside of the SO_2-polluted zone, calculated using

15 Eq. (2) in Davis et al. (2019). For each cell, spectra were recorded around solar noon in September in Toronto, Ontario (43.773 N, -79.506 W) between 12:53 and 13:26 local time at α = 90°, 30°, 15°, 8°, 4°, and 2° above the horizon, followed by a 90° measurement without the gas cell. This second zenith measurement was used as the Fraunhofer Reference Spectrum (FRS) in the fit. The time between the 2° and 90° measurements in one sequence (both containing the SO_2 cell) was less than 13 minutes. The FRS were obtained less than 35 minutes after the beginning of the respective sequence of cell measurements. Each

20 recorded spectrum was the average of 1000 spectra with an integration time of ~115 ms. The experiment was repeated for both gas cells by placing a 400 nm short-pass filter (Edmund Optics TECHSPEC® OD 2 #47-285) within the telescope between the MAX-DOAS lens and the SO_2 gas cell. The fused silica filter had a thickness of 3 mm, a cut-off wavelength of 400 nm, and a transmission wavelength range of 250-385 nm. The blocking optical density was ≥2.0, and the transmission was >85% in the transmission range. Spectra collected using the filter were fit against a FRS collected by measuring a 90° spectrum

25 without a gas cell but including the filter.

Trace gas differential Slant Column Densities (dSCDs) were obtained using the DOAS method (Platt and Stutz, 2008) with the DOASIS software (Institute of Environmental Physics, Heidelberg University, 2009). All spectra were corrected for dark current and electronic offset, and wavelength calibrated using measurements of a Mercury (Hg) lamp. Included in all fits were a Fraunhofer Reference Spectrum (FRS), Ring spectrum, a 3rd order polynomial, and absorption cross-sections of SO_2 at 293K

30 and O_3 at 293 and 223 K (Bogumil et al., 2003). The shift and squeeze terms were allowed for the fit components with the Ring spectrum terms linked to the FRS terms and the O_3 cross-section terms linked to the SO_2 cross-section 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

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(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 the modifications are non-commutative but are applied in the reverse order by the analysis procedure (Lampel et al., 2017). The cross-sections were obtained from the MPI-MAINZ UV/VIS Spectral Atlas of Gaseous Molecules of Atmospheric Interest (Keller-Rudek et al., 2013). The reported uncertainty in the SO_2 absorption cross-section is ~3% (Bogumil et al., 2003). DOASIS fits dSCDs using an iterative algorithm based on the Levenberg-Marquardt method that finds the optimal solution by minimizing a cost function. The cost function includes the deviation between the measured spectrum and the spectrum modelled using the components included in the fit. Details on the DOASIS fitting algorithm can be found in Kraus (2006). The SO_2 dSCDs were fit in DOASIS with varying fitting windows using λ_{low}= 303-318 nm and λ_{high}= 310-340 nm in ~0.2 nm increments. The "retrieval interval mapping" technique (Vogel et al., 2013) was used to visualized and systematically evaluate the variations in the SO_2 dSCDs. The dSCDs are displayed as contour plots where λ_{low} and λ_{high} are the first and second dimensions, and the dSCDs are denoted using a colour scale.

For each calibration gas cell (higher and lower), four scenarios were fit: i) the base case (B) with no filter and no offset function, ii) no filter with offset function enabled (B+O), iii) with filter and offset disabled (B+F), and iv) with both filter and offset enabled (B+ F+O). SO_2 dSCDs were considered "accurate" if within ±10% of the higher calibration cell value and ±50% of the lower calibration cell value, 2.2×10^{17} and 2.2×10^{16} molec cm^{-2}, respectively. The background SO_2 in the atmosphere in Toronto was assumed to be negligible (<1 ppb) because there are currently no significant sources in Toronto (ECCC, 2018). A few industrial sources of <1600 tonnes of SO_2 yr^{-1} were present south-west of Toronto (ECCC, 2018), but the measurements were conducted under North-Easterly wind conditions. Typical hourly average mixing ratios of SO_2 in northern Toronto are <0.5 ppb (Ontario Ministry of the Environment, 2019).

3 Results

Examples of spectral retrievals of SO_2 from the α=2° spectrum in the base case (no filter and offset function disabled) are shown in Fig. 1.

3.1 Higher Concentration Reference Cell

SO_2 dSCDs fit from the α=2° and α=30° measurements using the higher concentration cell are shown in Fig. 2 with varying fitting windows for the four scenarios. The deviations of the SO_2 dSCDs from the expected value of 2.2×10^{17} molec cm^{-2} (fit errors) are shown in Fig. 3, where purple and green colours indicate under- and over-estimation, respectively. Grey and black areas indicate that the dSCD under- and over-estimated the expected value by more than 8×10^{16} molec cm^{-2}, respectively. For the base case, the windows with λ_{low} <307 nm ("low wavelengths") underestimated the expected SO_2 dSCD, as indicated by the grey areas in Fig. 2 (B) and the purple areas in Fig. 3 (B). The addition of the short-pass filter increased the accuracy of the SO_2 dSCDs for most windows, especially in the low wavelengths (Figs. 2 & 3 (B+F)). These results suggest that stray light originating from wavelengths >400 nm increased the underestimation of SO_2 dSCDs at low wavelengths. Stray light is a well-

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known source of interference in spectroscopic measurements that reduces accuracy and can obscure weak spectral lines (Kristensson et al., 2014). Ideally, a spectrometer's detector receives only light with the correct spectral bandwidth window at each pixel (Lindon et al., 2000). Stray light is additional light of an incorrect wavelength that enhances the background signal in ways that can vary across the spectral range (Kristensson et al., 2014). Sources of stray light include imperfections in the diffraction grating, leakage of light into the instrument, and scattering off mirrors and dust inside the instrument (Lindon et al.,

5   2000). Stray light results in apparent negative deviations from Beer's law (Choudhury and Prayagi, 2015), causing an underestimation of the retrieved SO_2 dSCD by "filling-in" the measured intensity reduced by SO_2 absorption features and an underestimation of the real optical density (Bobrowski et al., 2010). Stray light has an enhanced effect at low wavelengths because of the low measured signal and sensitivity near the lower end of the actinic spectral range (Choudhury and Prayagi,

10 2015). Many fitting windows with λ_{low}<307 nm and λ_{high}< 320 nm still underestimated the SO_2 dSCD even with the filter (Fig. 2 (B+F)). The remaining underestimation is likely due to stray light originating from <400 nm and effects of non-linearity between the column density and measured optical density because of the relatively large differential optical densities of SO_2 of >0.08 in the regions of strong absorption below 307 nm (Fig. 1) (Kern, 2009; Platt and Stutz, 2008). See Fig. 3.21 in (Kern, 2009) for percentages of underestimation by the retrieved column density of the actual column densities (1×10^{17} to 1×10^{19} SO_2

15 molec. cm^{-2}) for windows in the 300-320 nm region and a spectrometer with similar spectral resolution (0.8 nm). Enabling the offset function increased the accuracy of the SO_2 dSCDs of many windows compared to the base case (Figs. 2 & 3 (B+O)). The offset function resulted in slightly more windows with accurate dSCDs than the filter for windows with λ_{low} <311 nm because the offset function attempts to compensate for all the stray light, not just the stray light originating from >400 nm (Fig. 2 (B+F) & (B+O)). The use of both the offset function and the filter slightly improved the dSCD accuracy for a few windows

20 compared to the filter or offset function alone, mostly for windows with large λ_{high} (>324 nm) (Fig. 2 (B+F+O)).
Fitting windows produced more accurate SO_2 dSCDs from spectra measured at higher α (90° & 30°) compared to the lowest α (2° & 4°) in the base case (Figs. 2 & 3 (B) & S1). Windows with λ_{low} <307 nm underestimated SO_2 dSCDs more from the 2° compared to the 30° measurements (Fig. 3 (B)). The spectra collected at higher α are expected to produce more accurate SO_2 dSCDs because of the greater UV signal intensity (Fig. 4). The impact of stray light on fits from the lower angle spectra is

25 further increased because the visible light intensity, a potential source of stray light, is the same or higher compared to measurements at higher α (Fig. 4). The difference in the accuracy of SO_2 dSCDs between low and high α spectra decreased with the use of the filter or the offset function (Figs. 2-3), an expected result.
Fitting windows with λ_{low} >312 nm often overestimated the SO_2 dSCDs for all scenarios, as indicated by the green and black areas in Fig. 3, probably because the SO_2 absorption features become relatively weak (Fig. 4). Fickel and Delgado Granados

30 (2017) proposed the use of the higher wavelength fitting window of 314.7-326.7 rather than 310-322 nm for SO_2 column densities between 10^{17} and 10^{18} molec. cm^{-2}. In contrast, the results of this study found that SO_2 dSCDs from the higher range were less accurate than those from the lower range. The threshold for using fitting windows with higher wavelengths due to large optical densities may be greater than 10^{17} molec. cm^{-2}.

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The SO$_2$ dSCDs exhibited a dependence on the features of the SO$_2$ absorption cross-section for λ_{low} <307 nm for the base case (Figs. 2-3 (B)) that will be discussed in section 3.3.

3.2 Lower Concentration Reference Cell

Figs. 5 and 6 show the SO$_2$ dSCDs and their deviations from the expected value (fit error), respectively, for the lower concentration measurements for all the scenarios. Purple and green areas in Fig. 6 indicate dSCDs were under- and over-estimation, respectively. Black and grey areas indicate dSCDs over- and under-estimated by more than 2.0×10^{16} molec cm^{-2}, respectively. The SO$_2$ dSCDs from the base case exhibited a dependence on the SO$_2$ absorption that will be discussed in section 3.3. In the base case, the lower concentration measurements had fewer windows that produced accurate SO$_2$ dSCDs compared to the higher concentration measurements (Figs. 2 & 5 (B)). Most of the fitting windows produced SO$_2$ dSCDs that were >100% over- or under-estimated for the lower concentration 2° spectrum (Figs. 5 & 6 (B) & S1). In contrast, the lower concentration 90° measurement exhibited accurate SO$_2$ dSCDs for all fitting windows with λ_{low} < 311 nm (Fig. S1). This difference highlights that measurements at lower α experience greater inaccuracies from the reduced solar intensity and greater impact of stray light. While the higher concentration dSCDs from the 2° measurements were consistently underestimated for windows with λ_{low} <307 nm, the lower concentration measurements often overestimated the dSCDs (Figs. 5 & 6 (B)). This overestimation in spite of the influence of stray light could be due to interference from O$_3$ since the similarity between the absorption features of SO$_2$ and O$_3$ can introduce instability in the retrieval (Kraus, 2006; Rix et al., 2012). The deviation of the dSCD from the true value can depend on the SO$_2$ concentration rather than exhibiting a consistent bias for a fitting window. The use of the filter or offset function increased the accuracy of the SO$_2$ dSCDs for most windows for spectra measured at angles ≤15° (Fig. 3 & 6 (B+F), (B+O)). The improved accuracy due to the filter indicates that stray light originating from wavelengths >400 nm significantly decreased the accuracy of the SO$_2$ dSCDs for fitting windows at both lower and higher wavelengths. Unexpectedly, the use of both the filter and offset function for the 30° measurement reduced the accuracy of the SO$_2$ dSCDs compared to the base case for some windows with λ_{low}<307 nm and λ_{high}<320 nm (Fig. 6 (B+F+O)). Since the stray light to signal ratio is expected to be lower for the higher elevation measurements, and the filter already reduced the stray light, the offset function may have incorrectly estimated the relatively small amount of remaining stray light at some wavelengths. The offset function may have added unnecessary freedom to the fit, increasing instability and inaccuracy in the dSCD. Also, the offset function compensates for stray light by assuming the stray light is proportional to the measured intensity (see Eqs. 11-12 in Supplemental). If light from wavelengths outside the fitting window contributes to stray light, this assumption is invalid, and the offset function may increase uncertainty in the fit. The short-pass filter may be the preferred method of reducing the impact of stray light compared to the offset function because the filter directly addresses rather than modelling the source of the problem. However, the problems from using both the filter and offset function can be mitigated by using a fitting window with λ_{low}≥307 nm.

3.3 Dependence of the dSCD on the SO$_2$ Absorption Features

In the base case, the SO$_2$ dSCDs exhibited an inverse relationship with the depth of the differential SO$_2$ absorption features for windows with λ_{low}< 307 nm and λ_{high}<330 nm for non-zenith measurements (Figs. 2 & 5 (B)). The variation in the SO$_2$ dSCD

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as a function of λ_{low} from the $\alpha=2^o$ measurements, given λ_{high} of 315 nm and 324 nm, are shown in Figs. 7 and 8, respectively. The SO_2 dSCDs varied up to 3.4×10^{16} and 3.0×10^{16} molec cm^{-2} for a 0.4 nm change in λ_{low} for the higher and lower concentration measurements, respectively (Figs. 7-8). Note that for the lower concentration measurement, the difference in the retrieved SO_2 dSCDs between using λ_{low} of 304 nm and 308.5 nm is an order of magnitude in the base case (Fig. 7). For both concentrations, using the filter or enabling the offset function reduced the dependence of the dSCDs on λ_{low} (Figs. 7-8) and increased the accuracy of many of the low wavelength fitting windows (Figs. 3 & 6). The SO_2 dSCD dependency was increased by stray light, exhibiting the greatest underestimation when λ_{low} coincided with an SO_2 absorption peak. Errors due to stray light are enhanced in wavelength regions where absorption is high (Choudhury and Prayagi, 2015). The measured signal was further reduced surrounding an SO_2 absorption peak (e.g., ~304.4 nm) compared to an absorption minimum and stray light "filled-in" the decreased intensity due to the absorption maxima. If an absorption peak is the strongest SO_2 feature included in the fit, the resultant deviation between the modelled and measured spectrum in the peak region requires the fit algorithm to underestimate the SO_2 dSCD to minimize the cost function (see Supplemental for fitting algorithm details). The inverse relationship between the dSCD and the SO_2 absorption features was strongest at $\lambda_{low} <307$ nm because absorption was greatest and solar signal was smallest (Figs. 4, 7 & 8). The dSCDs exhibited less dependence on the λ_{low} when $\lambda_{low} = 307\text{-}311$ nm due to increased solar intensity and weaker SO_2 absorption (Fig. 4). For both higher and lower concentration measurements, the anti-correlation of the SO_2 dSCD in the base case was more pronounced for windows with the $\lambda_{high}= 324$ nm than $\lambda_{high}= 315$ nm (Figs. 7-8).

3.4 Fit Uncertainties and Accuracy

The uncertainty in the SO_2 dSCD reported by the fitting algorithm and the actual deviation from the expected value shall be referred to as the "fit uncertainty" and the "fit error," respectively. 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. The divergence is due to factors including assumptions about the independence of errors, and the presence of spectral noise 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. The fit uncertainties from the 2° spectrum are shown for the higher and lower concentration measurements in the left column of Figs. 9 and 10, respectively. The fit uncertainties for the base case were the greatest for windows with $\lambda_{low} <306$ nm and $\lambda_{high} < 315$ nm, and with $\lambda_{low} >312$ nm (Figs. 9 & 10 (B)). The purple and black regions in Figs. 9 and 10 indicate that fit error was greater than the fit uncertainty, and the green regions indicate that fit error was less than fit uncertainty. For the higher concentration measurement in the base case, the fit error was significantly greater than the fit uncertainty (by $>2.2\times10^{16}$ molec cm^{-2}) for most windows when $\lambda_{low} <305$ nm (black regions in Fig. 9 (B)), corresponding to fit uncertainties that were 20-50% of the fit errors (Fig. S2). Therefore, fitting windows for the higher concentration measurements in low wavelength regions (impacted by stray light and non-linearity effects) can not only

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produce less accurate SO_2 dSCDs but also exhibit larger divergences between fit uncertainty and error (Figs. 2, 3 & 9 (B), S2). For the lower concentration measurement, the fit error was >1.1×10^{16} molec cm^{-2} greater than the fit uncertainty for most windows in the base case (black regions in Fig. 10 (B)). The use of the filter or enabling the offset function reduced the fit uncertainties by up to 50% and decreased the difference between the fit errors and uncertainties, particularly for windows with

5 λ_{low} <309 nm (Figs.9, 10, S2). Note that when the filter or offset function was used, increasing λ_{high} > ~ 320 nm or decreasing the λ_{low} < ~307 nm decreased the fit uncertainty but not the fit error for some windows (Figs. 6 & 8).

4 Summary & Recommendations

Measurements of calibration gas cells with column densities of 2.2×10^{17} and 2.2×10^{16} molec cm^{-2} SO_2 were conducted using a mini-MAX-DOAS instrument with an OceanOptics USB2000 spectrometer. In the base case, SO_2 dSCDs were least accurate

10 and had the largest fit uncertainties for fitting windows with λ_{low} <307 nm and >312 nm due to stray light and low solar signal, and weak SO_2 absorption, respectively. Fitting windows exhibited less accurate SO_2 dSCDs for spectra recorded at lower compared to higher α due to reduced UV signal. Therefore, choosing an accurate fitting window is particularly important for measurements at low α. Windows with λ_{low} <307 nm generally underestimated SO_2 dSCDs from higher concentration measurements for all scenarios. In contrast, many windows with λ_{low} <307 nm from the lower concentration measurements

15 overestimated the SO_2 dSCD that were overestimated from the higher concentration measurement. In the base, the SO_2 fit uncertainties were significantly less than the actual known fit error for many windows for both concentration measurements. Using the short-pass filter or the offset function increased the accuracy of the SO_2 dSCDs, decreased fit uncertainty, and decreased the difference between the fit uncertainty and error compared to the base case for most windows. Some low wavelength windows continued to underestimate the SO_2 dSCDs despite the filter for the higher concentration measurements.

20 The remaining underestimation was probably due to significant stray light originated from <400 nm and non-linearity in the relationship between the column density and measured optical density due to large optical depths of SO_2 at these lower wavelengths (e.g., >0.08). A low pass filter with lower cut-off wavelength (i.e., $\lambda_{cut-off}$ = 340 nm) may address the first factor, as may the use of spectrometers with reduced stray light. A spectrometer with an improved spectral resolution should help reduce the impact of the second factor (Kern, 2009). SO_2 dSCDs exhibited an inverse dependence on the depth of the

25 differential features in the SO_2 absorption cross-section in the base case. The dependence decreased with the use of the short-pass filter or offset function, implying that stray light contributed to the dependence. Using both the filter and offset function decreased the accuracy of the lower concentration dSCDs of SO_2 for some windows with λ_{low}<307 nm and λ_{high}<320 nm compared to the base case. Increasing the λ_{high} greater than ~ 320 nm tended to decrease the fit uncertainty but not necessarily the fit error for measurements with the filter or offset function.

30 Note that this study focused on the impact of two retrieval parameters (the fitting window wavelength and offset function) but that several other parameters can be varied in the SO_2 dSCD fit. These parameters include the order of the DOAS and offset function polynomials and the choice of the literature cross-sections for the trace gases. The DOAS analysis could also be expanded to include a correction to reduce impacts of the wavelength dependence of the Ring effect in the near UV due to aerosol and multiple Rayleigh scattering, as described in Langford et al. (2007). Additional factors that could impact the

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retrieved dSCD include the solar zenith and azimuth angles during measurement. A limitation of this study is the lack of measurements at high solar zenith angles (near dawn and dusk) when the SCDs of O_3 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 O_3 and SO_2 cross-sections. Future studies could repeat these experiments by measuring at different solar geometries and varying the other fit parameters. Also, SO_2 the column densities measured in this study were chosen to be representative of a range typical of polluted urban settings. Greater SO_2 column densities ($>1\times10^{18}$ 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).

Based on the results of this study, it is recommended that fitting windows for SO_2 have λ_{low} >307 nm to avoid the effects of stray light, low solar signal, and, for higher column densities, effects of non-linearity between the measured optical depth and the column density for optical densities >>0.05, and λ_{low} <312 nm because of weak SO_2 features. Fitting windows are recommended to have λ_{high} less than ~320 nm to avoid increased underestimation of the fit error by the fit uncertainty unless there are concerns about interference by large O_3 absorptions, such as at high SZA. A fitting window should not be chosen only because it has a smaller fit uncertainty since it does not guarantee a more accurate dSCD. A short-pass filter with a cut-off close to the λ_{high} of the SO_2 fitting window improves the accuracy of MAX-DOAS SO_2 measurements. In the absence of a filter or if a filter would conflict with other species to be determined (e.g., NO_2), the offset function should be used to compensate for stray light. Even in the case that SO_2 and NO_2 are to be fit simultaneously, a filter with $\lambda_{cut-off}$ = 550 nm may reduce stray light. A short-pass filter may be preferred over the offset function for reducing stray light impacts because the filter removes stray light while the offset function mathematically compensates for stray light by assuming it is proportional to the measured intensity (see Eqs. 11-12 in Supplemental). The offset function may increase fit error if this assumption is invalid or if little stray light is present. If a short-pass filter or the offset function is used, the 307.5-319 nm fitting window for mini-MAX-DOAS measurements of SO_2 is recommended. 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.

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Appendix A List of symbols and acronyms used in this paper.

Acronym	Expansion
α	Viewing Elevation Angle
$\lambda_{cut\text{-}off}$	Cutoff wavelength of Short-pass Filter
λ_{high}	Upper Limit Wavelength of Fitting Window
λ_{low}	Lower Limit Wavelength of Fitting Window
(B)	Base Case Measurement (No Filter and Offset Function Disabled)
(B+F)	Measurement with Short-Pass Filter
(B+F+O)	Measurement with Short-Pass Filter Fit using Offset Function
(B+O)	Measurement with Fit using Offset Function
dSCD	Differential Slant Column Density
FRS	Fraunhofer Reference Spectrum
HCHO	Formaldehyde
MAX-DOAS	Multi-Axis Differential Optical Absorption Spectroscopy
molec cm^{-2}	Molecules per square centimetre
nm	nanometres
NO_2	Nitrogen Dioxide
O_3	Ozone
ppb	Parts Per Billion
SCD	Slant Column Density
SO_2	Sulphur Dioxide
UV	Ultraviolet
VCD	Vertical Column Density

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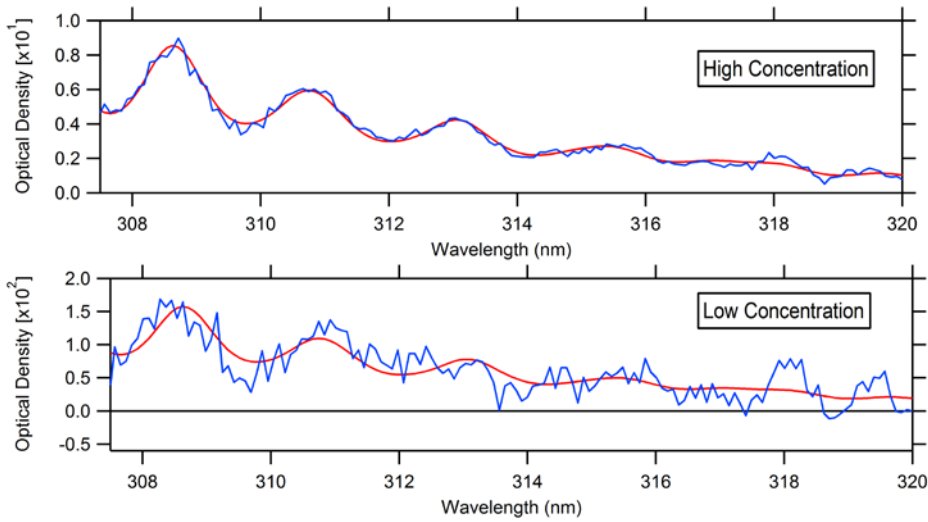
Figure 1 Examples of spectral retrievals of SO_2 from the base case (no filter and offset function disabled) from spectra measured at 2° viewing elevation angle using the fitting window 307.5-320 nm. Retrieved dSCDs were $2.23(+/-0.08)\times10^{17}$ molec cm^{-2} and $4.10(+/-0.66)\times10^{16}$ molec cm^{-2} for the higher and lower concentration measurements, respectively.
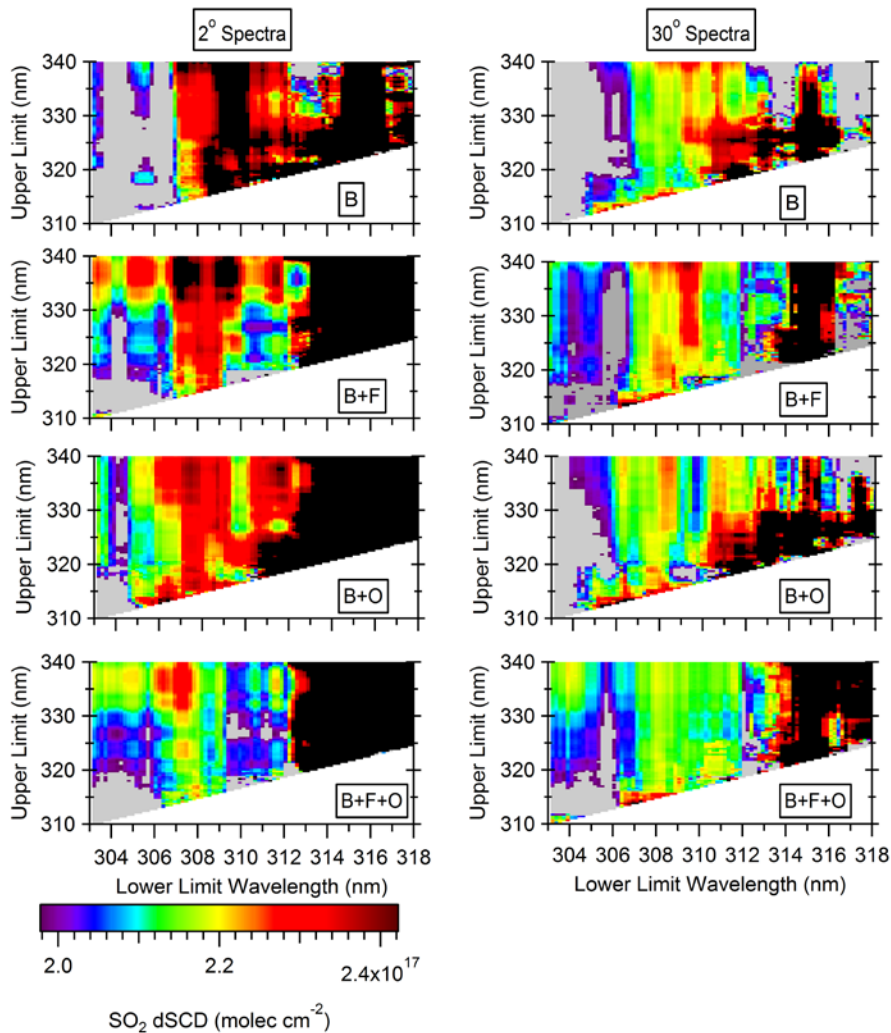
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Figure 2 SO$_2$ dSCDs fit from higher concentration measurements at 2° (left) and 30° (right) elevation angles for the base case (B), with offset (B+O), with filter (B+F), and with filter and offset (B+F+O). Grey and black areas indicate dSCDs were ≥10% less and >10% more than the expected value, respectively. The true value of the cell is 2.2×10^{17} molec cm^{-2} (yellow).
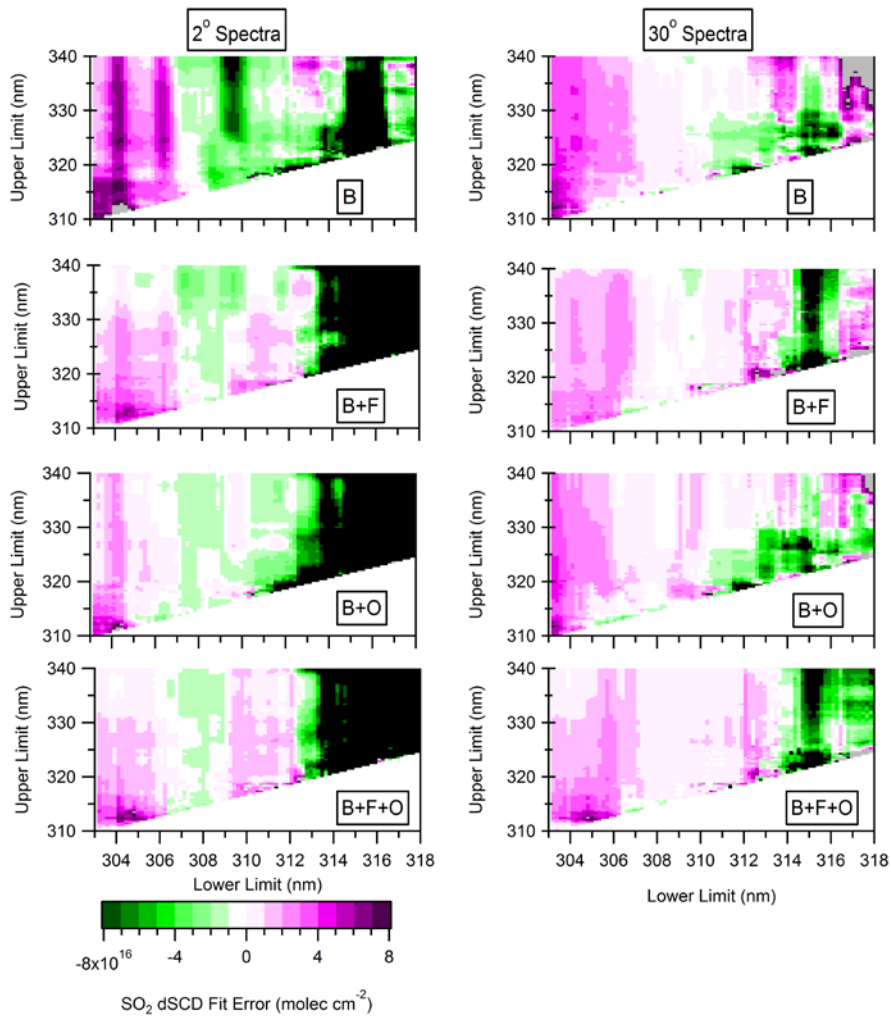
Figure 3 Higher concentration fit errors (deviations of SO_2 dSCDs from the expected value of 2.2×10^{17} molec cm^{-2}) from the measurements at 2° (left) and 30° (right) elevation angles for the base case (B), with offset (B+O), with filter (B+F), and with filter and offset (B+F+O). Purple and green areas indicate under- and over-estimation of the expected value, respectively. Black and grey areas indicate dSCDs over- and under-estimated by more than 8.0×10^{16} molec cm^{-2}, respectively.
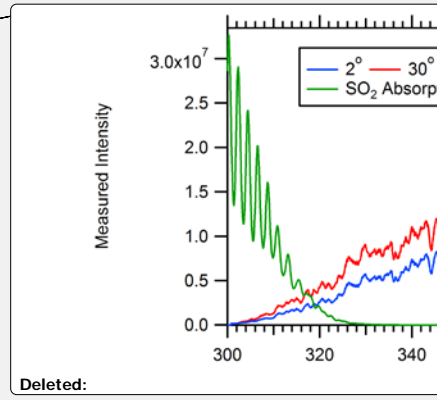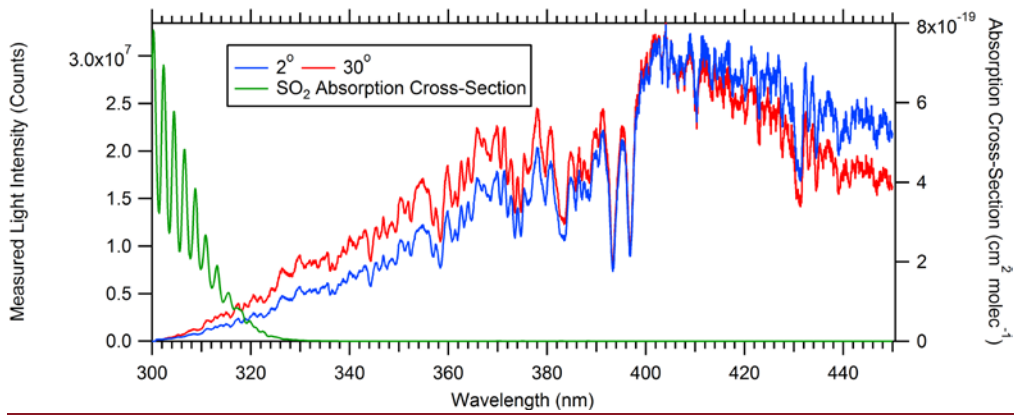
Figure 4 Comparison of the measured spectral intensity for the 2º and 30º viewing elevation angle spectra with the lower concentration cell without the short-pass filter, and the absorption cross-section of SO_2 smoothed to the spectral resolution of the instrument.
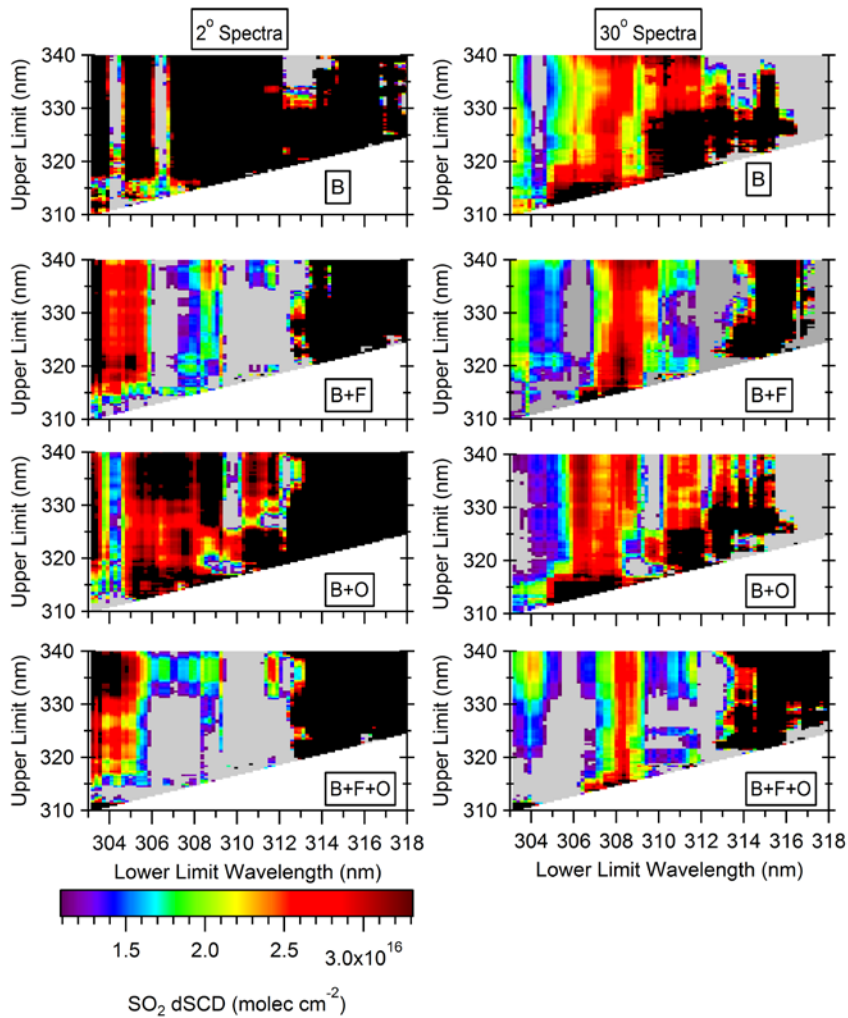
Figure 5 SO_2 dSCDs fit from the lower concentration measurements at 2° (left) and 30° (right) elevation angles for the base case (B), with offset (B+O), with filter (B+F), and with filter and offset (B+F+O). Grey and black areas indicate dSCDs that were <50% less and >50% more than the expected value, respectively. The true value of the higher concentration cell is

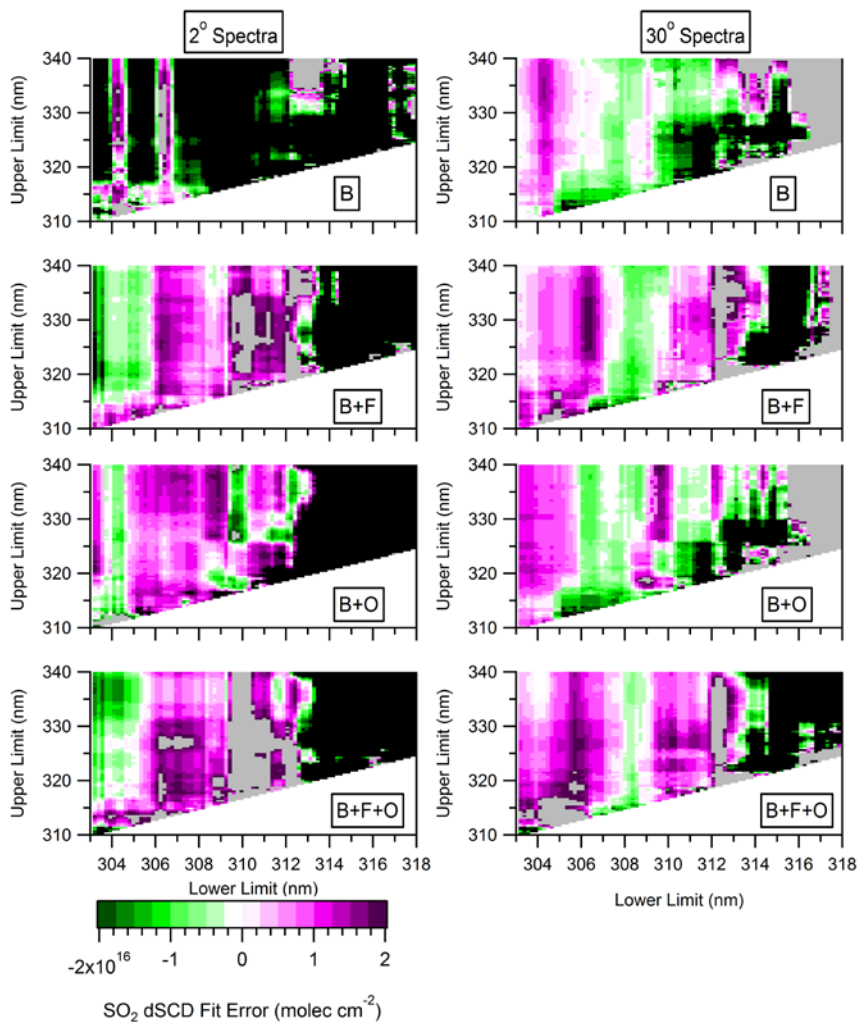5 2.2×10^{16} molec cm^{-2} (yellow).

Figure 6 Lower concentration fit errors (deviations of SO_2 dSCDs from the expected value of 2.2×10^{16} molec cm^{-2}) from the measurements at 2º (left) and 30º (right) elevation angles for the base case (B), with offset (B+O), with filter (B+F), and with filter and offset (B+F+O). Purple and green areas indicate dSCDs were under- and over-estimation, respectively. Black and grey areas indicate dSCDs over- and under-estimated by more than 2.0×10^{16} molec cm^{-2}, respectively.
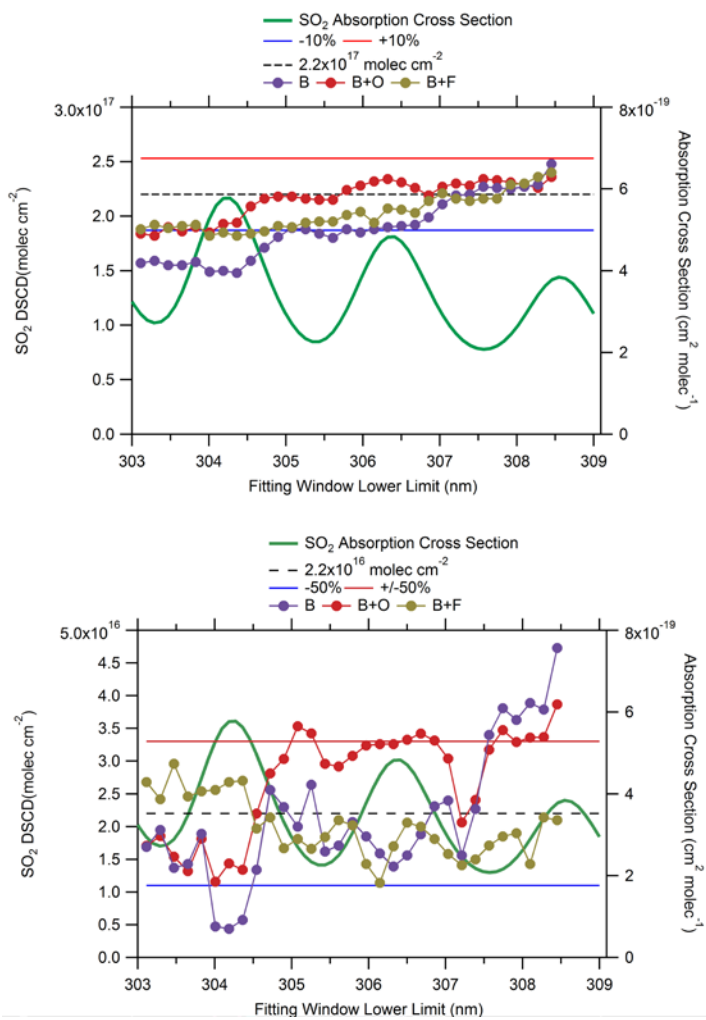
Figure 7 SO$_2$ absorption cross-section and variation in the SO$_2$ dSCD with λ_{low} with λ_{high} = 315 nm for higher (top) and lower (bottom) concentration measurements for the base case (B), with offset (B+O), and with filter (B+F).

Figure 8 SO$_2$ absorption cross-section and variation in the SO$_2$ dSCD with λ_{low} with λ_{high}= 324 nm for higher (top) and lower (bottom) concentration measurements for the base case (B), with offset (B+O), and with filter (B+F).
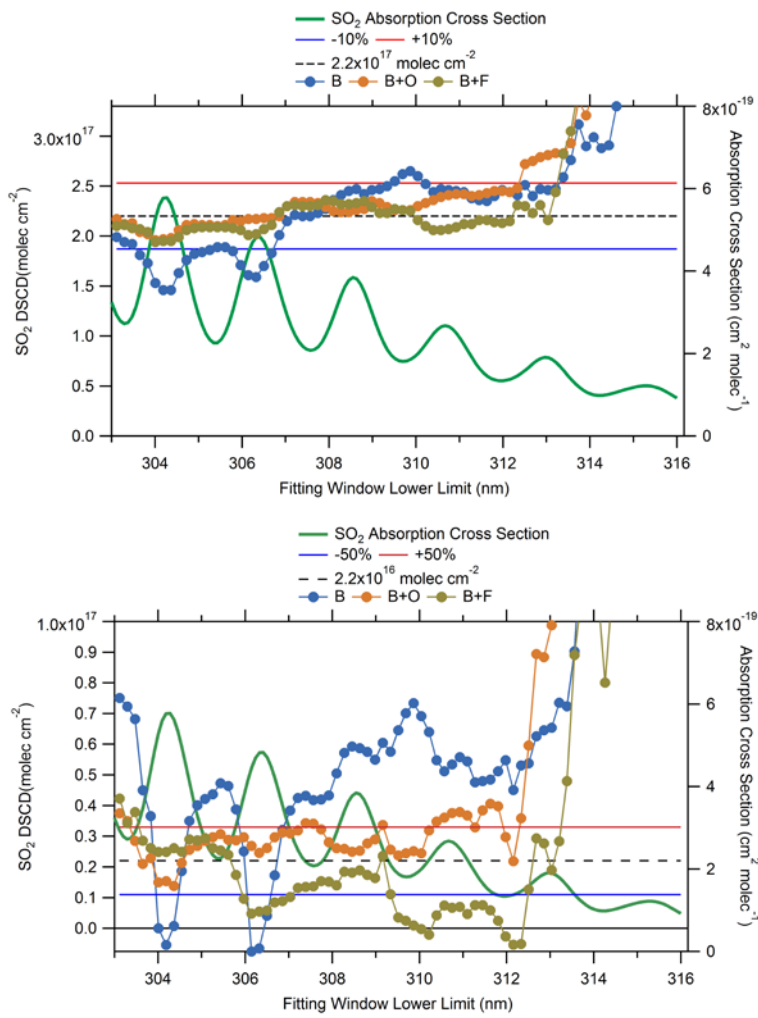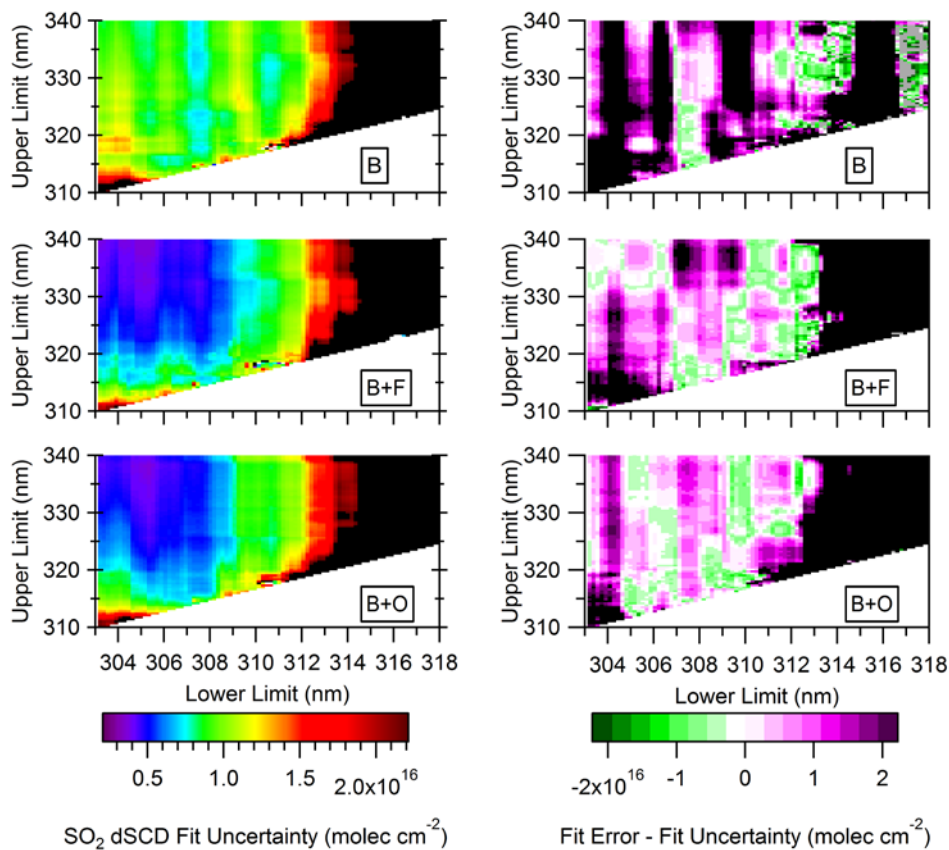
Figure 9 Higher concentration SO_2 dSCDs fit uncertainties (left) and difference between fit error and uncertainty (right) from spectra measured at 2° elevation angle for the base case (B), with offset (B+O), and with filter (B+F). Black areas indicate errors $>1.1\times10^{16}$ molec cm^{-2} for absolute error (left) and $>2.2\times10^{16}$ molec cm^{-2} for the difference (under-estimation) between actual and fit error.
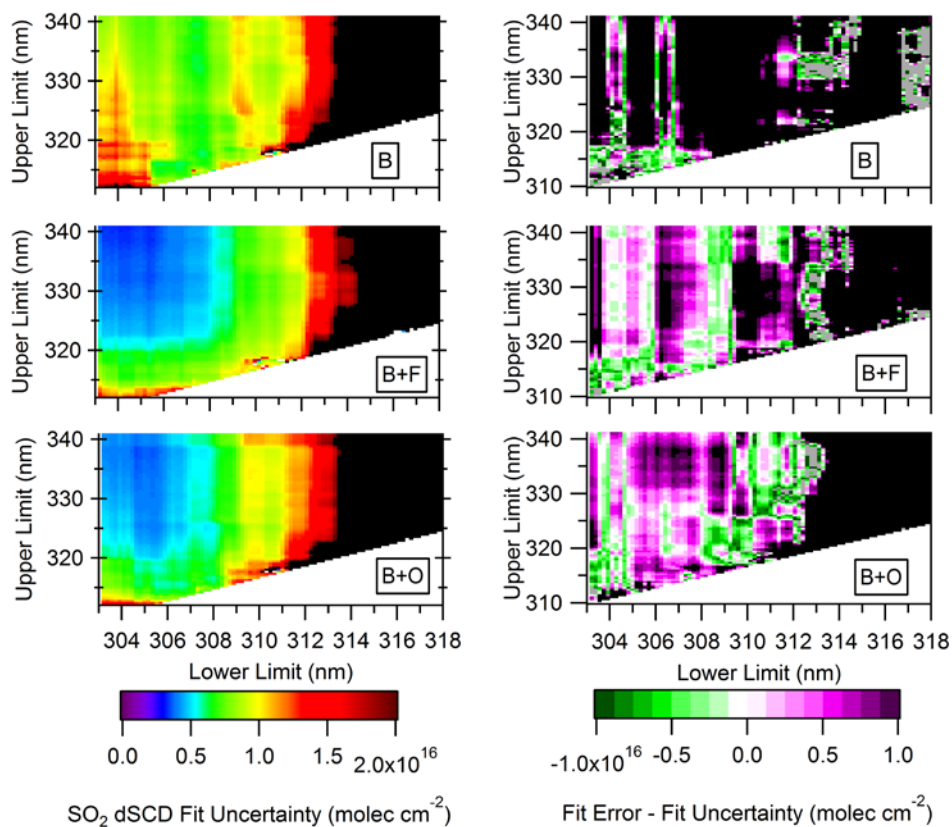
Figure 10 Low~~er~~ concentration SO_2 dSCDs fit errors (left) and difference between fit uncertainty and error (right) from spectra measured at 2° elevation angle for the base case (B), with offset (B+O), and with filter (B+F). Black areas indicate errors of >2.2×10^{16} molec cm^{-2} for absolute error (left) and >1.1×10^{16} molec cm^{-2} under-estimation of the fit error by the fit uncertainty.

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