Interactive comment on "Sulphur dioxide (SO_2) vertical column density measurements by Pandora spectrometer over the Canadian oil sands" by Vitali E. Fioletov et al.

Anonymous Referee #2
Received and published: 14 April 2016

The paper presents the retrieval of SO2 column by Pandora sun-photometer, and discusses an application to an area in Canada with elevated concentrations of SO2. It is a well presented paper with sufficient innovation, demonstrating the capabilities of Pandora to use used for monitoring the SO2 in addition to ozone and NO2. The subject is relevant for AMT and the quality of the paper is good to be accepted for publication in AMT.

We would like to thank the reviewer for the evaluation and comments that helped us improve the manuscript.

However, before publication I recommend to the authors to address the following issues:

General comments:

1, 17: The fitting uncertainty of 0.05 DU is true only for 60% of the data.

The fitting uncertainty was just a part of the total uncertainty as was also noted by Reviewer #1 who suggested to remove that sentence. We removed the sentence.

2, 27: Delete "visible" since SO2 does not absorb in this range.

Corrected

3, 19: Please clarify: Is 0.6 nm the FWHM or the width of the base of the slit function?

Or it is the average pixel width of the CCD (i.e. the full spectral range divided by the number of pixels)?

0.6 nm is the FWHM. We added this to the text.

3, 24: Subtracting a constant offset to correct for stray light does not make any sense in DOAS retrieval, because it is a smooth function which is finally removed by the polynomial fitting.

In the first order approximation, stray light adds a bias to the measurements. Therefore the offset correction is done before taking the Log. The fitting algorithm uses Log(X-S) where S is stray light and X is the signal. While it can be re-written as Log(X-S) = Log(X) – Log(1-S/X) and Log(1-S/X) can be fit by the polynomial function, it may not be the best approach, particularly if the spectral window is wide. In any case, this stray light correction is a part of the Pandora standard processing software provided by the manufacturer that we do not discuss in this study.

We added to the text that this stray light correction is a part of the Pandora processing software.

5, 3: It would be good to show on Figure 2 the residual noise which is a measure of the signal to noise ratio and hence the fitting uncertainty.

We added that plot, although the same information is available from the HCHO fit that is basically a flat line

5, 18: Please elaborate briefly on the "synthetic reference spectrum". How it is determined?

Is it one spectrum or a synthesis of more spectra? Does it correspond to a zero SO2 column? In not, what is the SO2 amount corresponding to the reference spectrum used?

In order to minimize noise, the synthetic reference spectrum is derived from an average of the logarithms of about 100 low integration time spectra measured near noon in Toronto where SO2 is low. We added this information to the text. While it is still possible that some SO2 signal is presented in the reference spectrum, the suggested calibration procedure accounts for it.

5, 29: 90% of the data have fitting errors below 0.15 DU. Where the upper limit of 0.35 DU comes from?

The initial data filtration was done based on the integration time. 90% of data that have passed through that filter have the statistical fitting uncertainties less than 0.15. Among the remaining 10%, there are still some measurements that can be used. We changed the text to mention the remaining 10%

.

5, 30: The discussion in this paragraph is rather vague: How one can detect that a measurement is artificially elevated by an amount of up to 1 DU? How these cases are detected and processed with another reference spectrum, and why with this reference spectrum gives better results compared to the synthetic spectrum? It is stated that data are filtered based on the standard error, what is the threshold value?

All data were processed with the both reference spectra and with several spectral windows. Then all retrieved SO_2 values for each measurement were compared. In general, the 306-330 nm spectral window and the synthetic spectrum give the best results, but occasionally when data are very noisy, these fits find the “wrong” solution with some small wavelength shift and elevated SO_2. As a result, the SO_2 values retrieved with the 306-330 nm spectral window and the synthetic spectrum were up to 1 DU different from the retrievals for the other reference spectrum or for the same spectrum, but different fitting windows. When this occurred, we simply used SO2 values retrieved with the prescribed reference spectrum. As mentioned, such cases were rare and occurred when the data were really noisy with the statistical fitting uncertainty >0.2 DU.

We changed this paragraph to:

“All data were processed with the both reference spectra and with several spectral windows. Then all retrieved SO_2 values for each measurement were compared. We encountered one practical problem related to the fitting algorithm that appears when the SO_2 amount is close to zero and the measurements are relatively noisy (e.g. due to thin clouds). In general, the 306-330 nm spectral window and the synthetic spectrum give the best results, but on some occasions, that fitting algorithm finds the best fit with a small wavelength offset and an artificially elevated SO_2 value (by as much as 1 DU compared to the values for the other reference spectrum or for the same spectrum, but different fitting windows). Only 2-3% of the data are affected by this error, but they are very noticeable on time series plots. A simple filtering by the standard error of retrieved SO_2 (<0.2 DU) and/or by the wavelength offset removes these erroneous data, but it can also remove some valid observations. As mentioned, there are two options for the reference spectrum: an independently measured extraterrestrial spectrum (“prescribed reference spectrum”) or generated from the measurements themselves (“synthetic reference spectrum”). Such problematic cases were processed with the prescribed spectrum that appear to give better results in this situation than processing with the synthetic reference spectrum used for all other retrievals”

6, 24-26: I don’t understand this sentence “the low percentiles are close to the same percentiles for clean conditions”. Could you please make it clearer? Up to this point there has been no discussion about the VCD of SO2 associated with the reference spectrum. Here it is implied that this value is determined based on the “low” percentiles. How is this done? Is the average value for one of these percentiles considered as the SO2 column in the reference spectrum?

If there is no SO_2 in the atmosphere (Case 0), then the mean corresponds to SO_2 in the reference spectrum and the location of percentiles is determined by the noise. If we assume that the noise is Gaussian with a known standard deviation, then the mean in Case 0 can be also calculated from any percentile value because the Gaussian distribution is determined by only two parameters. In the real atmosphere of Ft McKay, we assume that 10% (or 25%) of the lowest values correspond to conditions with no SO_2 in the atmosphere (e.g. when the wind is from the west where there is no sources). The values of these percentiles therefore should be the similar to those in the Case 0. Then if we know the standard deviation, we can calculate where the mean would be for Case 0. The standard deviations are known and they are discussed a couple of paragraphs below. Note that all of this is an attempt to improve the accuracy of the method at the level of a few tenths of a DU. Otherwise, the average value for one of these percentiles can be used as the SO_2 column in the reference spectrum as pointed out by the reviewer and as it was done for NO_2 by Herman et al., 2009.

We added some text to the previous paragraph and changed this paragraph to:

"… If we assume that the noise is Gaussian with a known standard deviation, then the mean can be also calculated from any percentile value because a Gaussian distribution is determined by only two parameters. This can be used to determine the "no SO_2" atmosphere mean value in the case of real atmosphere.

If we assume that SO_2 is present even in a fraction of all observations at an otherwise SO_2-free site, then the mean value will be elevated compared to the SO_2-free "clean" atmosphere and therefore it cannot be used as a reference in the calibration procedure. However, the low percentiles (e.g., 5th, 10th or 25th) of slant column values are close to the same percentiles for "clean" conditions as they correspond to conditions with no SO_2 in the atmosphere (e.g. when the wind is from the west where there is no sources). This making them suitable for determining the absolute slant column amount in the reference spectrum as the mean value for the "no SO_2" atmosphere. There are two potential complications: first, the low percentiles could be biased low relative to zero SO_2 conditions due to random errors, thereby resulting in scattering of data points. The lower the percentile value, the larger that bias. Second, the standard deviation of the scattering increases with the air mass factor as the signal strength declines resulting in higher errors and lower values in the low percentiles."

6, 28: This justification is not very accurate: With increasing airmass factor the measured radiation decreases but the absorption signal increases due to the longer path length through the SO2.

We are talking about low percentiles here. We assume that they correspond to conditions with no SO_2 in the atmosphere. The paragraph was modified as described above to make this clearer.

7, 1: What is meant by "distances" between percentiles? Is it the difference between the intercepts of the two regressions?

Corrected to "the difference between the 25th percentile intercept and 50th or 10th percentiles intercepts for VCDs are +0.16 DU and -0.12 DU respectively"

7, 27: Figure 5 and the correlation coefficient of 0.7, does not give the impression of a very good agreement between the two datasets, so the statement "tracks each other very well" is too strong statement.

Changed to "tracks each other reasonably well"

8, 19: There is no experimental evidence that the SO2 plum was above the ground. I would say "was probably above the ground"

We agree. Corrected as suggested.

9, 28: With six numbers it is not safe to calculate the “average” and “standard deviation”.

Maybe it would be better to provide the range of differences for the six cases.

Table 1 gives a sense of the range of differences. We wanted to describe aircraft-Pandora differences as a single number and used the standard deviation for this purpose.

Technical comments:

2, 20: Replace “modification” with “type”

Corrected

3, 26: Replace “the interval” with “an interval”

Corrected

4, 27: It is not obvious to what “etc” refers. Perhaps it is better to remove it.

Corrected

5, 12: “values retrieval” is not proper English. Please revise.

It was a typo. It should be “values retrieved”. Corrected.

11, 20: Replace “characteristics” with “quantities”

Corrected