

Interactive comment on “Long-path averaged mixing ratios of O₃ and NO₂ in the free troposphere from mountain MAX-DOAS” by L. Gomez et al.

Anonymous Referee #2

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General comments

This manuscript attempts to utilize a unique geometry of MAX-DOAS at an elevation angle of zero degrees from the mountaintop as a new method to estimate the effective path in the free troposphere. Then, the estimated path is used to convert the differential slant column densities of O₃ and NO₂ into their mixing ratios averaged over the path. Because the estimated path is important for a DOAS-based measurement technique, the subject is appropriate for AMT. However, the authors have made assumptions that seem very difficult to justify. Additionally, I have identified some areas that need much more clarification and additional discussions. After these issues and the other concerns described below are adequately addressed, I recommend publishing this manuscript.

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Major comments

1. I was confused in several places in Section 1.2. First, the authors state, "it is assumed that for both geometries the scattering altitude is the same and is close to the station level." I cannot accept this assumption. Additionally, Fig. 2 does not support the assumption; it indicates that (1) the station level is $h(s)$, which is different from the scattering altitude of $h(s) + h$ for observations at an elevation angle of zero degrees and (2) the direct sunlight measurement is represented for an elevation angle of 90 degrees, while the MAX-DOAS should measure the scattered sunlight. The authors might claim that Fig. 2 is a schematic diagram, nevertheless the definition of the scattering heights in Fig. 2 indicates that for both geometries the scattering altitudes are not the same and differ from the station level by h .

The assumption must be supported by a radiative transfer (RT) model. Indeed, the authors have included discussion using the SDISORT RT model in Section 2. However, their approach using the differential box-AMF is not appropriate for discussing the scattering altitude. They argue that the scattering takes place below 3 km for elevation angles of both zero and 90 degrees, as the differential box-AMF is very small above 3 km. If this logic is correct, how do they explain the differential box-AMF for other sets of elevation angles (e.g., for 1 and 90 degrees), which show significant values of differential box-AMF at least up to 10 km? If the authors want to discuss the scattering altitude, the box-AMF is a better parameter than the differential box-AMF. However, I suggest that they use the most direct parameter, which is the scattering altitude estimated using a RT model. I understand that the authors wanted to utilize a unique feature of the differential box-AMF vertical profile for elevation angles of zero and 90 degrees. Please interpret the feature properly, if the assumption "for both geometries the scattering altitude is the same and is close to the station level" is unnecessary.

Second, the authors have used correction factors f and f' to account for a SZA difference. I understand that this correction is valid for the column density of target gas above the scattering altitude. While this study targets the column density below the

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scattering altitude, it is unclear how this correction functions. Please clarify this issue in the manuscript.

Third, in order for Equation 5 to be valid, we need to assume that the box-AMF (not the differential box-AMF) is constant at altitudes above the scattering altitude. Is this supported by a RT simulation? Additionally, for the calculation of d' with the RT model, a constant concentration has been assumed from the top of the atmosphere to the station level, but this is obviously invalid for O₃ and NO₂.

As described in Section 1.3, O₃ was retrieved from the 430-500 nm wavelength region. To my knowledge, this region is poor for the O₃ retrieval. Please discuss the quality of O₃ retrieval using this wavelength region. Specifically, is there any interference with other fitting parameters (DSCDs for other gases or polynomial coefficients)?

3. From Figs. 7 and 8, the MGA values do not agree with in situ values at times, even when both MGA and in situ data are available. This is, of course, independent of the availability of in situ measurements. Indeed, the authors consider only such simultaneous cases, but then argue that the MGA and in situ data are in agreement when considering error bars. What uncertainty do the error bars represent? I feel that the differences seen with the common data in Fig. 8 (10-30 ppbv) are too large to support the validity of the MGA method. Considering this and the inadequately-justified assumptions mentioned above, I am skeptical of the validity of the MGA methodology, which the authors are proposing.

4. I strongly suggest that the English throughout the manuscript be checked by a native speaker.

Specific comments and technical corrections

Throughout the manuscript, please use DSCD, not SCD, as a parameter retrieved from MAX-DOAS. Please use either alpha or IEA consistently.

(page 8236, lines 9-10): "mixing ratios concentrations" should be "mixing ratios."

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(page 8236, line 10): Please state the magnitude of errors quantitatively.

(page 8236, lines 10 and 11): "concentrations" and "concentration" should be "mixing ratios" and "mixing ratio," respectively.

(page 8236, line 17): "Observation" might be a better word here than "Distribution."

(page 8237, line 2): "know" should be "known."

(page 8237, lines 27 and 28, and page 8238, line 19): "Honninger" needs an umlaut over the "o".

(page 8239, line 21): Perhaps "results mainly of" should be "results mainly from."

(page 8242, line 5 and other places): "thickness" is preferable to "width."

(page 8242, line 6): "If the optical path ... after the scattering is..." should be "If the optical paths ... after the scattering are..."

(page 8243, line 8): What contribution comes from the station level?

(page 8243, lines 21-23): What is the statistical meaning of the "molecular error"? Is it the 1-sigma random error? I do not think "molecular error" is an appropriate term.

(page 8244, line 22): What is meant by "the dominant synoptic wind exists"?

(page 8245, line 7): What exactly do the authors mean by "single scattering O₃ differential box-AMFs"? I do not think that the box-AMFs calculated in this way are only for O₃. "single scattering" seems unnecessary.

(page 8245, line 10): "widht" should be "width", although "thickness" is preferable.

(page 8245, line 22): "photometer" should be "sun photometer."

(page 8246, line 17): Why do the authors use forecast data? Are any reanalysis data available?

(page 8246, lines 22-24): The authors state, "the relative azimuth was set to zero,"

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although Table 2 indicates a relative azimuth of 180 degrees. Additionally, even if no appreciable difference is observed when the daily solar azimuth variation is considered, I suggest making RT calculations under actual azimuth conditions for each measurement to simplify the discussion.

(page 8246, line 25): Perhaps, "de optical path" should be "optical paths"?

(page 8247, line 4): It is unclear what "the assumed geometry" means? Do the authors mean that AMF-MGA relies more on the RT simulation?

(page 8247, line 5): This states that a similar diurnal evolution is seen for O4-MGA and AMF-MGA. Additionally, both quantities exhibit periodic patterns. It is possible that this is due to inadequate assumptions made in calculating both quantities, such as those I mentioned above (given as specific comments).

(page 8247, line 26): It is unclear what "light period" means.

(page 8247, lines 26-28): I do not understand the sentence starting, "As a result of the MBE..."

(page 8248, lines 3-5): I do not think that the O3 value from the ozonesonde at the Izana level agrees well with the estimated MGA values, because it differs by more than 10 ppbv.

(page 8248, line 9): What is meant by "observed differences"? I believe that MGA values do not agree with in situ values at times, even when both MGA and in situ data are available, as mentioned above.

Table 2: "Wave length" should be "Wavelength."

Fig. 5: Although the differential box-AMF is small in the upper troposphere and lower stratosphere, the contribution of these altitudes to the DSCD O3 can be significant as the O3 concentration is high there. I suggest checking this by adding a plot of vertical profiles of (O3 concentration) \times (differential box-AMF).

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Fig. 7: The black and gray points are very difficult to distinguish.

Fig. 9: Why are the NO2 values measured with in situ instruments around noon on days 204 and 205 not as large as those on other days? On days 204 and 205, the agreement between the MGA and in situ NO2 values is good, but the differences in O3 are large, compared to other days. Please clarify this in the text. Additionally, why does NO2 increase around noon, when O3 does not exhibit a decrease due to MBE? It might help if the authors include the H2O results in this discussion.

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 8235, 2013.

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