Atmos. Chem. Phys. Discuss., 15, C11323–C11330, 2016
www.atmos-chem-phys-discuss.net/15/C11323/2016/


Atmospheric Chemistry and Physics Discussions
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15, C11323–C11330, 2016

Interactive Comment

# *Interactive comment on* "Estimates of free-tropospheric $NO_2$ and HCHO mixing ratios derived from high-altitude mountain MAX-DOAS observations in the mid-latitudes and tropics" *by* S. F. Schreier et al.

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Received and published: 11 January 2016

We would like to thank the reviewer for his / her useful comments.

MAXDOAS data from two high mountain stations at mid and tropical latitudes are analysed to obtain estimations of the background concentrations of NO2 and HCHO in the free troposphere. The analysis makes use of the novel technique MGA extended toward the UV spectral region. Radiation data are compared with synthetic ones to evaluate the accuracy of the measurements and results are discussed considering the



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aerosol loading (AOD) and the influence of the biomass burning in the area. Results provide new and additional information on the free troposphere minor species chemically active, a region where data are scarce. The manuscript is clearly written and figures are illustrative. I recommend the article for publication after addressing the comments below.

Specific comments:

- The applied technique is quite sensitive to the amount of aerosols present in the air. However, there is little information in the paper on how this has been treated in the data analysis. AOD data based on MODIS (in the visible?) show mean values over 0.2 on 5 out of the 8 months considered in the study. In such conditions the errors of the approach increases notably compared to a Rayleigh atmosphere. In page 31795, lines 10-12 lower limits for considering too much aerosol loading at each spectral range is established. How are these limiting paths calculated?. Is there any "visibility" device at the stations to correlate with the obtained paths? Have the MAX-DOAS data themselves used to retrieve aerosols as part of the rejection criterion? A more detailed description on filtering criterion concerning the atmospheric visibility would be needed. If data with AOD larger than 0.1 passed the filter, it would be useful also to estimate the error in the computed paths.

We agree that aerosols play an important role in this type of measurements. The AOD values are obtained from the MODIS instrument and represent extinction coefficients integrated over a vertical column. As most of the aerosol is expected to be found in the boundary layer, let's assume 80% (see Gonzi et al. (2015) for typical biomass burning injection heights), the values are of course not representative for the level of the measurement instruments. They are too high. If we follow the recommendations made by Gonzi et al. (2015) than we can assume that AODs at the station levels, at least for Pico Especjo, are lower than 0.1. We have added a discussion on this comment:



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“For example, Gonzi et al. (2015) have estimated biomass burning injection heights using active fire area and fire radiative power from MODIS data in combination with a parameterized plume rise model. They found that 80% of the injections remain within the local boundary layer. Consequently, trace gases and aerosols are only lifted into the free troposphere when the active fire area and convective heat flux exceed a certain threshold. For the Pico Espejo site, it is expected that the possibility of injections reaching the free troposphere increases towards the end of the dry season with increasing fire activity. Due to a lack of ground-based measurements of AOD at the two stations that are representative for the altitude of the station, monthly gridded means of AOD from the MODIS instrument on board Terra and Aqua satellites have been downloaded from ftp://ladsweb.nascom.nasa.gov/allData/51/ (Remer et al., 2008) and averaged over both products and selected regions (see Table 3). The MODIS instruments have 36 channels covering the spectral range from 410 to 14400 nm and representing three different spatial resolutions of 250 m, 500 m, and 1 km. The AOD product used in our study is retrieved at 550 nm and has a spatial resolution of 250 m. Again, the MODIS product provides an extinction coefficient integrated over a vertical column with probably most of the aerosol load being located below the measurement stations. Nevertheless, the effect of aerosols on hOPL can still be quantified for the Pico Espejo site as about 20% of the aerosol load is expected to be found in the free troposphere, following the recommendations made by Gonzi et al. (2015).”

Unfortunately, there were no visibility devices at the stations. We therefore filtered the data by making some assumptions on the data. One assumption is to use a lower limit for the hOPL. These lower limits are obtained by testing different values. The values that we propose are a compromise between “loosing not too many measurements” and “still provide clear sky cases”. We have added the following text to the manuscript:

“As no instruments to obtain information on atmospheric visibility were available at the stations, we have tested different lower limits of hOPL as a filter criterion and found that 17.5 km and 30 km in the 346-372 nm fitting window and 12.5 km and 22.5 km in



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the 338-357 nm fitting window are good compromises for Zugspitze and Pico Espejo, respectively (see Fig. 7).”

As we can only speculate that AOD at the station level and above is smaller than 0.1, we argue that our filter criteria are the only way to remove measurements that are not representative.

- FOV of the instruments is not mentioned in the paper, neither references to previous publicactions. They are relevant for the reasons exposed below (page 31789).

We have now added some information about the instrument’s field of view and included two references for more information:

“Scattered sunlight entering the telescope, either from the zenith or horizon window, is focused by lens to reduce the field of view before it reaches the optical fibre mount. During the instrument’s operation at the two measurement stations, a field of view with an opening angle of $\sim 1^{\circ}$ was achieved (Oetjen, 2009 and Peters, 2013). Consequently, the signal in the horizontal path might be slightly affected by the contribution of trace gas absorption at lower altitudes (up to 500 m below the measurement stations at the end of the hOPL). Nevertheless, the mixing ratios as presented in Sects. 6.3 and 6.4 for NO2 and HCHO, respectively, are still considered to be representative for the free troposphere.”

- 31784, line 26. It is more accurate to use “minimize” than ”cancel out” since local effects contribute to the hOPL, as well.

We agree with this comment and have now replaced “cancel out” by “minimize” in the text (see Page 3, Line 27).

- 31789, line 15. If the average terrain height below the path at Pico Espejo is of only 150 m, and the path length is of 20-30 km, typical FOV of $1^{\circ}$ would hit the ground. The quality of the signal should be affected by the contribution of the ground spectrum. A comment on how this geometry affects the measurements should be included in the



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text.

To our understanding, an opening angle of about 1° (full FOV = 2°) does not hit the ground for the Pico Espejo case. There is a height difference of more than 4500 meters between the mountain station and the terrain height below. At the end of the path length (e.g. 20-30 km), light from a few hundred meters below the level of the mountain station might enter the horizontal light path. This is still clearly above the boundary layer and should not affect our argumentation that elevated values of NO2 and HCHO are found in the free troposphere. We have now added some information in the text (see first comment on FOV above):

"Scattered sunlight entering the telescope, either from the zenith or horizon window, is focused by lens to reduce the field of view before it reaches the optical fibre mount. During the instrument's operation at the two measurement stations, a field of view with an opening angle of $\sim 1^\circ$ was achieved (Oetjen, 2009 and Peters, 2013). Consequently, the signal in the horizontal path might be slightly affected by the contribution of trace gas absorption at lower altitudes (up to 500 m below the measurement stations at the end of the hOPL). Nevertheless, the mixing ratios as presented in Sects. 6.3 and 6.4 for NO2 and HCHO, respectively, are still considered to be representative for the free troposphere."

- 31794, line 3-6. Measurements of larger paths than those obtained for a Rayleigh atmosphere are also possible due to the use of a room-temperature O4 cross-section. Spinei et al. (AMT, 2015) have shown that too large paths are obtained when using room temperature cross-sections (i.e. Hermans) in low effective-temperature conditions, which I assume is the case at Pico Espejo. I suggest the authors to estimate the error in the path due to the temperature dependence based on the Spinei paper.

Thank you for pointing this out. We have now considered the Spinei et al. (2015) publication and estimated errors that can be expected when a room temperature laboratory-measured O4 cross-section is used for the estimation of optical paths. We have now



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added the following paragraph:

"Recently, Spinei et al. (2015) have shown that too large $O_4$ slant column densities are obtained when using laboratory-measured $O_4$ cross-sections (e.g. Hermans et al. (1999)) in low effective-temperature conditions. They report a temperature dependence in the $O_4$ absorption cross-section from 231 to 275 K at about 9±2.5% per 44 K rate in the 335-390 nm spectral window and suggest a small correction factor of 0.94±0.02 at 231 K when using $O_4$ cross-sections measured at room temperature. Following the recommendations made by Spinei et al. (2015), an overestimation of up to 6% in hOPL and thus, an underestimation in $NO_2$ and HCHO mixing ratios of up to 6% can be expected in our study due to the use of a room temperature $O_4$ cross-section."

- 31796, line 4-7. I guess the authors make use of MODIS because AOD devices on the stations are lacking. However, since MODIS averages over an area with probably a lower mean heigh than the observing point, the correlation shown in figure 8 and conclusion of table 3 are missundertanding. I suggest explaining this subject in more detail and provide some information on MODIS (size of the footprint, mean altitude, etc). Again, interpretation of section 6.2 (relies on the correlation Xno2-AOD. If AOD is not that above the station, it must be outlined.

We agree with this comment and have now added more information on the MODIS AOD product and mean altitude of aerosols (e.g. injection height of biomass burning). We have now outlined that no representative AOD products are available at the mountain stations and thus, we have used a column averaged satellite-derived AOD product. We have now added the following paragraph to the manuscript (see first comment on AOD/MODIS above):

"For example, Gonzi et al. (2015) have estimated biomass burning injection heights using active fire area and fire radiative power from MODIS data in combination with a parameterized plume rise model. They found that 80% of the injections remain within



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the local boundary layer. Consequently, trace gases and aerosols are only lifted into the free troposphere when the active fire area and convective heat flux exceed a certain threshold. For the Pico Espejo site, it is expected that the possibility of injections reaching the free troposphere increases towards the end of the dry season with increasing fire activity. Due to a lack of ground-based measurements of AOD at the two stations that are representative for the altitude of the station, monthly gridded means of AOD from the MODIS instrument on board Terra and Aqua satellites have been downloaded from ftp://ladsweb.nascom.nasa.gov/allData/51/ (Remer et al., 2008) and averaged over both products and selected regions (see Table 3). The MODIS instruments have 36 channels covering the spectral range from 410 to 14400 nm and representing three different spatial resolutions of 250 m, 500 m, and 1 km. The AOD product used in our study is retrieved at 550 nm and has a spatial resolution of 250 m. Again, the MODIS product provides an extinction coefficient integrated over a vertical column with probably most of the aerosol load being located below the measurement stations. Nevertheless, the effect of aerosols on hOPL can still be quantified for the Pico Espejo site as about 20% of the aerosol load is expected to be found in the free troposphere, following the recommendations made by Gonzi et al. (2015)."

- 31796, line 10. Typo: remove "of"

We have now removed "of" in the text (see Page 15, Line 4).

- 31796, line 6. "averages" ->"averaged"

We have now changed accordingly (see Page 14, Line 24).

- Check the spectral range in which spectrometers are operating. Different numbers appear along the text.

We have checked the spectral ranges along the text. There are 4 different numbers: 346-372 nm for the $NO_2$ retrieval, 338-357 nm for the HCHO retrieval, 321-410 nm for the spectrometer, and 330-440 nm for the RTM simulations.

In addition to the reviewers' comments, we have performed some minor changes: - In the ACPD version, References from Table 2 are not included in the reference list. We have now added them to the reference list.

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Interactive comment on Atmos. Chem. Phys. Discuss., 15, 31781, 2015.



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