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Atmospheric Chemistry and Physics Discussions

Interactive comment on "MAX-DOAS measurements of NO_2, HCHO and CHOCHO at a rural site in Southern China" *by* X. Li et al.

Anonymous Referee #2

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In this paper, the authors report on MAX-DOAS measurements at a rural site in China during the PRIDE-PRD2006 campaign. The measurements cover NO2, HCHO, and glyoxal for a period of 9 clear days. Tropospheric columns, mixing heights and surface layer concentrations are derived from the MAX-DOAS measurements and compared to NO2 in-situ observations, OMI satellite retrievals and CMAQ model simulations. The main results are that all three absorbers appear to be concentrated in the boundary layer, that NO2 surface values agree well with in-situ observations and reasonably well with OMI tropospheric columns, while the model systematically overestimates NO2 values. The HCHO and CHOCHO observations are interesting in that HCHO has an unusual diurnal variation and the absolute values of the two columns, as well as the ratio CHOCHO / HCHO are larger than expected. The latter could indicate local influence or a difference between previous studies and the situation in Southern China.

The paper is overall well written, clearly describes measurements and data analysis and reports on interesting results. I therefore recommend it for publication in ACP after minor revisions.

I do have however a couple of questions and suggestions to the paper:

1) The model predicts higher NO2 than observed and the authors interpret this as too large NOx sources. They also report unusually high OH levels. Are these high OH levels prescribed / reproduced by the model? If not, could the model have a too long lifetime for NO2 which would then lead to too large NO2 values at the right emission strength?

2) The measurements nicely illustrate that CHOCHO is mixed to higher altitudes than HCHO. The authors explain this by the fact that CHOCHO is produced at a later stage of the VOC oxidation chain when the boundary layer has grown. However, I do not really see why this should lead to more CHOCHO at higher altitudes as we can assume that the boundary layer is relatively well mixed in the afternoon and similar vertical distributions can be expected for all species in the BL with no pronounced surface source. If the precursors of CHOCHO are in the free troposphere, then the HCHO produced from them should also be above the BL for which there seems to be indication on some but not all days. I would therefore argue that the observations are indicative of VOCs above the BL and that the assumption of a box profile for these species is not fully appropriate. Alternatively, NO2 and HCHO must have continuous surface based sources that explain why they are not well mixed in the BL.

3) I'd suggest to add the aerosol mixing heights from Li et al., 2010 to Fig. 6. This would make it obvious that only CHOCHO follows the evolution of the aerosol mixing heights. This could indicate that the source of CHOCHO and aerosols is the same while NO2 and HCHO are from other sources.

4) Why are figures 9 and 10 shown as log-log display? Was the linear fit performed in log-space or on the original data? What is the reason for forcing the regression lines

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through 0? These choices have a large impact on the results and need to be well justified or changed.

5) I'm not at all convinced by the "good" agreement between ground-based and OMI NO2 columns, in particular for the case including all data. OMI results are more or less constant for ground-based measurements covering more than one order of magnitude! The argument that OMI misses the NO2 because of clouds is also not convincing – first, the authors explain that over their site, it was cloud free so OMI should have seen the NO2. Second, the TEMIS product has a cloud correction scheme that should compensate for such effects. I believe that this points needs more discussion and a linear display of the results would help.

6) Some discussion at the beginning of the paper is concerned with details of the profile retrieval and how it was set-up. However, at a later point it is explained that in fact not the more complex 3 parameter model is used but rather a simple box layer model as already applied in previous studies. I do not see why a complicated method is introduced only to be abandoned and suggest to limit the description to the method actually employed.

7) Why was a log scale used for Fig. 11? I think a linear scale would be more appropriate (and more clearly show the large variation of Rgm for the columns which is quite an interesting result.

Minor comments:

There is a relatively large number of minor grammar points of which I list some below. Thorough proof reading is recommended before submission of the revised version.

p3984, l17: I don't think MAX-DOAS is that novel anymore

p3985, description of geometric approach. I don't think that single scattering is the point – the important assumption is that the last scattering was above the absorber layer. Also, RTM calculations are always needed to derive trace gas profiles.

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P3985, l13: Give the routinely => Given that routine

P3985, l18: on assumptions of => on assumptions on

P3985, l25: Boersma et al do not compare to MAX-DOAS

P3986, l5: what is large photochemical turnover? Why to high HCHO concentrations indicate large turnover – couldn't they just indicate high VOC levels?

P3987, l7: in most of => most of

P3987, l13: conditions favors => conditions favor

P3988, l2: what is "spectrum sampling"?

P3988, l8: record => recording

P3988, l25: for O4 => for the O4

P3990, l9: the norm for exponential factor => the normalisation factor

P3990, l11; and we found => and found

P3990, l11: under these => under the

P3990, l12: most of the trace gases were => most of the trace gas was

P3991, l1: applied for => applied to

P3991, l20: It would be good to explain already here what was used for g and SSA

P3991, l20: Was NO2 from the first retrieval in fact used in the HCHO and CHOCHO analysis or is NO2 included as an interfering species?

P3992, l9: This section is confusing – is this about SSA and AOD measured by MAX-DOAS? If not, what is the relevance of the data here?

P3993, l17 and in many other places: in (these 9) days => on (these 9) days

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P3994, l12 kept stable => remained stable

P3994, l22: pattern having => patterns having

P3994, l26: in the similar way => in a similar way

P3995, l25: than the obtained => than that obtained

P3996, l25: neither in Celarier et al., nor in Chen et al., any comparisons between MAX-DOAS and in-situ are reported

P3997, l21Though similar => Though a similar

P3997, l22 when compare => when compared

P3998, l4: instruments at => instruments measure at

P3998, l26: be 3-4 times of => being 3-4 times larger than

P3999, l22 PRD was identified => PRD being identified

P3999, l24: given HCHO => given that HCHO

P4000, l20: the lifetime => the lifetimes

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 3983, 2012.