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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Four years of ground-based MAX-DOAS observations of HONO and NO_2 in the Beijing area" *by* F. Hendrick et al.

Anonymous Referee #1

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In this manuscript, Hendrick et al. report on several years of MAX-DOAS observations of HONO and NO2 in and close to Beijing. Using a profiling algorithm they retrieve both vertical columns and surface mixing ratios of the two quantities and investigate the diurnal and seasonal variations, the correlations between NO2, HONO, and aerosol and the behaviour of the HONO/NO2 ratio. Using their measurements, they then investigate the rate of OH production from HONO and compare it to that from O3, finding that HONO is the dominating OH source in Beijing during winter time.

The paper is clearly structured, well written and covers a topic relevant for ACP. The long-term NO2 and HONO data sets in a Chinese megacity are very interesting and the analysis provides insights into the diurnal and seasonal variations as well as the links between NO2, HONO, and aerosols. However, I do have some concerns and needs

for clarification with respect to the retrieval and the data on which the whole paper is based. I therefore cannot recommend the paper for publication in ACP before these points have been addressed satisfactorily.

Major Comments

My main concern is that the retrievals, in particular the surface mixing ratios, have much larger uncertainties than suggested in the manuscript, and that aerosols, which are important for both the retrieval and the interpretation are not shown and discussed enough. More specifically, I have the following points:

1. The uncertainties given for the NO2 and HONO surface mixing ratios appear very optimistic to me – considering the possible impacts of varying aerosol loads and properties, clouds and horizontal inhomogeneities which all contribute to the uncertainty of the inversion, I find it difficult to believe that the uncertainty for the NO2 surface mixing ratio is as small as the 11% quoted in the table. Please comment. Is this value for individual observations or monthly averages?

2. The authors show an example for winter where BL height is low. As stated in the text, BL height can be as large as 3 km in summer, which would be the top of the scale in Figs 2 and 3. How do the profiles look like for a summer case? Is the same a priori shape used? If so, how realistic is that? Please add summer figures.

3. In Fig. 3 it can be seen, that the NO2 measured in the lowest 4 viewing directions is constant. In my opinion, this can only be the case if the light path for these viewing directions is limited by strong aerosol scattering (as is to be expected for Beijing) or if the NO2 layer extends to higher altitudes (which doesn't seem to be the case). I'm really surprised that the averaging kernels for such strong aerosol scattering still indicate that two independent layers can be retrieved in the lowest 500 m. Please comment. As aerosols are really important under these

observation conditions, I think the retrieved aerosol profiles and properties need to be shown as well for the examples.

4. In Fig. 2 and 3, the retrieved profiles of NO2 and HONO differ significantly with HONO being much more concentrated at the surface. How does this agree with the conclusion of NO2 being the main source of HONO? Is that a typical result or just a coincidence? It will be interesting to see the aerosol profile (the other prerequisite for HONO formation discussed).

5. Fig. 4, please add number of days per month contributing to the averages

6. Fig. 4, 5, and 8: please add AOD time series for comparison

7. The fact that HONO VC and VMR behave so similar could have a number of reasons: Either, the vertical profile shape is constant over time, or HONO is well mixed in the BL, or the DOF is too small to retrieve an independent surface mixing ratio. In the text it is stated, that retrievals with DOF < 0.7 are excluded, but for determination of surface mixing ratios which are more than the vertical column scaled by the a priori profile shape this is not sufficient. I think this points needs more discussion and the reader needs information on how independent the surface mixing ratio values really are from the columns. This could be done by either limiting the retrievals to those having larger DOF values or at least by indicating the average DOFs in Fig. 4.

8. It is not clear to me what drives the very large correlation coefficients found between NO2, HONO, and aerosols – are that changes during the day or changes from day to day? Given the systematic differences in diurnal behaviour shown in Fig. 7, I would guess that the correlation is driven by day to day changes. It would be good to also include examples showing data for all three quantities on higher time resolution for one day (15 minutes or hourly) and one month (daily) so that the reader has a clearer picture of the temporal variability.

9. How large is the correlation between NO2 and aerosol, and does that tell us something about the formation process of NO2 (using the same argument as for the correlations for HONO)? Or do these data just tell us that all three pollutants have high values in polluted conditions and low values on clean days? I think that the interpretation of the correlations as evidence for chemical formation processes is oversimplified and needs to be complemented by the evaluation of other possible explanations.

Minor Comments

P 10630, L 17: sensitivity of the measurements => sensitivity of the retrievals

P 10631, L 2: Isn't absorption strength rather than concentration the important point here?

P 10361, L1: Do you really believe that the "total retrieval error" on the NO2 VMR in the lowest 200 m is 4%? I think this is unrealistic considering the large number of uncertainties in this type of inversions!

P 10640, L9: "To conclude, MAX-DOAS is shown to be a useful and reliable technique for monitoring HONO near-surface concentrations and vertical column amounts in polluted areas." I think this is not the main point of the paper. Also, I think this is not shown in the paper (you would need independent validation to support this claim).

Fig. 1, top: If differential optical density is shown, why is the signal not centred around 0 as is the case for NO2?

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 10621, 2013.