Reply to Anonymous Referee #1

First, we would like to thank Anonymous Referee #1 for his/her helpful comments.

In this manuscript, Hendrick et al. report on several years of MAX-DOAS observations of HONO and NO_2 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 NO_2 surface mixing ratio is as small as the 11% quoted in the table. Please comment. Is this value for individual observations or monthly averages?

We agree that the error budget presented in the ACPD paper was underestimated mainly because potential forward model error sources were not investigated. In the revised manuscript, we have included the impact of the aerosol loads, which is one of the main forward model error sources. The uncertainty related to aerosols is found to be about 20-25% on the retrieved NO_2 and HONO surface concentrations. It increases the total uncertainty on the surface concentrations (individual retrievals) to about 28-33% for HONO (instead of 24-26% previously) and about 24-30% for NO_2 (instead of 11-16% previously). The errors related to the presence of clouds and to horizontal inhomogeneity are more difficult to quantify since they require extensive radiative transfer calculations which are beyond the scope of the present study. It should be noted that both issues are currently investigated by the NDACC UV-vis Working Group (http://www.ndacc.org/) within the framework of the EU project NORS (http://nors.aeronomie.be).

Recommendations on these topics will be formulated by the end of the project (July 2014).

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.

The BLH ranges typically between 1 to 3 km throughout the year at local noon but it is most of the time lower than 100m in the early morning and late afternoon according to ECMWF analyses. We found that 0.5 km was a good compromise for SH, especially regarding the sensitivity of the retrieval to the lowest altitude layers and the overall information content. Moreover, sensitivity tests performed on MAX-DOAS retrievals of formaldehyde at the Xianghe station showed that results obtained using SH=0.5 km agree generally within 25% with those obtained using ECMWF reanalysis BLH data for SH, as illustrated in Figure 1 below. The sensitivity test with SH=1 km presented in the paper already provides a reasonable estimate of the uncertainty related to the choice of SH.

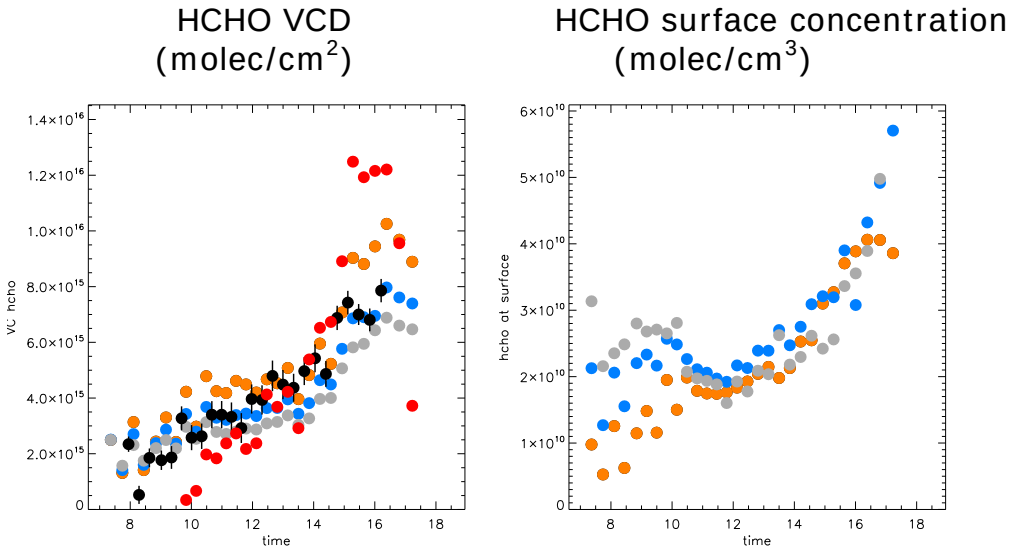

Figure 1: Impact of the choice for SH on the retrieved HCHO VCD and surface concentration (day 67 in 2011 at Xianghe). Blue is for SH=BLH_{ECMWF}, grey is for SH=0.5 km, orange is for SH=2.5 km, black is for direct-sun measurements, and red is for the geometrical approximation.

Figures 2, 3, and 4 below show examples of HONO, NO_2, and aerosol retrievals for summer conditions using exponentially decreasing a priori profiles with SH=0.5km.

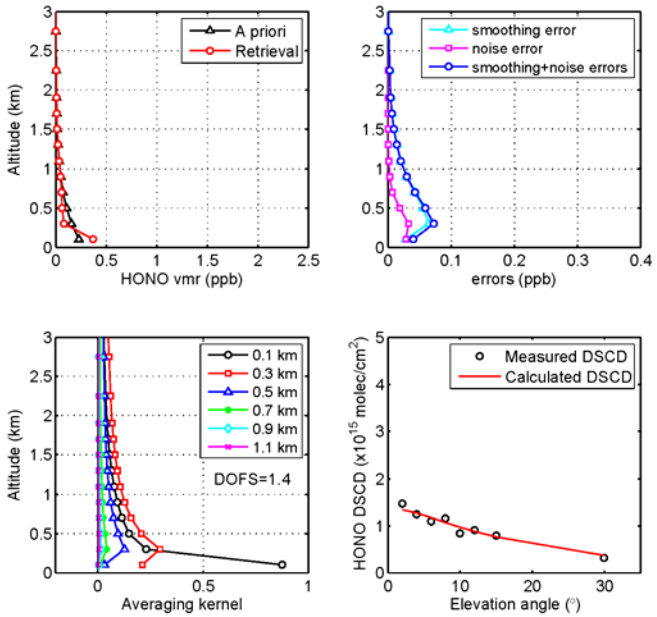

Figure 2: Example of HONO vertical profile retrieval (Beijing, 31 July 2008, ~07:00 local time). The upper plots display the a priori and retrieved profiles (left) and the smoothing and noise errors (right). Averaging kernels and fit results (comparison between measured DSCDs and those calculated with the retrieved profile) are shown in the lower plots. Error bars on the measured DSCDs are the DOAS fit errors.

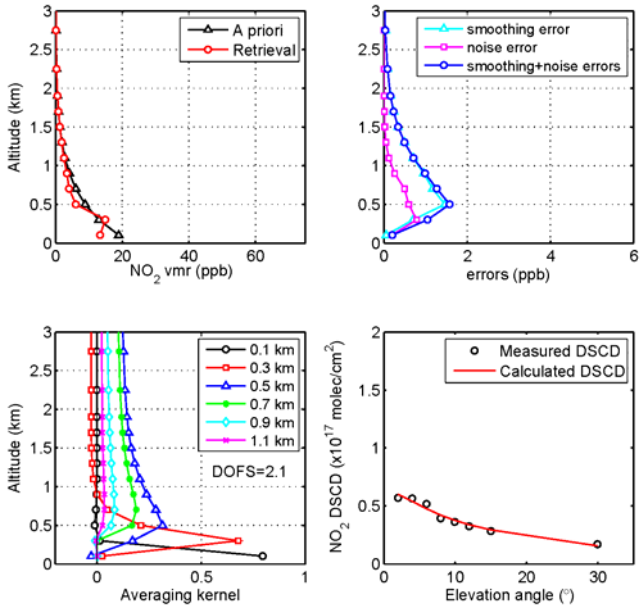

Figure 3: Same as Fig. 2 but for NO_2.

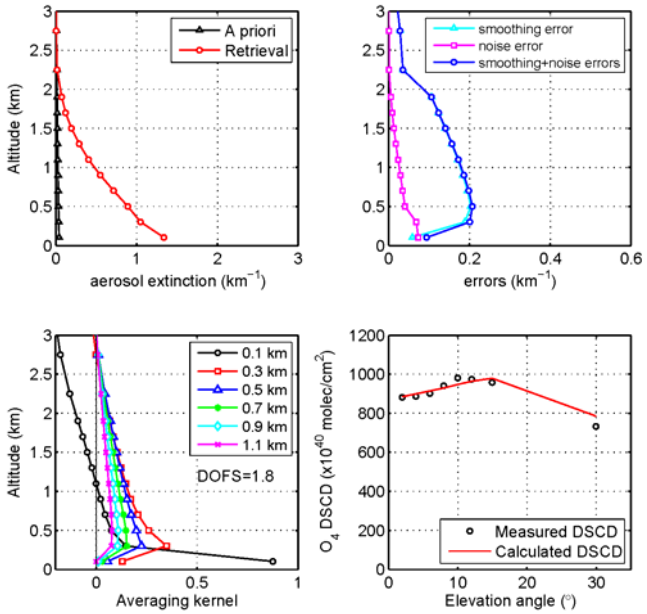

Figure 4: Same as Figs 2 and 3 but for aerosol extinction vertical profile retrieved from O_4 DSCDs at 360 nm.

As in winter conditions (see Figs 2, 3, and 4 in the revised manuscript), the vertical gradient of HONO concentration is stronger than for NO_2. The comparison of winter and summer averaging kernels shows that the vertical sensitivity is similar for the three retrievals (sensitivity to the first layer and total column for HONO and aerosols while in case of NO_2, the retrieval is sensitive to the first two layers in addition to the total column).

We decided not to include the above three figures in the revised manuscript because (1) similar features are obtained for winter and summer conditions (we mention this point in the revised manuscript), (2) the main purpose of these HONO and NO_2 retrieval examples is to illustrate the main input/output parameters involved in the retrieval and not so much their geophysical interpretation (the examination of a larger set of profiles is needed to do that), (3) four new figures have been already added to the revised manuscript in response to other Referees' comments.

3. In Fig. 3 it can be seen, that the NO_2 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 NO_2 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.

We have added the corresponding example of aerosols retrieval in the revised manuscript (see Fig. 4). This figure shows large aerosol extinction coefficient values in

the layers close to the ground. Therefore, as suggested by Referee #1, a strong aerosol scattering is responsible to the near-constant NO_2 slant column density measured in the lowest four viewing angles. In case of NO_2, we found that the averaging kernels are most of the time similar for low and high aerosol loads. It is likely related to the high absorption strength of this molecule and its large concentration in the Beijing area.

4. In Fig. 2 and 3, the retrieved profiles of NO_2 and HONO differ significantly with HONO being much more concentrated at the surface. How does this agree with the conclusion of NO_2 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).

We have added the corresponding aerosol retrieval example in the revised manuscript (Fig. 4). As noted by Referee #1, the winter and summer retrieval examples (see Figs 2, 3, and 4 in the present document and in the revised manuscript) indicate that the vertical gradient of HONO concentration is stronger than for NO_2. Moreover, the comparison of mean daytime HONO and NO_2 profiles normalized by the VMR in the 0-200 m layer (see Fig. 5 below) shows that it is a typical behaviour. A stronger vertical gradient for HONO is not in contradiction with NO_2 being the main source of HONO because the heterogeneous conversion of NO_2 to HONO might occur for a large part at the ground surface, on soils and buildings (while the rest likely takes place at the surface of aerosols).

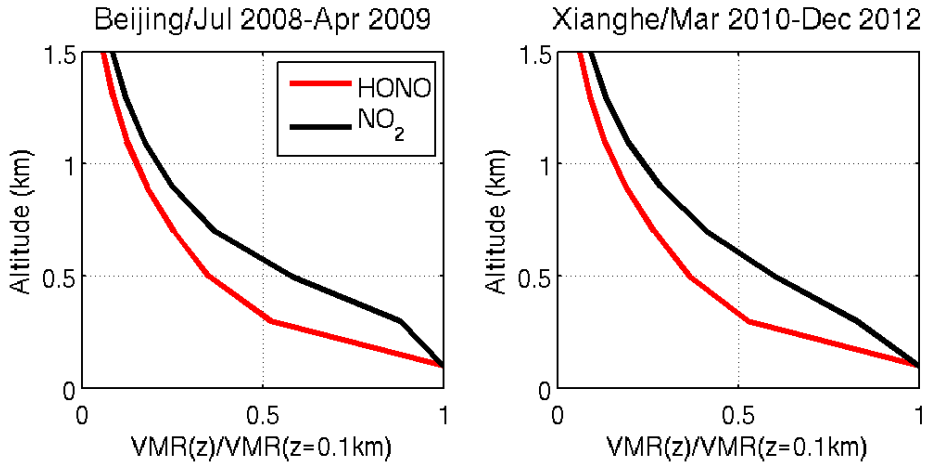

Figure 5: Mean daytime (local noon ± 2h) HONO and NO_2 vertical profiles normalized by the VMR value in the first layer (0-200m).

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

Fig. 6 below shows the number of days per month contributing to the averages as well as the monthly-averaged DOFS. The number of days used for the calculation of monthly means shows a seasonality with a maximum in fall/winter/early spring (~ 25-30 days) and a minimum in summer (~15 days). The reason for this decrease in summer is the low daytime HONO amounts observed during this period making the OEM-based retrieval

less stable with retrieved profiles showing spurious oscillations with negative values, leading therefore to a larger number of rejected scans.

We decided to only mention the number of days in the revised manuscript and not to include Fig. 6 below.

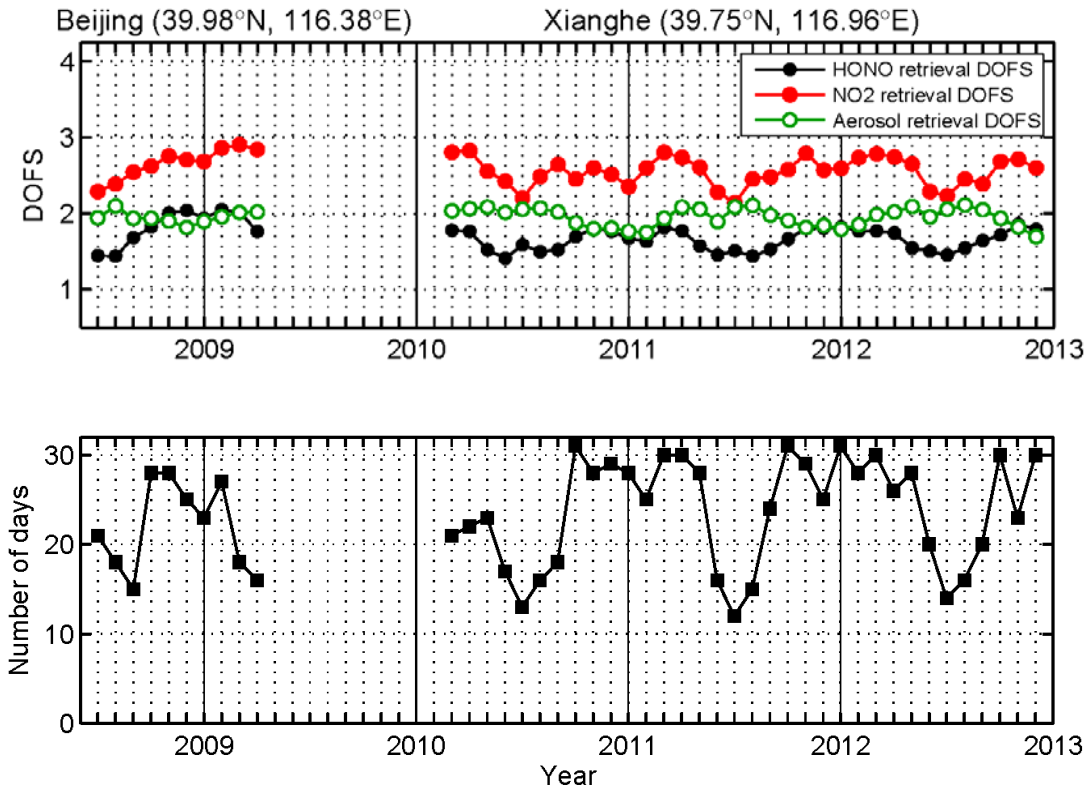

Figure 6: Number of days used to calculate monthly means in Fig. 7 of the revised manuscript (lower plot) and corresponding mean DOFS for HONO, NO_2, and aerosol retrievals (upper plot).

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

We have added the AOD retrieved at 360 nm in the three figures. The AOD shows a distinct seasonality with a maximum in spring/summer and a minimum in winter. Such a seasonal variation of the AOD over Beijing was also reported by Yu et al. (2009) using AERONET observations. It can be mainly attributed to particles emitted from massive agricultural fires in the region surrounding Beijing during the May-July period with a peak in June (Xia et al., 2013) as well as to long-range transport of dust particles during spring/summer (Yu et al., 2009). Regarding the AOD diurnal cycle, there is no marked variation, with values around 1-1.5 throughout the day at both stations, except in Beijing in summer where the AOD increases during the morning, with a maximum value of 3 around 11:00 LT.

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.

We agree with the reviewer. The monthly averaged DOFS are presented in Fig. 6 above. The mean DOFS is seen to range between 2.0 and 3.0 for NO_2, and 1.8 and 2.2 for aerosols, indicating that the retrieved concentration or extinction coefficient at surface is independent from the corresponding VCD or AOD. It is also the case for HONO during the late fall/winter/early spring period with a DOFS around 1.8-2.0. In summer, the DOFS decreases to values around 1.5, suggesting that the surface concentration is to some extent not strictly independent from the retrieved VCD and a priori profile shape during this period.

This discussion on the mean DOFS has been added in the revised manuscript.

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.

We have added a figure showing the day-to-day changes for one summer month and one winter month at both stations (Fig. 10 in the revised manuscript). We see that within one month (summer or winter), the short-term variations of the daily means exhibit exactly the same patterns, with peaks and troughs on the same days for both trace gases and aerosols. Simply put, the three pollutants have high values in polluted days and low values on clean days. Although a strong correlation is expected between NO_2 and HONO, since NO_2 is recognized as the main precursor of HONO, the same is not true for e.g. the correlation between NO_2 and aerosols. The high correlation is therefore likely mainly of meteorological origin, given the relative similarity in the spatial distribution of aerosols and NO_x, which both have a strong anthropogenic component. We have therefore to admit that the role of aerosols as mediator for heterogeneous HONO formation is not proven by the correlation between HONO and aerosols, although it might contribute to it. The manuscript has been modified in order to provide a more balanced view of the possible causes for the observed correlations.

9. How large is the correlation between NO_2 and aerosol, and does that tell us something about the formation process of NO_2 (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.

See response to the previous comment. We have added the correlation between NO_2 and aerosols in Fig. 9 of the revised manuscript. The correlation between NO_2 and aerosols is indeed also very high, in the 0.6-0.9 range at both stations, as now mentioned in the text.

Minor Comments

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

Corrected.

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

Right. This has been corrected.

P 10361, L1: Do you really believe that the "total retrieval error" on the NO_2 VMR in the lowest 200 m is 4%? I think this is unrealistic considering the large number of uncertainties in this type of inversions!

See our reply to major comment #1.

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).

We agree on the fact that thorough validation of MAX-DOAS HONO retrievals with other independent techniques like LOPAP and LP-DOAS would be needed to claim that MAX-DOAS is a reliable technique for monitoring HONO in polluted areas. The problem is that, to our knowledge, such correlative data at both Beijing and Xianghe stations are not available. However, we have added in the revised manuscript a comparison with other HONO measurements performed in or in the vicinity of megacities in East Asia. The agreement with our HONO data is found to be rather good, suggesting that, combined with the error budget presented in the paper, our HONO retrievals give reasonable results. We therefore replaced "…useful and reliable technique…" by "…useful technique….".

Fig. 1, top: If differential optical density is shown, why is the signal not centered around 0 as is the case for NO_2 ?

The reason is that absolute cross-sections of HONO have been used in the DOAS retrieval. The differential absorption features are well marked for HONO and the absorption background is very low, in contrast to NO_2.

References:

Li, Y., An, J., Min, M., Zhang, W., Wang, F., and Xie, P.: Impacts of HONO sources on the air quality in Beijing, Tianjin, and Hebei Province of China, Atmos. Env., 45 (27), 4735-4744, 2011.

Xia, X., Zong, X., and Sun, Li: Exceptionally active agricultural fire season in mid-eastern China in June 2012 and its impact on atmospheric environment, J. Geophys. Res. Atmos., 118, 9889-9900, doi:10.1002/jgrd.50770, 2013.

Yu, X., Zhu, B., and Zhang, M.: Seasonal variability of aerosol optical properties over Beijing, Atmos. Environ., 43, 4095-4101, 2009.