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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Exploring the atmospheric chemistry of nitrous acid (HONO) at a rural site in Southern China" *by* X. Li et al.

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Reply to Referee #2

We thank Anonymous Referee #2 for his/her comments on our paper and the recommendation for publication in ACP.

Specific comments

Comment: 1. Extremely high levels of HONO (5 ppb) were measured and suggested as a record for rural areas. However, as mentioned by the authors, the abnormally high HONO was due to the influences of a cable-burning event. Thus, I think the data of that episode should be excluded from the analysis for "urban atmospheric chemistry" or, at least, should not be highlighted as a record.

Answer: During our study, we did not exclude the time periods when cable or biomass burning events occured in the surrounding areas of the measurement site, i.e. 24 and 25 July 2006. As shown in Figure 1, the NO/NO_X ratios in these periods were below 50%, even smaller than in the previous nights. This indicates that the detected airmasses were already aged. However, given the long nocturnal HONO lifetime it is difficult to associate the observed high HONO concentrations to chemical formation or direct emissions. However, we still like to include these data for several reasons: 1. They refer to a ≈10% of the dataset and the general conclusions are not biased. 2. These events are typical in rural/agricultural areas in countries where waste burning is not strongly regulated by legislation. 3. These days were also included in the papers by Hofzumahaus et al. (2009) and Lu et al. (2012). According to the comment we removed the statement "are among the highest ever reported" from the abstract.

Comment: 2. Elevated HONO/NO_2 ratios were observed during afternoon in this study, indicated high HONO/NO_2 in night time. This finding should have very important implications for the daytime budget of HONO. Unfortunately, the authors did not make further discussions, i.e. why the high HONO/NO_2 in PRD occurred during daytime.
Answer: Compared to other studies, our observed elevated HONO/NO_2 ratios during afternoon is due to the formation of HONO is more efficient via other mechanisms than via the conversion from NO_2. This conclusion is based on the fact that (1) no correlation was found between P_M and NO_2 (as shown in Fig. 9, and Fig. 2 and Fig. 3 in the reply to Referee #1), and (2) the P_M (0.77 ppb h^{-1}) is much larger than the heterogeneous conversion from NO_2 to HONO (which can be calculated as $C_{HONO} \times \overline{[NO_2]} \approx 0.024 \times 2 = 0.048$ ppb h^{-1}). We modify the text so that the observed different behavior of HONO/NO_2 in Backgarden than in other places is emphasized and explained.

Comment: 3. Weak correlation between aerosol surface density and HONO/NO_2 ratio was observed and, accordingly, the formation of HONO on aerosol surface was suggested to be small. However, as shown in Figure 6c, the correlation is rather obvious and the low r^2 value is due to the interferences of some data points. I'd like to suggest

dividing the data into groups and rechecking the aerosol effects.
Answer: The correlation of HONO/NO_2 against aerosol surface density (S_{aw}) was checked on the daily basis. Although r^2 in some days is higher than that in Fig. 6c, in general we did not find a prominent relationship between HONO/NO_2 and S_{aw} (i.e. r^2 is below 0.4). The $\gamma_{NO_2 \rightarrow HONO}$ calculated for each day are in the range of (1–6)$\times 10^{-5}$, which seems too high for ambient aerosols. We thought the data points mentioned by the referee are those in the range of HONO/NO_2>0.08 and S_{aw}<1.5. Excluding these data points, r^2 increased to 0.347. However, when we refer to the time periods where these data points belong to, we did not find a significant difference from the time before and after in terms of the meteorological conditions (e.g. wind speed, wind direction, RH) and trace gas (e.g. NO, NO_2, O_3) concentrations. Therefore, we could not exclude these data points from the correlation analysis in Fig. 6c.

Comment: 4. The surface density of soot was estimated as $(1-\omega)\times S_a$ (p27609). Considering that the single scattering albedo of aerosols is affected by a lot of microphysical properties like size distribution and mixing state of BC and scattering components, I disagree with such an approximation. This could also be one of the causes for the unreasonable gamma values.
Answer: As we pointed out in the text, the surface area was estimated using a number of rough assumptions and the resulting $\gamma^{\mathrm{soot}}_{\mathrm{NO_2 \rightarrow HONO}}$ is too high, similar to findings of other groups. We think that this information is important for the reader since it (indirectly) supports the conclusions drawn by Aubin and Abbatt (2007), Sörgel et al. (2011), and Wong et al. (2011).

Comment: 5. Strong correlation between P_M and HNO_3 was revealed. In addition to gaseous HNO_3, will nitrate aerosols also go through the reaction (R7)? In this case, considering the high levels of nitrate aerosols in PRD region, the contribution of nitrate could also be significant.
Answer: Based on the advice of the referee we recalculated the J($HNO_3 \rightarrow$HONO) by using the sum of measured HNO_3 and aerosol nitrate. In this case, an even better

correlation is found (r^2=0.88, cf. Figure 1 in the answer to Referee #1). The original correlation between P_M and adsorbed HNO_3 was r^2=0.81 (This value changed due to a mistake which was detected when preparing the revised figures.). Moreover, the calculated J($HNO_3 \rightarrow$HONO)=2.5$\times 10^{-5}$ s^{-1} is closer to the value observed by Zhou et al. (2003). In the revised version we provide a new Fig. 10 which includes both correlations, the text will be changed accordingly.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 27591, 2011.

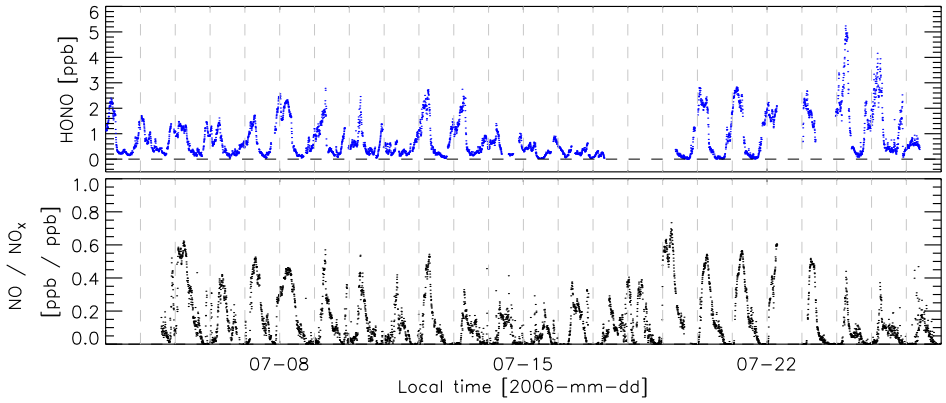

Fig. 1. Time series of HONO and NO/NOx at the Back Garden supersite in July 2006.