

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

Anonymous Referee #1

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General comments

This paper reports HONO measurements at a rural site in Southern China and high levels of HONO (up to a few ppb) were observed under polluted conditions. Using the concurrent measurements of OH as well as other trace gases and meteorological parameters, HONO budget was analyzed and it was found that HONO was mainly from NO₂ heterogeneous conversion on the ground at night. During the day a missing HONO formation rate was calculated and found to be relevant to the photolysis of adsorbed HNO₃ on the ground, with possibility of the contribution from soil nitrite. A surprising finding is that the missing HONO formation during the day was not related to the NO₂ heterogeneous conversion.

It seems to me that the conclusion of the missing daytime HONO production mainly
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from the photolysis of adsorbed HNO₃ is not very solid (see special comments below). It might be possible that the photolysis of adsorbed HONO₃ and soil nitrite contribute equally to the daytime HONO production.

Also it seems that there is a discrepancy between this work and the work by Su et al., Science, 2011. Su et al. (2011) showed that the HONO production from soil nitrite alone for the field measurements in Xinken in Southern China can explain most daytime HONO productions besides the OH+NO reaction. I thought the soil in Back Garden, where the field measurements for this study were made, is similar to the soil in XinkenSu, since both locations are within the Pear River Delta area. If so, soil nitrite should also play a significant role in HONO production in Back Garden as in Xinken. However, in this study, the authors attribute the daytime missing HONO mainly to the photolysis of adsorbed HNO₃ on the ground, although they do not rule out the possibility of the contribution from soil nitrite.

In general the paper is well written and reports important results. I support its publication in ACP after minor revision and ask the authors to consider the above main concerns and following special comments in their revision.

Special Comments

1. P.27593, L.12, I would suggest changing “...on atmospheric chemistry” to “...in atmospheric chemistry”. Also, L.18, “...generally lower than” to “...generally much lower than” or “...generally an order or more lower than” for a better text flow.
2. P.27595, L.12-15, I was surprised that a recent paper, Zhou et al., Geoscience, 2011, was not cited when the photolysis of surface adsorbed HNO₃ as a HONO source is discussed.
3. P.27597, the direct emission term is missing in Eq.(3), unless it has been included in PM (if this is the case, it should be mentioned in the text). Also, what about the dry deposition? On the same page at the bottom, where missing HONO formation is

discussed, Wong et al. (2011b) also did a similar analysis other than Kleffmann et al. (2005). It might be worthwhile to mention it here as well.

4. P.27598, L.19, it should be Table 1, not Fig. 1.
5. P.27601, L.8-10, the sentence "While the particle number size distributions were measured by a system consisting of a Twin Differential Mobility Particle Sizer (TDMPS) and an APS (TSI model 3321)" is not complete. Maybe remove "while".
6. P.27607, L.10, at what temperature are these rate coefficients calculated?
7. P.27612, L.7, the term, HONO_M, is missing definition at its first time appearance. I can guess it is the HONO concentration corresponding to P_M, or P_M/{first-order of HONO loss rate}, but it should be state clearly what it stands for. Also in the caption of Fig. 8, the definition (or brief description) of HONO_M should be included so it is self-explained and readers do not need to go back to the text to find its definition.
8. P. 27614, again Zhou et al., Geoscience, 2011 should be cited when the photolysis of surface adsorbed HNO₃ as a HONO source is discussed. Also the derived J(HNO₃→HONO) is about a factor of 5 higher than the value obtained in the lab by Zhou et al. and the data points in Fig. 10 is rather limited. Thus the conclusion that the daytime HONO production is mainly from the photolysis of surface adsorbed HNO₃ is not solid. Other processes (e.g. soil nitrite) maybe also contribute equally if not more importantly to the daytime HONO production.
9. Fig. 1, in caption, "refers" to "refer".
10. P.27629, Fig. 4, top panel: put the percentage number closer to each dashed line. Also it seems that higher aerosol surface density => higher HONO/NO₂ ratio.
11. P.27628, in the caption of Fig. 3, "...boxes represent 50%...", does it means between 25% and 75% percentile?
12. In Reference, Wong et al. (2011b) came up an parameterization of unknown

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HONO production and it might be worthwhile (should be easy to do) to compare the parameterization in PRD and that in Houston to see if there is any similarity.

13. Fig. 7, why choose 18:00-0:00 this time period?
14. Fig. 8, caption, should be "Black triangles" instead of "Black circles".
15. P.27613 top and Fig. 9, in order to rule out the importance of the photosensitized or photoenhanced reduction of NO₂ on surface, it might be worthwhile to look at the correlation between PM and JNO₂*[NO₂] (or NO₂-normalized PM vs. JNO₂) because both Wong et al. (2011b) and Ren et al. (Atmos. Meas. Tech., 4, 2093-2103, 2011) found good correlation between these (similar) two terms. The correlation between PM and a single term (JNO₂ or [NO₂]) only could be poor as also discussed in Ren et al. (2011).

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