

## ***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 #1**

We thank Anonymous Referee #1 for his/her comments on our paper. We understand that his/her major concern is the source of the missing daytime HONO production.

### **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 NO<sub>2</sub> heterogeneous conversion on the ground at night. During the day a miss-

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ing HONO formation rate was calculated and found to be relevant to the photolysis of adsorbed HNO<sub>3</sub> 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 NO<sub>2</sub> heterogeneous conversion.

It seems to me that the conclusion of the missing daytime HONO production mainly from the photolysis of adsorbed HNO<sub>3</sub> is not very solid (see special comments below). It might be possible that the photolysis of adsorbed HNO<sub>3</sub> 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 Xinken, 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 HNO<sub>3</sub> 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.

### **Answer to general comments**

The major issue of the comment is missing daytime HONO production. Based on the measured data during the PRD2006 campaign, we analyzed the relationship between the missing daytime HONO production (i.e.  $P_M$ ) and various parameters. These parameters include not only the different measured species (NO<sub>2</sub>, aerosol surface density, solar radiation, photolysis frequencies, etc.) but also the combination of some of them (e.g. NO<sub>2</sub> × H<sub>2</sub>O, NO<sub>2</sub> × H<sub>2</sub>O × aerosol surface density). Moreover, the analysis

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was done both on the entire dataset and on the daily basis. The analysis showed that the heterogeneous conversion of  $\text{NO}_2$  to HONO can not explain  $P_M$ . We found that the adsorbed  $\text{HNO}_3$  could be one source of  $P_M$ , given the good correlation between them and the calculated  $J(\text{HNO}_3 \rightarrow \text{HONO})$  being in the reported range. Since we had limited data points in Fig. 10 we described the adsorbed  $\text{HNO}_3$  as one *likely source* of  $P_M$ . This relatively weak conclusion reserves space for other possible sources, which unfortunately are not able to be quantified by our measured data. We agree with the referee that the soil nitrite could contribute to  $P_M$  in a similar amount as the adsorbed  $\text{HNO}_3$ . However, as we did not have any measurement on the soil properties, it is difficult to quantify the contribution of soil nitrite compared to adsorbed  $\text{HNO}_3$  to  $P_M$ . In addition, we do not know if the soil properties at Backgarden are the same as those at Xinken. This is because Backgarden is located at the north end of the PRD region while Xinken is located at the southeast end. The distance between the two sites is around 200 km. Backgarden site is surrounded by farmlands and forests. In contrast, Xinken is at the seaside (at the Zhujiang river estuary) and located in a land reclamation area which might not be representative for the Guangdong province. Also, the campaign performed at Xinken was in the autumn of 2004, while our measurements at Backgarden were in the summer of 2006. The meteorological conditions during the two campaigns were quite different.

### Specific comments

**Comment:** 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.

**Answer:** Changed in the revised version.

**Comment:** 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  $\text{HNO}_3$  as a HONO source is discussed.

**Answer:** We thank the referee for this advice. We will cite Zhou et al. (Nature Geoscience, 4, 440–443, 2011) in the revised version.

science, 4, 440–443, 2011) in the revised version.

**Comment:** 3. P.27597, the direct emission term is missing in Eq.(3), unless it has been included in  $P_M$  (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.

**Answer:** We will modify the explanation of Eq. 3 according to the referee's comments. The work by Wong et al. (2011b) will also be cited. The deposition lifetime is much smaller than the lifetime due to photolysis: for the daytime analysis we restricted the data to photolysis frequencies above  $8 \times 10^{-4} \text{ s}^{-1}$  corresponding to a HONO lifetime below 20 min. The deposition velocity is in the order of  $0.8 \text{ cm s}^{-1}$  corresponding to  $\approx 30 \text{ h}$  lifetime.

**Comment:** 4. P.27598, L.19, it should be Table 1, not Fig. 1.

**Answer:** Changed in the revised version.

**Comment:** 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".

**Answer:** Changed in the revised version.

**Comment:** 6. P.27607, L.10, at what temperature are these rate coefficients calculated?

**Answer:** At the temperature of 298K. Included in the revised version.

**Comment:** 7. P.27612, L.7, the term,  $\text{HONO}_M$ , is missing definition at its first time appearance. I can guess it is the HONO concentration corresponding to  $P_M$ , or  $P_M/(\text{first-order of HONO loss rate})$ , but it should be state clearly what it stands for. Also in the caption of Fig. 8, the definition (or brief description) of  $\text{HONO}_M$  should be included so it is self-explained and readers do not need to go back to the text to find its definition.

**Answer:** Changed in the revised version.

**Comment:** 8. P. 27614, again Zhou et al., Geoscience, 2011 should be cited when the photolysis of surface adsorbed  $\text{HNO}_3$  as a HONO source is discussed. Also the derived  $J(\text{HNO}_3 \rightarrow \text{HONO})$  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  $\text{HNO}_3$  is not solid. Other processes (e.g. soil nitrite) maybe also contribute equally if not more importantly to the daytime HONO production.

**Answer:** The paper by Zhou et al. (2011) is included in the revised version. Anonymous Referee #2 also pointed out the possible contribution of the adsorbed nitrate to  $P_M$ . We included the measured aerosol nitrate in the analysis of Fig. 10. As illustrated in the Figure A1, the x-axis is the averaged  $\text{HNO}_3$  and aerosol nitrate ( $\text{NO}_3^-$ ) concentration in the previous 24 h. The calculated  $r^2=0.88$  is higher than that in Fig. 10 (i.e. 0.81; this value changed from the previous version due to a mistake which was detected when preparing the revised figures.). Moreover, the calculated  $J(\text{HNO}_3 \rightarrow \text{HONO})=2.5 \times 10^{-5} \text{ s}^{-1}$  is even 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.

**Comment:** 9. Fig. 1, in caption, "refers" to "refer".

**Answer:** Changed in the revised version.

**Comment:** 10. P.27629, Fig. 4, top panel: put the percentage number closer to each dashed line. Also it seems that higher aerosol surface density  $\rightarrow$  higher HONO/ $\text{NO}_2$  ratio.

**Answer:** Changed in the revised version.

**Comment:** 11. P.27628, in the caption of Fig. 3, ". . .boxes represent 50%...", does it mean between 25% and 75% percentile?

**Answer:** Yes, the boxes are the percentile between 25% and 75%. We modified the figure caption of Fig. 3 in the revised version.

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**Comment:** 12. In Reference, Wong et al. (2011b) came up an parameterization of unknown 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.

**Answer:** Wong et al. (2011b) found a prominent relationship between the  $\text{NO}_2$ -normalized unknown HONO production and the  $J(\text{NO}_2)$  and global short-wave solar radiation ( $G$ ). Based on this relationship, they came up with a parameterization of the unknown HONO production. However, in our case, we did not see any correlation between these parameters (as illustrated in the Figure A2 and Figure A3). Therefore, we could not derive the similar parameterization of the unknown HONO production as in Houston. Moreover, according to Wong et al.(2011b), the unknown HONO production in Houston is related to  $\text{NO}_2$ . But our study suggests the unknown HONO production in Backgarden is more related to the adsorbed  $\text{HNO}_3$ . From Figure 10, we can provide a parameterization of the unknown HONO production as a function of the adsorbed  $\text{HNO}_3$ , i.e.  $P_M=(0.89 \pm 0.22) \times [\text{HNO}_3]_{ads} \text{ ppb h}^{-1}$ . The comparison with the results by Wong et al. (2011b) is included in the revised version.

**Comment:** 13. Fig. 7, why choose 18:00-0:00 this time period?

**Answer:** As explained in P.27608, L.4-5, the choose of 18:00–0:00 is to avoid the influence of the contribution of  $\text{OH}+\text{NO}$  reaction to the HONO formation. We include this statement in the figure caption of Fig. 7 in the revised version.

**Comment:** 14. Fig. 8, caption, should be "Black triangles" instead of "Black circles".

**Answer:** Changed in the revised version. Figure 8 will be updated to make the triangles better visible.

**Comment:** 15. P.27613 top and Fig. 9, in order to rule out the importance of the photo-sensitized or photo-enhanced reduction of  $\text{NO}_2$  on surface, it might be worthwhile to look at the correlation between  $P_M$  and  $J(\text{NO}_2) \times [\text{NO}_2]$  (or  $\text{NO}_2$ -normalized  $P_M$  vs.  $J(\text{NO}_2)$ ) 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  $P_M$  and a single term ( $J(\text{NO}_2)$  or  $[\text{NO}_2]$ ) only could be poor as also

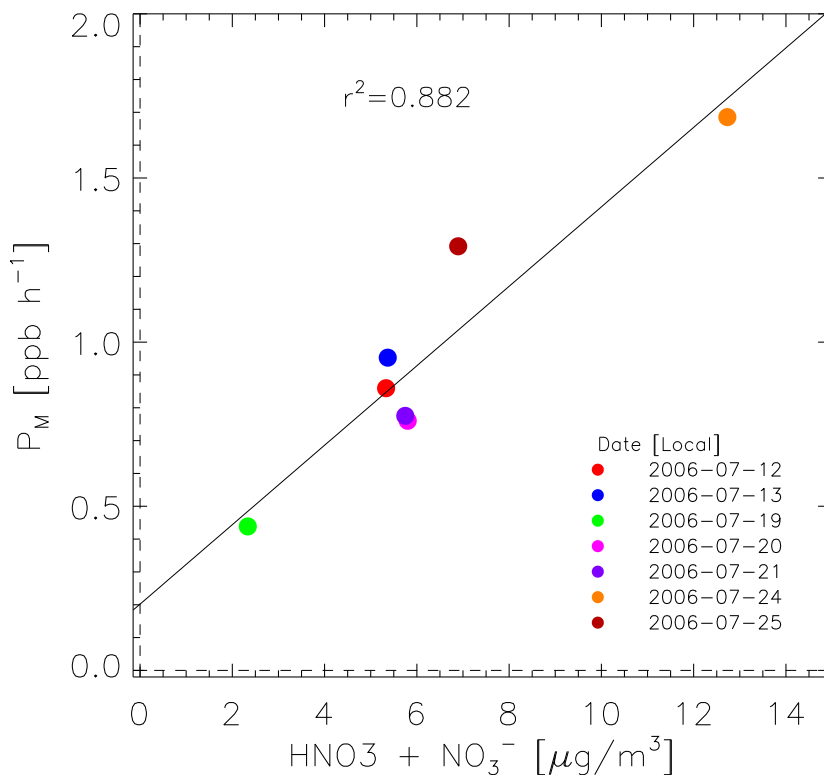
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discussed in Ren et al. (2011).

**Answer:** As described in the answer to Comment 12, we checked the correlations between  $P_M$  and  $J(\text{NO}_2) \times [\text{NO}_2]$ , as well as between  $P_M$  and  $G \times [\text{NO}_2]$ , see Figure A2 and Figure A3. Differently from the results by Wong et al. (2011b) and Ren et al. (2011), we did not find correlations between  $P_M$  and these quantities. This will be mentioned in the revised version.

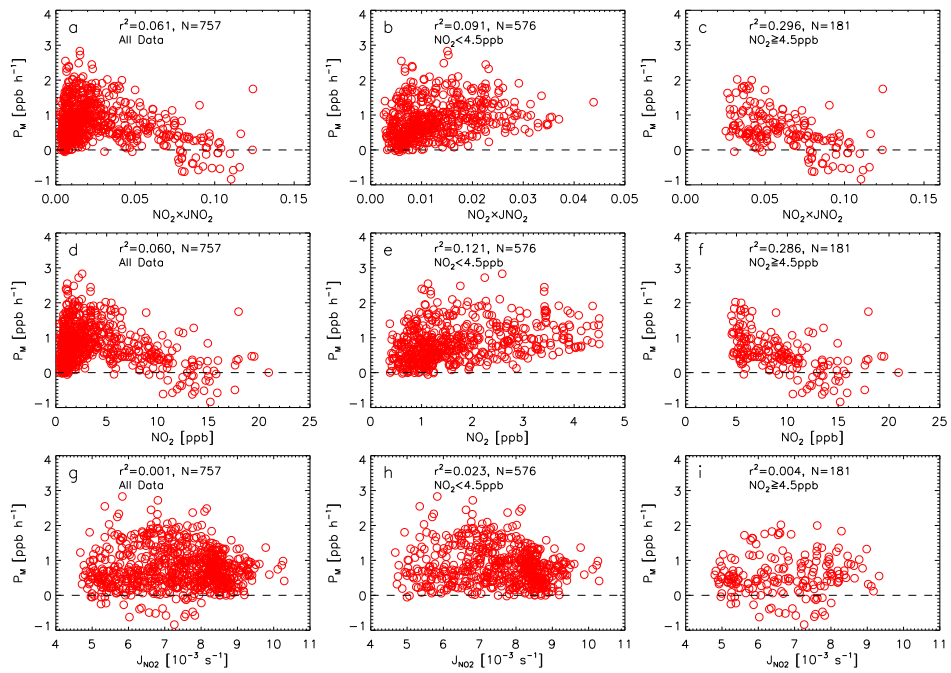
Interactive comment on Atmos. Chem. Phys. Discuss., 11, 27591, 2011.

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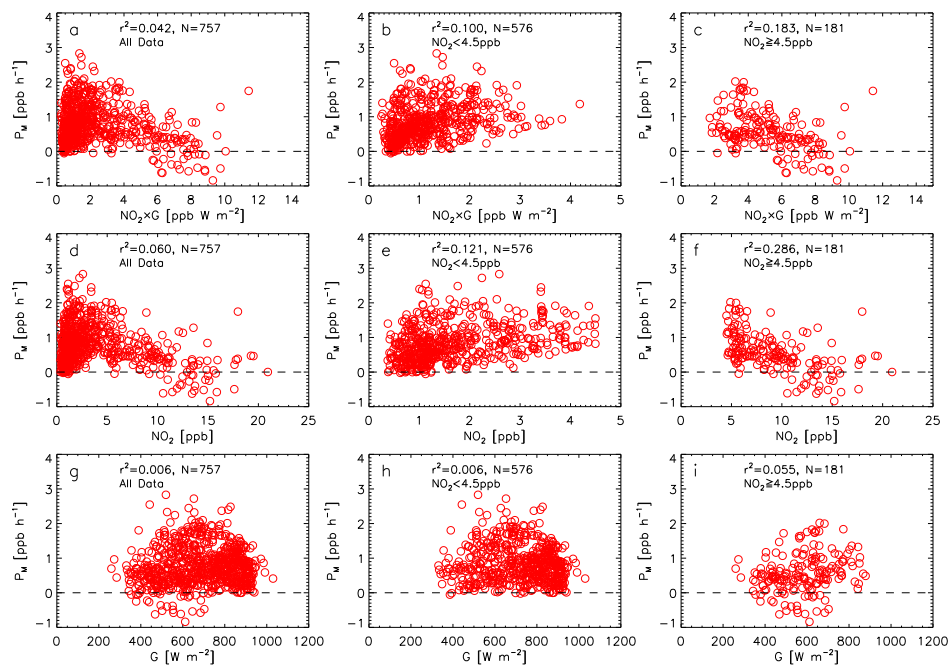
**Fig. 1.** Relationship between average noontime (11:00-13:00 LT)  $P_M$  and the averaged  $\text{HNO}_3$  and aerosol nitrate ( $\text{NO}_3^-$ ) concentration over the previous 24-h period.

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**Fig. 2.** Correlation of  $P_M$  against  $NO_2$ ,  $J(NO_2)$ , and  $NO \times J(NO_2)$ .

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**Fig. 3.** Correlation of  $P_M$  against  $NO_2$ , solar radiation ( $G$ , 300-2800 nm), and  $NO_2 \times G$ .

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