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Atmospheric
Chemistry
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Discussions

Interactive comment on "Measurements of HONO during BAQS-Met" *by* J. J. B. Wentzell et al.

Anonymous Referee #1

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The authors presented some high quality and interesting HONO measurement data during the 2007 Border Air Quality Meteorological Study in this manuscript. The content of the paper is appropriate to Atmospheric Chemistry and Physics. However, some additional discussion and revisions can be made to improve the manuscript. I have the following comments and suggestions for the authors to consider during the revision:

1. The strong correlations between daytime HONO production rate and [NO2*][H2O] (Figures 7-10, Table 3) indicates that: (1) NO2 is a major precursors for daytime HONO and (2) photochemical processes are involved in daytime HONO formation. However, the processes involved can be gas-phase reactions (e.g., R5), or photo-enhanced heterogeneous NO2-H2O reactions on surfaces (and at the presence of organics). The apparent k values (2.9-7.8 x 10-13 cm3 molecules-1 s-1) were significant than the highest laboratory value of 1.2 x 10-13 cm3 molecules-1 s-1 reported by Li et al (2008), suggesting that photo-enhanced heterogeneous processes (e.g., Stemmler,

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2006, 2007)are more important. I would suggest the authors to revise and expand the discussion in the section.

2. Moderate correlation between daytime HONO production and aerosol particle surface (Table 2) does not exclude the importance of aerosol particle surface as site for HONO formation reactions. In fact, the r2 is better with aerosol surface (0.31) than with NO2 (0.04), and NO2 was likely to be the dominant precursor for HONO at this site! A stronger correlation of 0.61 between HONO production and JHONO[NO2](particle surface) may suggest that aerosol surface may be quite important as a daytime HONO source (also see point 4 below).

3. When discussing impact of air mass origin on air chemistry, it is more appropriate to use the air back trajectory than the local wind direction. Southwesterly wind does not mean that the air mass comes from Toledo. It may come from somewhere in the eastern or northern quarter and loop around the site locally. The air back trajectories can be calculated using NOAA's online HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html).

4. According to Google map, the measurement site is only 4-5 km from the lake in the south and southwest. If the air is moving from that direction at 10 km per hour, it would take only <1/2 hr to get to the site from the lake. The authors should take the opportunity to examine the effect of lake on air HONO chemistry and to estimate the HONO production in the air vs on ground. In the south/southwesterly flows, if air mass move fast enough, the in situ HONO production in the air may become more important compared to the contribution from the ground surface processes, since lake is a net sink for HONO and since air mass contact time with the ground is short before arriving at the measurement site. I do see higher HONO/NO2 ratio in the southwesterly flows in both day and night (Figure 5). Does this suggest that majority of the HONO was produced in situ (in the air) rather than on ground? I would suggest the authors to look into 1 or 2 cases with significant wind speed from south and southwest.

5. Section 3.1, 1st paragraph: why HONO/NO2 is smaller than HONO/NOx? Are these 2 numbers derived from the same period of measurements? Since NOx = NO + NO2, NOx is always > NO2, and thus HONO/NO2 should be always > HONO/NOx.

6. P15304, L14-17: the so-called daytime "unknown" HONO source defined here includes those from k2[NO][OH] and dark heterogeneous processes, although they may be small.

7. P3, L16: replace "bult" with "built".

Li, S., Matthews, J., and Sinha, A.: Atmospheric Hydroxyl Radical Production from Electronically Excited NO2 and H2O, Science, 319, 1657–1660, 2008.

Stemmler, K., Ammann, M., Donders, C., Kleffmann, J., and George, C.: Photosensitized reduction of nitrogen dioxide on humic acid as a source of nitrous acid, Nature, 440, 195–198, 2006.

Stemmler, K., Ndour, M., Elshorbany, Y., Kleffmann, J., D'Anna, B., George, C., Bohn, B., and Ammann, M.: Light induced conversion of nitrogen dioxide into nitrous acid on submicron humic acid aerosol, Atmos. Chem. Phys., 7, 4237–4248, doi:10.5194/acp-7-4237-2007, 2007.

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