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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Daytime HONO Vertical Gradients during SHARP 2009 in Houston, TX" *by* K. W. Wong et al.

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Response to Referee #1

We would like to thank the reviewer for the helpful comments on our manuscript. Below are our responses (in italics) to the specific comments by the reviewer.

1) Overall, the text is very well written and structured. I especially appreciate the long but well worked out introduction. The only general technical comment I have is that the conclusion section should be shortened a bit to avoid any reiteration of discussion there.

The comments from the reviewer are well-taken. We shortened the conclusion and took out any repeated discussion in this section.

2) General scientific comment: The authors were obviously surprised about the significant gradient of NO2 at times when efficient mixing should even it out. This is referred to at several places in the manuscript and would deserve some more discussion and comparison to other studies. What are the expected sinks and how do these compare to the vertical mixing speeds? Is there an unknown sink for NO2? Since HONO to NO2 ratios remained very similar along the vertical profile, this of course could have some ramification for the unknown HONO source.

The vertical profiles of NO_2 are believed to be the cause of strong NO_x emissions at the ground and vertical mixing that is not fast enough to even out the vertical distribution in the lowest 300 m. NO_2-NO partitioning can vary NO_2 vertical gradients. However, due the lack of measurements of vertical profiles of NO and photolysis frequencies, it is hard to determine how NO_2-NO partitioning can affect the vertical profiles of NO_2 in the lowest 300 m. To investigate the unknown sink for NO_2, a modeling study will be performed in the future using a 1-D chemistry and transport model.

3) page 24368, line 16: . . .conversion on humid surfaces: I suggest to make this more explicit to mention both NO_2 heterogeneous hydrolysis (disproportionation) and reaction with organics on surface. The latter reactions (in the dark) are significantly faster than the disproportionation reaction on many different substrates.

The sentence "Heterogeneous reactions on fresh organic aerosols can play a role in HONO formation during rush hours (Ziemba et al., 2010; Wong et al., 2011)"

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was added to the text following the updated sentence "It is generally believed that heterogeneous NO_2 conversion on humid surfaces, either through disproportionation or reaction with adsorbed organics, is the most important formation pathway of HONO in the nocturnal boundary layer (NBL) (Finlayson-Pitts et al., 2003; Stutz et al., 2004; Wong et al, 2011)."

4) page 24369: discussion of role of NO2*. For the sake of completeness, the authors should also cite the response of Li et al. to the comment by Carr et al. (2009)

The reference Li et al., 2009 was added to the discussion of the role of NO_2^*.

5) page 24372, line 8: in the Arctic

Correction was made in the text.

6) page 24382, line 19: section 4: should this be 4.2; note that there is already a reference in the preceding line.

Correction was made in the text.

7) page 24385, top lines: in relation to the nitrophenol photolysis in the gas phase, nitrophenols formed in the particulate phase may also contribute to formation of HONO (Sosedova et al., 2011).

The sentence "Sosedova et al. (2011) showed that heterogeneous reactions of NO_2 on phenols can lead to the formation particulate-phase nitrophenols, which upon

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photolysis, can lead to formation of HONO." was added to the introduction. The analysis of heterogeneous HONO formation in Section 4.2.2, which showed that HONO formation occurs predominately at the ground instead of on aerosol, ruled out the possibility that photolysis of nitrophenols in the particulate phase is the dominant daytime HONO formation pathway.

8) page 24385, 2nd paragraph: how was aerosol nitrate measured? Could photolysis of nitrate be a significant sink for aerosol nitrate?

Aerosol nitrate was sampled at 70 m at University of Houston by Rice University. It is not clear what the role of nitrate photolysis as a sink of aerosol nitrate is. Observed diurnal variation of aerosol nitrate does not seem to depend on photolysis. The impact of photolysis on the loss of aerosol nitrate is interesting but not within the scope of this study.

9) page 24385 3rd paragraph: is there any impact of the complex urban ground surface structure on the difference between actinic flux and irradiance?

In this study, we analyzed HONO formation based on observations horizontally integrated over 4-5 km between University of Houston and Downtown Houston. In the vicinity of our measurements, the urban structures are mostly one- to two-story buildings. Therefore, the impact of urban ground surface structure is not expected to play a significant role on actinic flux and solar irradiance at the ground. However, buildings are expected to impact solar irradiance and actinic flux significantly for studies taking place mainly in compact urban areas with tall buildings.

10) page 24388 or in the vicinity: the authors could include a comparison to the recent

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study by Su et al. (2011) and also discussion thereof. This should probably also added to the introduction section.

The paragraph "A recent study by Su et al., (2011) suggested that soil nitrite can also be a strong source of daytime HONO. The emission of HONO from soil showed diurnal variation with a maximum at noon, with a magnitude similar to the observed missing HONO source." was added to the introduction. The sentences "Proposed photolytic HONO formation pathways that occurs on the ground include the photolysis of HNO_3, NO_2 conversion on humic acid and HONO formation from soil nitrite (Zhou et al., 2003; Stemmler et al., 2006; Su et al., 2011)." and "HONO formation from soil nitrite is not shown to depend on gas-phase NO_2 concentration, but on nitrite concentration in the soil, which depends on soil acidity and temperature (Su et al., 2011). We do not have sufficient data to evaluate if soil nitrite can be the daytime HONO source." were added to the discussion section of the paper. The sentence "Our results showed that it is also possible that photolysis of adsorbed nitric acid at the ground and soil nitrite could be important sources." were included in the conclusion section.

References

Li, S., Matthews, J., and Sinha, A.: Response to Comment on "Atmospheric Hydroxyl Radical Production from Electronically Excited NO_2 and H_2O", Science, 324, 336, 10.1126/science.1166877, 2009.

Sosedova, Y., Rouviere, A., Bartels-Rausch, T., and Ammann, M.: UVA/Vis-induced nitrous acid formation on polyphenolic films exposed to gaseous NO_2, Photochemical & Photobiological Sciences, http://dx.doi.org/10.1039/C1PP05113J, 2011.

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Su, H., Cheng, Y., Oswald, R., Behrendt, T., Trebs, I., Meixner, F. X., Andreae, M. O., Cheng, P., Zhang, Y., and Pöschl, U.: Soil Nitrite as a Source of Atmospheric HONO and OH Radicals, 333, 1616-1618, 10.1126/science.1207687, 2011.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 24365, 2011.

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Interactive Comment