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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Vertical profiles of nitrous acid in the nocturnal urban atmosphere of Houston, TX" *by* K. W. Wong et al.

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Response to Referee #2

We would like to thank the reviewer for the constructive comments. Our response to the comments are highlighted in italics in the following text.

Major comments:

1. The authors do not describe the assumed aerosol profile that is included in the model. How was the vertical aerosol profile determined? Are there any measurements

that could be used to constrain the profile?

Because no aerosol profile measurements were performed during the 2006 TRAMP experiment, the vertical aerosol profile was assumed to be uniform. The aerosol surface area was calculated based on aerosol measurements taken at 70 m altitude. Nocturnally averaged aerosol surface areas were determined and used for each of the three modeling periods.

"The aerosol vertical profile is assumed to be uniform." has been added to the model description and "However, please note that aerosol surface profile in our model is oversimplified." has been added to the discussion section to clarify this point.

2. Page 30148 lines 12 - 15: "HONO mixing ratios below 20 m, which were not observed by the LP-DOAS, showed that..." This is unclear. Was there an additional, in situ HONO measurement that was not described in the experimental section? If so, why was it not used to constrain the model?

The statement referred to the HONO mixing ratios below 20 m, as shown in the model. No additional observations below 20 m were available. This statement has been revised to "The modeled HONO mixing ratios below 20 m, which were not observed by the LP-DOAS, showed that. . . ".

3. Page 30135, line 22: The authors select three nights with distinct vertical gradients, and use these examples to conclude that HONO production at the surface is greater than HONO production on aerosols. I assume that the authors selected nights with strong vertical gradients because this indicates a stable nocturnal boundary layer. If so, that should be explained in the text. Also, I assume that they used O_3 and NO_2 (not HONO itself) to select nights with strong vertical gradients. If so, that should also

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be explained in the text. Unless these two points are clarified, it seems as if the selection of nights influences the conclusion – by selecting only nights with strong vertical gradients in HONO, one would logically reach the conclusion that HONO comes from the surface. Are other days (particularly days without strong vertical gradients) not well-represented by the 1-D model? What about comparing the diurnal average for the entire period to the model?

We selected the three modeling nights based on the NO_2 and O_3 observations, not HONO. Nights with distinct vertical gradients of NO_2 and O_3 were associated with stable boundary layer. Our observations indicate that nights with stable boundary layers always result in distinct gradients of HONO. The selection of the three nights has been clarified in the following revised sentences "Three periods, Sep 1-2, 7-8 and 11-12, (Figures 5a, 6a, 7a) were selected for a more detail analysis. These nights were selected based on the distinct NO_2 and O_3 vertical gradients, which indicate a stable atmosphere. HONO profiles were not considered in the selection of the nights. However, our observations during TRAMP show that nights with stable boundary layers result in strong HONO gradients."

We did not carry out any modeling studies on nights without strong gradients of NO_2 and O_3 because these nights were less stable. Our focus was on shallow stable nocturnal boundary layers because they allow a better separation of surface and aerosol chemistry.

4. On page 30137, line 5-6, the authors state that they believe "that the upper height interval was in the residual layer during both nights." In the conclusions, they state that HONO was often below 100 ppt in the upper height interval and care must be taken to interpret surface observations of HONO because they are not representative of the entire boundary layer. But the upper height interval arguably wasn't in the boundary

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layer. This inconsistency is confusing, and should be fixed throughout.

The upper height interval (130-300 m) was partially located in the residual layer, which was located at 200 m and 160 m for Sep 1-2 and 7-8. Any inconsistency has been fixed throughout the text. "The residual layer began at 200 m and 160 m respectively for Sep 1-2 and Sep 7-8, assuming the residual layer was located right above the nocturnal ground inversion (Day et al., 2010)." was added to the text.

5. The authors adjust the NOx emission rate and vertical transport in the model to match the observations. What is the sensitivity of the model to HONO/NO emission ratio? Could the HONO/NO emission ratio change during the night, with changes in vehicle fleet (more cars, fewer trucks)?

The following paragraph has been added to the text to discuss the sensitivity of HONO mixing ratio to changes in HONO/NO_x emission ratio, "It is also possible that the HONO to NO_x emission ratio varied throughout the night due to changes in vehicle fleet composition. Since there was insufficient information on fleet composition and vehicle type specific HONO/NO_x emission ratios, sensitivity runs were performed to study the effect of a possible change in emission ratios. Varying the HONO/NO_x emission ratios by $\pm$0.5% from the original value of 0.8%, i.e. to 0.3% and 1.3%, led to a 20% change in HONO mixing ratios and HONO/NO_2 ratios in all three height intervals during the rush hour period. During the rest of the night, HONO mixing ratios in the lower height interval varied by 13-19%, and by 13% and 4% in the middle and upper height intervals, respectively. The higher emission ratios could explain the rush hour HONO on 7-8 Sept but were still too low to explain the rush hour observations on 1-2 and 11-12 of September. As a HONO/NO_x emission rate of 1.3% is higher than any published value (see for example Kurtenbach et al, 2001, Kirchstetter et al., 1996) we conclude that direct HONO traffic emissions were most likely not the explanation

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for the unexplained rush hour HONO. ”

6. Page 30140 line 12 What are the VOC concentrations that are included in the model?

Model runs were initialized with VOC observations at 70 m, as shown in Table 2. Leuchner and Rappenglück, 2010 has been added as a reference to the data source. The sentence in the text has been revised to “Observed volatile organic compounds (VOC) concentrations at 70 m, assumed to be constant at all heights, were used in all three model runs (Leuchner and Rappenglück, 2010) (Table 2)”.

7. Was the friction velocity measured? How does it compare to the values assumed for the model? What are the time scales for vertical and horizontal mixing (described on pg 30141 line 22)?

Unfortunately, friction velocity was not measured during the experiment. The vertical transport timescale from the ground to 100 m in the NBL was about 10^3s and the horizontal transport timescale was about 10^4s assuming a distance of 20 km. The sentence “The vertical transport timescale at 100 m in the NBL was about 10^3s and horizontal transport timescale was about 10^4s for the area inside the Houston inner ring, for which our LP-DOAS observations are representative.” has been added to the text.

8. I don’t understand the statement on pg 30151 line 7-8 "Therefore addition of HONO by direction emission leads to a larger net HONO formation at the ground when vertical

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mixing is constant." Why would HONO production be related to HONO emission?

Increase of NO_2 and HONO emission will lead to an increase of both HONO formation (by NO_2 conversion) and HONO removal (by ground uptake). Our model calculations showed that the change of HONO formation exceeds that of HONO removal. Therefore, this leads to a larger net HONO formation, which equals HONO formation minus HONO loss. This sentence has been revised to clarify this point: "Therefore increased NO_2 and HONO from emissions leads to larger net HONO formation at the ground when vertical mixing is constant".

9. How does the surface area of buildings compare to the surface area of the ground and aerosol?

The surface area of buildings was not calculated or considered in the calculation. We believed that inclusion of the urban canopy will not change our results. However, the reviewer's point is well taken and we are working on a study of the effect of surface area of buildings on nocturnal chemistry.

Other comments:

Page 30131 line 2 NBL not defined in introduction. *NBL has now been defined. Sentence was revised to "stable nocturnal boundary layer (NBL)".*

Page 30131 lines 6 - 10 Add references for these two sentences. *Reference "Finlayson-Pitts and Pitts, 2000" has been added to these two sentences.*

Page 30132 line 1 Remove "[i]n the nocturnal boundary layer" because HONO can be formed during the daytime as well. *Corrected*

Fix "relatively humidity" throughout *Corrected*

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Table 1 - Give acquisition time for detection limits *Corrected*

Figures 4, 5, 6 - Add panel indicating the error between the refined model and the observations. *Three figures showing the errors between the refined and the observations will be added as supplemental information for the paper.*

Figure 9 - Simplify the figure. It is very difficult to distinguish the colors. *Figure has been modified so that the colors can now be easily distinguished.*

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 30129, 2010.

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Interactive Comment