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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 #1

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

General comments

Wong et al. present vertical profiles of HONO, NO_2 and O_3 obtained from long-path DOAS measurements in Houston, TX during three different nights in September 2006. The observed HONO profiles are compared with vertical HONO profiles derived from a 1-D chemistry and transport model after adjusting NO_x emissions and vertical turbulent

transport to make the modeled temporal and vertical profiles of NO_2 and O_3 fit the measurement. Finally, the model is used to quantify the contributions of different HONO formation and loss processes to the net HONO production at different heights.

The separation and quantification of different HONO formation and loss processes is an important and interesting topic. Therefore, this combined presentation of observational and modeling data merits publication. However, I do have a few major questions about the comparison of the observational and model results. Also, the manuscript needs some technical revision before publication.

Specific Comments (*response in italics***)**

1. Taking into account that the upper height interval was not reproduced well by the model, and that the night period on 11/12 September was not reproduced well by the model, I would ask the authors to remove their statement that "the observed HONO profiles were reproduced well by the model" from the abstract (p.30130, l.15-16).

This statement has been revised to "the observed HONO profiles were reproduced by the model for the modeling period of Sep 1-2 and 7-8 in the nocturnal boundary layer (NBL)".

2. While the introduction is nicely written and just about the right level of detail, I don't think that Figure 1 fits with the text. The authors may want to expand on their explanation of Fig. 1, e.g. explain the different arrow colors. It could also be helpful to indicate reactions R1-R3 in Fig. 1, and put labels on the different ground and aerosol surfaces.

Caption of Figure 1 has been revised to "Schematic figure of HONO chemistry in urban boundary layer, showing HONO formation from direct emission (purple arrow), gas-phase reaction R2 (cyan arrow) and heterogeneous reactions R3 (blue and red arrows). HONO loss processes such as photolysis (R1) and uptake on surfaces are

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indicated by black arrows." In addition, Figure 1 has been updated to include labels of reactions R1, R2 and R3.

3. In Fig. 2, I do not understand how the authors arrive at the averaging dimensions associated with the light path between 70 m and 300 m. How exactly is the upper height interval between 130 m and 300 m derived from the light path arrangements between Moody Tower (70 m) and the three retroreflectors at 20/130/300 m? What is the exact horizontal averaging of the upper interval as indicated by the light red box? It seems to be different from the horizontal averaging between Moody Tower and downtown Houston as noted on p.30134, l.17.

The following text has been added to clarify this point. "The concentration in the upper box was determined by subtracting the concentration of the middle light path scaled by the geometric overlap from the upper light path. Therefore, the concentration in the upper box was horizontally weighted more towards downtown". Figure 2 has been revised to include the derivation of the concentrations of the lower, middle and upper height intervals.

4. On p.30135, l.6, the authors mention that vertical gradients disappear in the morning when the boundary layer became well-mixed. It would be very helpful to add a complementary measurement to Fig. 3 that indicates the observed mixing state of the boundary layer. On that same note, do you have complementary measurements of atmospheric stability?

Temperature profiles showing atmospheric stability were available but with insufficient temporal resolution. Figure 3 would also become very complicated if temperature profiles were added to it. In addition, in-situ measurement of temperature profiles taken at University of Houston may not be representative for our LP-DOAS data, which averages over 4-5 km distance. We thus believe that using the LP-DOAS observations of O_3 and NO_2 to determine the mixing state of the boundary layer is the most appropriate

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approach.

5. P.30136, l.25: Please indicate sunset and sunrise in Figs. 4-6.

Nighttime data are now shaded in grey in Figures 4 to 6.

6. P.30137, l.7 and l.20: Can you quantify the positive correlation between HONO and NO_2?

For Sep 1-2 and Sep 7-8, the correlation between HONO and NO_2 has correlation coefficients R^2 of 0.80 and 0.90, respectively. On Sep 11-12, the correlation between HONO and NO_2 has R^2 of 0.59. The sentence "The correlation coefficients R^2 were 0.80 and 0.90, respectively for Sep 1-2 and Sep 7-8" has been added to the text. The sentence "However, HONO in the middle and upper interval showed a positive correlation with NO_2. " has been revised to "However, HONO in the middle and upper interval showed a slightly positive correlation with NO_2, with an R^2 of 0.59."

7. The used model is subdivided into 27 boxes, 9 of which are below the lowest observational height of the LP-DOAS of 20 m. I was left wondering how you initialized these nine lowest model boxes. Was there any additional observational data available closer to the ground? While you find the largest production and loss processes close to the ground (e.g. p. 30148, l.13-14), this is also where the model is not constrained by LP-DOAS observations. This raises the question how confident you are in the model results close to the surface, e.g. as presented on p.30147, l.12-20. A direct comparison with in-situ HONO measurements at the ground would be a very valuable addition to the manuscript.

LP-DOAS observations showed no vertical gradients of the trace gases, indicating the boundary layer was well-mixed, at the time of sunset on Sep 1 and Sep 7. Therefore, the lowest 9 boxes in the model were initialized with the same concentrations as in the boxes between 20 m and 300 m altitudes. For Sep 11-12, because vertical profiles of

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NO_2, HONO and O_3 were measured by the LP-DOAS, the model was initialized with vertical profiles of NO_2, HONO and O_3 based on the LP-DOAS observations. All other trace gases, such as SO_2, HCHO and VOCs were initialized with uniform concentrations over the 27 boxes based on LP-DOAS observations and/or in-situ measurement at 70 m altitude.

HONO measurements at the ground were not available for comparison. However, we are confident that the model results close to the surface are realistic. The following sentence "Since no observations were available below 20 m, the lowest 9 boxes, which are located below 20 m in the model, were initialized by extrapolating the LP-DOAS observations in lowest height interval." has been added to the text in the model initialization section.

8. P.30139, l.18-21: How is the aerosol surface area density initialized and parameterized in the model? Did you assume a uniform aerosol profile over the NBL (p.30148, l.18)? If so, all conclusions about HONO formation and uptake on aerosol surfaces and comparisons with ground surfaces should be made with great care. Furthermore, it should be clearly stated that the description of aerosol surface profiles is oversimplified.

With regard to the same topic: Is the gas phase transport of HONO to aerosol surfaces and to ground surfaces treated differently in the model? In fact, the transport to the surfaces may be the limiting factor in the heterogeneous conversion of NO_2 to HONO.

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

"The aerosol vertical profile is assumed to uniform." has been added to the model

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description and "However, please note that aerosol surface profile in our model is over-simplified." has been added to the discussion section to clarify this point.

Yes, a mass-transfer equation given by (Fuchs and Sutugin, 1971) is used to calculate the gas-phase transport of HONO onto aerosol surfaces. The transport to the surface is calculated in detail (see Geyer and Stutz, 2004a). Indeed the transport to and from surface is limiting. This was already explained in the text.

9. P.30140, l.12: Please give a reference for the typical VOC concentrations that were used in the model runs!

Model runs were initialized with VOC observations at 70 m, as shown in Table 2. Leuchner and Rappengluck, 2010 has been added as the 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 Rappengluck, 2010) (Table 2)".

10. On p. 30141, the authors compare the vertical mixing and the horizontal transport timescales. For the reader it would be useful to find typical values of these timescales in seconds or minutes presented in this section.

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

11. The model calculations showed an increase of the $HONO/NO_2$ ratio with height which was not reflected in the observations. The authors discuss their findings and

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conclude from sensitivity studies that the increase was due to excess HONO rather than the lack of NO_2, most likely due to an underestimation of HONO loss on aerosol surfaces (p.30144). However, there is no discussion of vertical mixing as a possible explanation. Could a different parameterization of vertical mixing also explain the model results?

We are not entirely sure that we understand this question. The comparison of the vertical O_3 and NO_2 profiles seems to indicate that the vertical mixing of reactive species is well captured by the parameterization we used. Vertical mixing can indeed change the HONO/NO_2 ratio, for example when air parcels with different ratios are mixed. However, this is captured in the model.

Please note that entire airmasses, which contain trace gas mixtures, are mixed and transported. Trace species are not mixed/transported individually. Consequently, to increase the HONO/NO_2 ratio due to mixing of two airmasses at one altitude, one of the air masses has to have an even larger HONO/NO_2 ratio. This again leads to the question how this airmass achieved the larger HONO/NO_2 ratio. Our model calculations show that the reason for the increase HONO/NO_2 ratio is due to the insufficient loss of HONO rather than the formation of HONO.

12. On p.30145, l.23-25, a deviation of the observed HONO/NO_2 ratio from the refined model results is explained by HNO3 conversion on fresh soot aerosol during rush hour. At what time did you observe the largest deviation?

The largest deviation of the observed HONO/NO_2 from the refined model results was observed between 5:30 and 6:03 CST, which was 6:30 and 7:30 local time, similar to observations by Ziemba et al., 2010. This sentence has been revised to "At 5:30 am CST, the observed HONO/NO_2 reached 5%, while the modeled ratio was only 2.5%".

13. Regarding vertical mixing: Can you explain the steep increase of eddy diffusivity starting around 03:30 CST as shown in Fig. 7? Did you compare the adjusted eddy

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diffusivities used in the model runs to any in-situ turbulence measurements in order to evaluate if vertical mixing is parameterized in a reasonable fashion in the model? This is a very important issue because vertical transport was found to be the dominant source of nocturnal HONO above 20 m in all model runs (p.30149, l.5-6).

Unfortunately, there was no in-situ turbulence measurement during this experiment for us to use or to compare with. Even if there was, in-situ turbulence data may not be representative for our LP-DOAS observations, which were average over 4-5 km light paths, because turbulence data at different locations can fluctuate greatly at night. It is very difficult to obtain turbulence data which are appropriate for the LP-DOAS data. Based on the NO_x emission pattern, the vertical profiles of NO_2 and O_3 were reproduced only with an increase of vertical mixing. In situ measurements of NO_2 at 70 m showed some fluctuation indicating possible vertical mixing during this time.

14. I like the discussion of two regimes of net HONO formation, a "transport sensitive" and a "NO_2 sensitive" regime on p. 30150. Please also indicate both regimes in Fig. 10.

Thank you. The two regimes are now indicated in Figure 10.

15. The authors repeatedly state that their model did not accurately reproduce the upper height interval because it was located in the residual layer. Still, they continue to evaluate and interpret HONO formation and loss rate profiles in section 6 up to 300 m, e.g. in Figs. 8 and 9, Table 3, as if the model had been shown to reproduce the profiles correctly. The authors should clearly explain how reliable they feel their conclusions are.

We had discussed this in the paper in the subsection on applicability of 1D model "However, care has to be taken in the interpretation of the model calculations of the upper interval (130-300 m) as advection may potentially play a role.". However, we agree with the reviewer that this should be better explained. We have thus added some more text

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and also added some numbers quantifying the uncertainty introduced by the residual layer modeling:

The sentence "The actual vertical profiles should be slightly stronger because the modeled NO_2 and HONO mixing ratios were overpredicted in the upper height interval." has been added to Section 5.2 in the explanation on Figure 8.

The sentences "Since the upper height interval was partially located in the residual layer where advection could play an important role, advection could potentially be a significant removal pathway of HONO in the residual layer." and "The inclusion of the upper height interval in our integration calculations leads to 20% uncertainty in HONO formation and loss on aerosol surfaces, 8% uncertainty in HONO loss due to reaction with OH and $<$ 1% uncertainty in other formation and loss process. Because these processes are relatively small, these lead to only 1% and 4% uncertainty respectively in total integrated HONO formation and removal." have been added to Section 6.1 in the discussion of the formation and loss rate profiles of HONO.

Technical Corrections

p.30130, l.22: Add "an" between "showed increase". *Corrected*

p.30131, l.3: Add "NO_x" between "stronger emission". *Corrected*

p.30131, l.6: Change "Nitrous acid, HONO is one" to "Nitrous acid (HONO) is one". *Corrected*

p.30133, l.1: Replace "occurs" with "occur". *Corrected*

p.30133, l.3: "such as buildings, plants etc, or on particles." looks odd! *Sentence has been revised as "such as buildings and plants, or on particles".*

p.30133, l.16: Change "gradients measurement" to "gradient measurements". *Corrected*

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p.30133, l.18: Change "aerosol surface" to "aerosol surfaces". *Corrected*

p.30135, l.10: Should mention that Fig. 3 also shows temperature. *Corrected*

p.30135, l.16: Change "condition" to "conditions". *Corrected*

p.30136, l.2: Add "the" between "at lower". *Corrected*

p.30136, l.3: Change "Difference" to "Differences". *Corrected*

p.30136, l.10: Change "Difference" to "Differences". *Corrected*

p.30136, l.18: Change "Difference" to "Differences". *Corrected*

p.30137, l.12: Add comma between "September respectively". *Corrected*

p.30137, l.24: Remove "and" *Corrected*

p.30138, l.2: Change "6% respectively on" to "6%, respectively, on". *Corrected*

p.30138, l.3-4: "HONO/NO_2 increased to 4% before midnight then was 3-4% throughout the night." looks odd. *Sentence has been revised to "HONO/NO_2 increased to 4% before midnight then remained above 3% throughout the night".*

p.30138, l.18-19: Change "model are based on (Kurtenbach et al., 2002, 2001)." to "model are based on Kurtenbach et al. (2001, 2002). *Corrected*

p.30139, l.10: Add "an" between "with emission". *Corrected*

p.30139, l.12: "currently included in the model include" should be changed. *Sentence has been revised to "currently considered in the model include. . . ".*

p.30139, l.16: Change "R3 and a NO2 reactive" to "R3 and an NO_2 reactive". *Corrected*

p.30139, l.22-23: Change "reactive uptake coefficient 10-4" to "reactive uptake coefficient of 10-4". *Corrected*

p.30140, l.2 and l.21: L should not be called "Monin-Obukhov length", but "Obukhov

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length". *Corrected*

p.30140, l.9-12: "Because vertical gradients of other trace gases. . . " seems incomplete. *Sentence has been revised to "Because other trace gases such as SO_2 and HCHO did not show any vertical gradients at this time, all trace gases except NO_2, HONO and O_3 were initialized with a constant vertical profile for this night".*

p.30141, l.24-25: Change "and trace gases distribution" to "and the trace gas distribution". *Corrected*

p.30142, l.6: Change "is the" to "are". *Corrected "is the" to "is"*

p.30143, l.14: Change "altitudes" to "altitude". *Corrected*

p.30143, l.26: Remove comma after "September". *Corrected*

p.30147, l.9: Change "mixing ratios profiles" to "mixing ratio profiles". *Corrected*

p.30147, l.24: Change "increases" to "increased". *Corrected*

p.30148, l.1: Change section heading to "HONO formation and loss rate profiles". *Corrected*

p.30149, l.2: Remove "HONO". *Corrected*

p.30150, l.1: Change section heading to "Dependence of the net HONO formation at the ground on vertical mixing and NOx emission". *Section title seems fine, no changes are made.*

p.30150, l.7: Add comma after "Consequently". *Corrected*

p.30150, l.17: Add "the" between "that impact". *Corrected*

p.30151, l.1: Add "the" between "of emission". *Corrected*

p.30151, l.23: Change "substantial" to "substantially". *Corrected*

p.30152, l.6: Add "the" between "during morning". *Corrected*

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Interactive Comment

p.30152, l.11: Change "or" to "and/or". *Corrected*

p.30146, l.2-3: What does "both modeling periods" refer to? *Sentence has been revised to "both modeling periods, Sep 1-2 and 7-8".*

p.30159, Table 2: I assume you show mixing ratios in ppb. Please give the units of the presented values. *Table title has been revised to "Initial concentrations in ppb for model simulation".*

p.30163: Fig. 3 also shows temperature measurements. Please modify the figure caption accordingly. *Figure caption has been modified to include temperature measurements.*

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