Atmos. Chem. Phys. Discuss., 12, C12950–C12970, 2013
www.atmos-chem-phys-discuss.net/12/C12950/2013/
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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Modeling of daytime HONO vertical gradients during SHARP 2009" *by* K. W. Wong et al.

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Received and published: 27 February 2013

Response to Reviewer #2

We would like to thank the reviewer for the helpful comments. Please find our responses in italic in the following.

General comments:

In the manuscript by Wong et al., vertical gradients of HONO, recently measured during daytime in the atmosphere (Wong et al., 2012), have been modelled and highly interesting results have been obtained. Caused by the unusual high sensitivity

of the DOAS during the former campaign, daytime HONO could be precisely detected and compared to different model runs in the present study. Since also gradients could be measured during daytime, the different discussed photochemical HONO sources (volume vs. ground), used in different model runs, could be compared to the measurements and potential sources identified. Since HONO has an important impact on the radical budget of the lower troposphere and since the source reactions are still under controversial discussion, the study is of high general interest for atmospheric scientists and should be published in ACP after some corrections. Besides some minor comments and technical corrections, I have two major concerns with the manuscript, which may be considered.

Major concerns:

1) In the manuscript, different model cases are studied to describe unknown daytime sources of HONO in the lower atmosphere. One important parameter is the irradiance used to parameterize the photochemical ground surface source, which is a very good approach compared to former J(NO2) parameterizations. In the model, a cubic parameterization of the irradiance with J(NO2) was used, which shows however some deviations to the observations (see Fig. 1, green and grey dashed) during morning and afternoon. Why isn't the measured light intensity used and the model constrained to that parameter (the same holds for the measured photolysis frequencies, see below)? The diurnal variation (shape) of the irradiance used here to parameterize the ground source is important to distinguish between surface or volume sources and to describe the daytime maximum in HONO/NO2. A wrong parameterization may lead to different interpretation of the results.

Response: The reasons for using a cubic parameterization of the irradiance with $J(NO_2)$ are: First, it is the simplest way to describe the photolytic HONO source in the model which, as in many atmospheric chemistry models, includes calculations of

photolysis frequencies, but not the solar irradiance. Second, as there were no solar irradiance observations in the early morning of one of the days we needed to find a parameterization that covered this time period.

Regarding the differences to the observations during the morning and afternoon, the model showed deviations to the observed visible solar irradiance but not to the UV solar irradiance (see Figure 1). Our previous studies suggested that the photolytic surface source of HONO is more likely to be related to UV solar irradiance than to the visible solar irradiance, thus the parameterization of the HONO source should be sufficiently accurate to allow interpretation of the results. To address this concern we added the following sentence on Page 27784 at line 18 "The modeled solar irradiance is within 5% of the observed UV solar irradiance, which we found previously to better correlate with the photolytic surface source of HONO than the visible solar irradiance (Wong et al., 2012)."

2) For the best model case, both, photochemical ground and aerosol HONO sources were identified. While the high contribution of the ground surface source can be well ex- plained by laboratory studies taking into consideration the much higher surface area of the ground compared to particles, the used particle surface kinetics is much faster than any reaction known from laboratory studies (see also own comments by the authors, e.g. in the conclusion). Since the photosensitized conversion of NO2 was used here to describe the daytime HONO source, the kinetics will not be different on aerosols or ground surfaces (compare Stemmler et al., 2006 and 2007). Soot was also proposed, however, caused by the fast deactivation this can clearly not explain the observations (see several former studies on this reaction) and would lead to even steeper gradients (fresh soot only near to the ground). In addition, even for a potential photosensitized NO2+soot reaction, recently proposed by Christian George's group, gammas of max. 10ˆ-6 were observed (here: 10ˆ-3, or 4x10ˆ-4 used). Thus, the results that particles source are also important, can at least

not be explained by any lab results. Either there are still unknown particle reactions (but: many different surfaces have already been studied, caused by the high importance. . .) or there are still some significant uncertain- ties in the model, which could be:

a) In model calculations, a flat ground surface at 0 m altitude was only considered, whereas in reality the measurements took place between the university and down town Houston, with very high buildings (up to 300 m). Since the averaged contribution of the postulated aerosol source was quite small (7-16 %, see table 3), the experimental results may be also well explained by only one single photosensitized surface source (gamma 6x10ˆ-5), but also on the higher building surfaces, which may also contribute to ca. 10 % of all surfaces, e.g. in the middle layer, at least in the downtown area. This may alternatively explain the higher HONO levels at higher altitude. The authors may think about a rough estimation of the average S/V ratio of buildings in the three layers used (take a "footprint" area of the buildings at the corresponding height for photolytic lifetime of HONO) and take that into consideration for the photosensitized ground surface source used. May be than, no additional aerosol source would be necessary, which would be a very important conclusion for scientist working in that field (stop to look for any aerosol sources of HONO. . .).

Response: We understand the reviewer's concern about building surfaces. Between the University of Houston and Downtown, where the LP-DOAS system measured, the buildings are mostly one and two stories high. While building surface can be sources of HONO in the lowest 6 m of the atmosphere in this case, we think that the building surface are not able to explain the missing HONO sources at higher altitudes. However, it will be interesting to study how building surfaces will contribute to the formation of daytime HONO. This will be future work on this project but is not in the scope of this study.

b) The authors used the solar radiation to parameterize the vertical mixing (see,

page 27786, line 27-28). Although I am not a meteorologist, the surface temperature should be however a better parameter compared to the radiation (heating of the ground in- duce the turbulent mixing). The surface temperature maximum is however typically shifted to later daytime compared to the maximum in the radiation. Thus, in the early afternoon, there should be the highest mixing (compare also BLH). Now, by comparing with the measured NO2, both, the mixing parameters (L in equation (1)) and the emissions strength were adjusted. If the mixing is however larger during the afternoon compared to the modelled value, the necessary emissions have to be also increased to describe the measured NO2 concentrations. This would lead to a more realistic diurnal emission profile of NO2 and HONO, which is linked to that of NO2 (0.008), see Figure 2. In the calculations by the authors, the increase of the HONO (and NOx. . ..) emissions between the minimum and the afternoon rush hour is only marginal (ca. 30-40 %), whereas the variation of urban traffic density during that time (11-18 h) is typically much higher (factors). If a higher mixing in the afternoon would be used i) the emission minimum would be shifted to later time and ii) the afternoon emissions would increase, which is more realistic. By the different NO2 dependent source reactions, the emission profiles have a strong influence on the model results and may significantly change the interpretation of the source regions. Here additional model calculations are recom- mended.

Response: Vertical mixing in our model is parameterized by eddy diffusivity which can be calculated from micrometeorological parameters such as friction velocities and the Monin-Obukov length as described in section 2.2 of the paper. However, there is a lack of observations of these parameters during the SHARP field campaign and our model does not have a meteorological component. Therefore we made the simplification that eddy diffusivity has a maximum at noon for all model runs. This assumption is supported by previous observations, which show a maximum of eddy diffusivity around solar noon (Horvath et al., 1998; Constant et al., 2008). While the eddy diffusivity maximum may be a little later during the day in urban area the maximum tends to

be broad enough that our assumption should be good enough. To clarify this, on Page 27786 line 28, we modified this sentence "Vertical mixing during the day is assumed to be proportional to solar radiation, i.e. maximum at noontime for all model runs." to "Due to the lack of micrometeorological observations during the experiment, vertical mixing during the day is assumed to have a maximum at noontime, when solar radiation peaks, for all model runs. This assumption is supported by previous measurements of eddy diffusivity (Horvath et al., 1998; Constant et al., 2008)."

While we do not have detailed hourly emission data for our days a sharper and larger morning rush hour emission maximum and a broader but smaller afternoon rush hour maximum of the NOx emissions is not unreasonable. For example, Berkowicz et al. (2006) and Marr et al. (2002) show such emission profiles for weekdays. The cause for these "asymmetric" profiles is the combination of light and heavy duty traffic, the latter is often decreased in the late afternoon thus leading to lower NOx emissions compared to the morning. To further clarify that the resulting diurnal emission profile is reasonable, we included the following sentence in this section: "The shape of NOx emission profile is similar to those reported by Berkowicz et al. (2006)."

We have performed sensitivity calculations, varying both eddy diffusivity and emission profile. The profiles shown in Figure 1 and the parameterization chosen for eddy diffusivity give the best comparison between observations and model. This has been clearly explained in section 2.2.2.

The following references have been added:

Berkowicz, R., M. Winther, M. Ketzel, Traffic pollution modeling and emission data, Environ. Modell. Softw., 21, 454-460, 2006.

Constant, P., L. Poissant, R. Villemur, Annual hydrogen, carbon monoxide and

carbon dioxide concentrations and surface to air exchanges in a rural area, Atmos. Environ., 42, 5090-5100, 2008.

Horvath, L., Z. Nagy, T. Weidinger, Estimation of dry deposition velocities of nitric oxide, sulfur dioxide, and ozone by the gradient method above short vegetation during the tract campaign, Atmos. Environ., 32, 7, 1317-1322, 1998.

Marr, L., D. Black, R. Harley, Formation of photochemical air pollution in central California 1. Development of a revised motor vehicle emission inventory, J. Geophys. Res., 107, D6, 4047, 2002.

Special comments:

Page 27778, top: I am missing some references on former field observations on the radiation dependence of the daytime source (topic of the present manuscript), e.g. Elshorbany, Sörgel, etc.

Response: Actually, these references were already included in the following sentence in the Introduction, "The formation rate of daytime HONO by unknown pathways has been estimated in rural and urban regions in the range of (1– 35) $\times$ *10* ^{6} *molec.* $cm^{-3}s^{-1}$ *(Acker et al., 2006a; Zhang et al., 2009; Elshorbany et al., 2009; Kleffmann et al., 2005; Zhou et al., 2002; Su et al., 2008; Sörgel et al., 2011a; Ren et al., 2010)." Therefore, no changes are made in the text regarding this comment.*

Page 27779, line 4: If also low altitude gradients should be also considered here (Zhou et al., 2001), than there are many other studies available especially for polar regions (e.g. Beine,. . .). I would recommend only using those covering i) a higher altitude range and ii) not polar regions. Please add also a reference to the study by Häseler et al., since also here up to 1000 m altitude was considered.

Response: We have included the reference. The sentence has been modified to "However, only a few observational studies have been performed to measure daytime HONO vertical profiles (Kleffmann et al., 2003; Zhang et al., 2009; Villena et al., 2011; Zhou et al., 2001; Häseler et al., 2009)."

Page 27779, lines 4-9: Here apples and oranges are compared. i) In Kleffmann et al., 2003, no daytime gradients were measured. They were measured in a different campaign and published in Kleffmann, 2007. In addition, not the HONO gradients, but those of the HONO/NOx ratio were shown. While HONO/NOx did not show a gradient (similar to Villena et al., 2011), there were clear gradients in HONO (again similar to Villena et al.). Thus, both studies are in excellent agreement.

Response: We used Kleffmann et al. (2003) as the reference because daytime vertical profiles were measured in a similar setup as by the same group at that time. However, we agree with the reviewer that Kleffmann 2007 is a more appropriate reference. The reference has been corrected to Kleffmann 2007.

Regarding the vertical gradient of HONO, Kleffmann 2007 state on page 4 of their publication that: "In agreement with the DOAS data, no strong gradients of HONO could be observed during daytime with the LOPAP instrument."

Page 27779, line 11-12: Fluxes of HONO were already frequently measured since 2001 in polar regions ("only recently, 2011. . ."). Page 27779, line 23: No daytime gradients measured in that study, see above (only daytime model calculations in Vogel et al., 2003).

Response: To correct this, the sentence "Flux measurements of HONO have only recently been developed" has been changed to "Flux measurements of HONO

have been carried out to study the daytime sources of HONO".

The reference has been corrected to Kleffmann (2007) from Kleffmann et al. (2003).

Page 27782, line 16-18: Also for the photolysis frequencies, measured values could be constrained to the model to further improve the model results, if the motivation of this study is to identify the missing HONO source (and not to develop a general 1 D model for HONO).

Response: We agree with the reviewer in principle. However, because the days we used in this study are all sunny days, the modeled photolysis frequencies describe the measurements very well, as we have shown in Figure 1. Using measured photolysis frequencies, instead of the model parameterization, would thus not improve the results of our manuscript.

Page 27782, line 21: What is the height of the lowest layer in the model? If 0.1 m (the lowest number I found in the text) than the use of uptake coefficients is not recommended, since gamma values >10ˆ-5 (used here) will be limited by molecular diffusion near to the ground. In this case, better diffusion corrected deposition velocities (used a residence model) should be used.

Response: The height of the lowest layer in the model is 1×10^{-4} m. To clarify this, we have modified the sentence in the Introduction (P27782 L5) from "The model subdivides the lowest 3000 m into 32 grid cells, with cell heights decreasing logarithmically below 1 m to take into account the inefficient vertical transport near the ground. " to "The model subdivides the lowest 3000 m into 32 grid cells, including 5 grid cells with cell heights decreasing logarithmically below 1 m to take into account the inefficient vertical transport near the ground."

Page 27783, line 19:

The uptake coefficient used is very high. E.g. in a tunnel study by Kurtenbach et al., an uptake coefficient of ca. 10ˆ-6 was observed on real tunnel surfaces, also in lab studies on humic acids (Stemmler et al., 2006) much smaller values than 10ˆ-5 were observed in the dark.

Response: This uptake coefficient was measured on an asphalt surface by Trick (2004). We also use the HONO uptake coefficient measured in the same study in our paper.

Page 27784, equation (2)?Shouldn't it be: Irradiance = Irradiance(max.) x J(NO2)ˆ3/J(NO2)noonˆ3 ?

Response: The reviewer is right. This has been corrected.

Page 27784, line 23: While the uptake coefficient for the photolytic reaction is quite reasonable and of the same order of magnitude compared to lab studies, the difference between dark and photolytic NO2 uptake in other laboratory and field studies is typically much higher than used here (factor 6 here, compare 27783/line 19, and factor 20-100 in other studies). This may also explain the overestimation of HONO in the morning in some model runs, see below.

Response: The difference between the dark and photolytic NO_2 reactive update coefficient in our study is, for example, within the range of laboratory measurements performed by George at al. 2005. In their study, the illuminated reactive uptake coefficients of NO_2 can be 1.4 times to 20 times larger than the dark uptake coefficients. Other studies report changes in the same range. Therefore, we do not think that the

difference between the photoenhanced and the dark NO_2 uptake coefficient used in our model is unrealistic.

We have tested the dark NO_2 uptake coefficient in our previous modeling study on nocturnal HONO vertical gradients and found that this uptake coefficient worked well to describe our observations. However, it should be noted that the dark uptake coefficient originates from measurements on asphalt (Trick 2004) and is larger than those typically reported from other laboratory studies. This is most likely an effect of the larger effective surface area of asphalt. The comparison is thus not the same as in many laboratory studies, where uptake coefficients are compared between dark and illuminated highly simplified surfaces.

Nevertheless, the reviewer has a point that there is still a lot of uncertainty in the uptake coefficient and more laboratory and field experiments are necessary to confirm the uptake coefficient we used in this study.

Page 27785, equation (4): Numbers too high, see general comment.

Response: We agree with the reviewer that this number is larger than the reported values. However, this is the value that best reproduce the observations. In our conclusions, we clearly state that: "The reactive NO_2 uptake on aerosol implied by our model study is higher than those reported from laboratory studies (for example Stemmler et al., 2007; Woodill and Hinrichs, 2010), and the reason for this discrepancy is currently unclear. It is possible that other mechanisms, thus far not considered, are acting in the atmosphere."

Page 27787, line 6, Fig. 2: A complete diurnal emission profile is recommended to better identify also the afternoon rush hour.

Response: We have expanded Figure 2 to include a more complete diurnal emission profiles.

Page 27788, line 6 and Fig. 3: Since emissions (and meteorology) were adjusted by the measured NO2 data, the agreement is trivial and almost infinite parameterisations could give the same results (increase/decrease of both, the turbulence and the emissions. . .). More important is the correct description of the gradients. Here the model could be improved. E.g. on the 21th, the measured NO2 gradient around noon is much steeper than the modelled, while it fits well around the afternoon. I. e. around the afternoon (16 h) the turbulence is well described and the atmospheric turbulence reaches its maximum, while it is over- estimated around noon. The most reasonable reason is the parameterization of the turbulence by the radiation, see general comments. Since HONO sources (topic of the manuscript. . .) are linked to the turbulence and the NO2 profile, this should be first optimized (e.g. by constraining the turbulence and emissions every day/daytime individually to match exactly the NO2 profile), before HONO should be studied and discussed. This recommendation is based on the assumption that the goal of the manuscript is to better understand and identify the daytime sources of HONO by comparing a model and individual measurements (that is how I understood the manuscript). If the goal is however, to develop a general model on the HONO chemisty, this comment, and also some general concerns may be ignored.

Response: We have already addressed this issue in an earlier comment. Vertical mixing in the model is parameterized by eddy diffusivity, which is described to have a maximum at noon in the model. Since we do not have any observations of eddy diffusivity during the field experiment, we made an assumption that vertical mixing has a maximum at noontime. To better constraint the emissions in the model, eddy diffusivity is the same for all three days except in the early morning when eddy diffusivity is also adjusted to match strong NO_2 gradient. For the rest of the day, NO_x

emissions are adjusted to best match the observations of NO_2

Page 27789, line 23-35: This is not correct for the dark reaction, see table 3. Here NO+OH is of much higher importance (ca. 22 %) compared to the dark conversion of NO2 on the ground (ca. 8 %), which is also in good agreement to other model and field studies on daytime HONO.

Response: The reviewer is correct. The sentence has been modified to "Daytime HONO during this model run was predominately from the gas-phase formation from NO and OH Contribution from the dark heterogeneous conversion at the ground is less significant"

Page 27790, line 6: Nice to see the daytime maximum of HONO/NO2 now also for a DOAS study!

Response: Yes, the daytime maximum of HONO/NO_2 ratio clearly indicates a photolytic source of HONO.

Page 27791, end of para. 3.2: Alternative explanation: the missing HONO source on high buildings, see general comment.

Response: As already explained in the general comment, the buildings below the LP-DOAS light path are generally one- to two-story high. Therefore, we do not think the missing HONO source is due to high buildings.

Page 27792, end of the page: Should be reformulated: The results confirm other studies, in which even the high rate coefficient from Li was used (Ref. to other model studies. . .; here, also the value from Li et al. is used). If the much lower values (<1/10) from Carr et al., etc. were used, the reaction would be of even smaller

importance. . .

Response: To clarify this, the sentence "The gas-phase mechanism through NO_2 is too slow to reproduce the observed daytime HONO mixing ratios, confirming other studies that found this mechanism to be unimportant (Carr et al., 2009; Amedro et al., 2011)." is modified to "Even with the rate constant suggested by Li et al. (2008), the gas-phase mechanism through NO_2 is too slow to reproduce the observed daytime HONO mixing ratios. This confirms other studies that found this mechanism to be unimportant (Carr et al., 2009; Amedro et al., 2011)."

Page 27793, line 16:?Value is still too high, see general comment.

Response: This has been addressed in the general comment.

Page 27794, lines 11-13: This is a very good point! Thus, first the NO2 profiles have to be optimized, see comment above.

Response: This has been addressed in a previous response.

Page 27795, line 14-16: That is reasonable: Kurtenbach et al. studied a vehicle fleet with significant contribution of diesel vehicles (higher HONO emissions). Maybe the range of HONO emissions between the studies of Kirchstetter et al. (US, tunnel without trucks, lower limit) und Kurtenbach et al. should be used. In addition, the dark reaction may be overestimated (see above).

Response: The emission ratio of HONO used in the model is on the high range of reported values. However, because we use the same ratio for our previous studies (Wong et al., 2012), we would like to be consistent with our previous studies. Due to the diurnal variation of vehicle fleet, the ratio can have a diurnal variation. It is possible

that the dark reaction may be overestimated, but it is less likely because it describes the nighttime HONO (not shown here) and the early morning HONO well. Therefore, we concluded that the direct emission is being overestimated or the loss of HONO is being underestimated at this time.

Page 27796, lines 9-10: Although that conclusion is what I expect, I do not understand how the authors obtained that result. The uptake coefficient of the photochemical reaction was only <6 times higher than during the dark (max. 6x10ˆ-5, see Figure 1, compared to 1x10ˆ-5). Averaged over the daytime, the difference between both sources should be only ca. a factor of 3. Thus, even when the different HONO yields are considered, the difference in the model cannot be "more than a factor of 10"? Both NO2 reactions are on the ground. . .

Response: Because the photoenhanced HONO formation is parameterized to have a 100% yield of HONO from NO_2 instead of 50% yield in the dark formation, the largest difference between both sources is a factor of 12 at noon, as described on Page 27996, lines 9-10. Averaged over the day, the difference between both sources is about a factor of 6.

Page 27796, lines 10-17: To average the ground source over 300 m is a good idea to compare the importance of the different sources! However, than, also the emission source should be averaged over 300 m. On contrary, here the emission is described as a volume source only for the layer 0.1-1 m? Thus, the numbers are orders of magnitude too high, should be 3x10ˆ5 cm-3 s-1, much smaller than the photolytic ground source.... Again apples and oranges are compared.

Response: The purpose of this section is to show the height dependence of the different sources and sinks of HONO in the boundary layer. The ground sources and sinks are given as a flux in unit of molecule per area per time, in contrast to all other

sources, which are given in unit of molecule per volume per time. The reviewer's desire to compare the difference sources and sinks is addressed in section 4.2 where we converted the ground sources and sinks to the same unit by averaging it over the lowest 300 m

Fig. 9:

This figure is too busy and several lines (e.g. P(ground), P(ground photo), E, L(ground)) are absent or cannot be seen. To improve, I recommend i) to use thinner lines so that the interested reader may zoom in to identify, ii) to use a non-linear scale (zoom the x and y axis around zero, logarithmic is clearly not possible for the negative values. . .), iii) use 300 m average values for all near ground processes, see text page 27796, lines 10ff, iv) delete d[HONO]/dt: is always zero (PSS fulfilled. . .). In addition, it is not clear, why the vertical transport term goes from -10ˆ7 to $+$10ˆ7 at the ground?

Response: We have tried the reviewer's suggestion to change the line thickness of some lines. However, it does not help much because some of the lines overlap. We have also tried to change the color or use a non-linear scale, but have decided that the current configuration is the best. Another reason to leave Figure 9 unchanged is that we would like to have consistent scales in both Figure 9 and Figure 10.

Regarding the 300 m average value for all near ground processes, because the purpose of this figure is to show the vertical dependence of the sources and sinks, we think it is not appropriate to convert all the near ground processes to averages over the lowest 300 m. Averages over the lowest 300 m are shown in Figure 10 instead. The reviewer has suggested us to delete the d[HONO]/dt line. However, this line is necessary to close the HONO budget, as HONO is not in a steady state.

The value of the vertical transport is negative at and near the ground and be-

comes positive as altitude increases. Because the strongest sources of HONO are at and near the ground, vertical mixing transports HONO upward leading to a loss of HONO at and near the ground and serves as a source of HONO above. This has been explained in the text therefore no changes are made.

Fig. 10:
This figure could be also improved by i) showing a non-linear y axis scale (zoom in around zero), ii) using thinner lines.

Response: We tried to change the scaling and the line thickness, but the figure did not become clearer. We thus kept it as is.

Page 27797, line 23-27 and page 27801, top of the page: Although I generally agree to the comment that the fluxes of HONO should be considered for the OH budget calculations, the differences to prior PSS calculations will not be as large as can be suggested from the numbers presented here. For example, here a large contribution by HONO deposition is calculated. However, the deposition takes place from the laminar layer at the ground to the surface, were transport typically limits the uptake (for the high gammas used). Since HONO is formed by the NO2 also at the surface, directly a third of that HONO deposite before leaving the layer. I.e. most of the HONO which deposits (total deposition flux used here), never escaped the laminar layer and thus, will not contribute to any HONO fluxes at >1 m were typically the measurements took place. Thus, for typical measurement heights the error by ignoring the deposition during daytime is marginal! This can be clearly seen from the results by the authors. In the present study, an altitude averaged HONO daytime source of 6x10ˆ6 cmˆ-3 sˆ-1 was calculated (see page 27796, lines 12-13), which is almost the same compared to the experimental study by Wong et al., 2012 (see their figure 5) using the same data and where much simpler PSS approach was used. So if no gradient measurement are available (which is certainly the best approach!), still

these simpler calculations are recommended and will give reasonable results.

Response: We believe this discussion is based on a misunderstanding between the upward and downward flux vs a net flux of HONO. In our case deposition refers to the uptake of HONO on a surface, while photo-enhanced conversion of NO_2 is the cause for the upwards flux. If one combines the two into a net upwards flux the contribution of deposition is indeed minor and ignoring dry deposition may still lead to reasonable PSS approach using atmospheric observations which are typically above the laminar layer (see Figure 10). Nevertheless for a complete interpretation of the system and to link uptake coefficients to observations both fluxes should be considered.

Our comments on page 27797 were mostly focused on the vertical transport to higher altitudes which can be a larger sink of HONO than photolysis in the 0 – 20 m altitude range. In our previous study Wong et al. 2012, the PSS calculations were based on an altitude average HONO daytime source over the layer 20-70 m, thus removed from this altitude range. However, most surface observations are taken below 20 m, where vertical transport is a strong removal pathway as indicated by our study. In this case, the PSS approach will underestimate the source of HONO if vertical transport is not taken into account.

Page 27798, line 17-19:?Should be: “The daytime averaged total. . .” Number is also integrated over the time. . .

Response: Correction has been made. This sentence has been modified from “The total production of HONO integrated over the lowest 300 m of the atmosphere was (6.8– 10) $\times$ 10^{15} molec. cm^{-2}, which was balanced by its removal.” to “The daytime total production of HONO integrated over the lowest 300 m of the atmosphere and time was (6.8– 10) $\times$ 10^{15} molec. cm^{-2}, which was balanced by its removal.”

Page 27799, line 8: This conclusion is unclear. If the gammas on particles would be as high as used here (they are not, see above) than formation on particles should be especially important near to the ground, where the particles are emitted (strong gradients at least for primary particles expected near to the emission source)?

Response: There is no information available about the aerosol gradients near the surface during this field campaign. Aerosol scattering measured by a ceilometer by University of Houston showed no obvious daytime vertical gradient of aerosol above 70 m. It is possible that there is a strong gradient for primary particles near the emission source. However, most aerosol and aerosol mass in urban areas are of secondary nature and would thus not show a strong vertical gradient. Finally, the surface area offered by the surface in the lowest 20 m of the atmosphere is many times larger than that of the aerosol and consequently surface formation will dominate.

Page 27800, lines 12-14: While this argument is true for any dark reaction, it will not hold for a photoenhanced reaction, which typically scales linearly with the irradiance. However, for a porous sur- face the light will not enter deep pores. In addition, even for any rough upper irradiated surfaces, the formation rate will be same compared to a flat surface, since the higher surface area of rough surfaces will be exactly compensated by the lower photon density per surface area.

Response: The reviewer may be right on this. We agree that light will not enter deeply into a porous surface. However, we believe that the formation rate on an uneven surface will be larger than that of a flat surface. It will of course depend on the structure of the surface and angle of light incidence. This will require additional laboratory studies before any decision or comments can be made at this point. To soften this comment we changed the sentence in the manuscript to: "*However, the true atmospheric surface area available for chemistry is most likely larger than the*

geometric surface area used in the model, thus explaining the need for a larger uptake coefficient in the model .''

Technical corrections:

Please check all references, there are still several errors, e.g. with the given names of the authors. In addition, the strange numbers (e.g. Acker et al.: 27777, 27778, etc.) behind each reference is unclear and should be deleted.

Response: References have been checked. The strange numbers behind each reference indicate the page number that the reference is cited. They are added by ACPD.

Second names of some authors not specified Carr et al., Dibb, et al., George et al., Goncales et al., He et al., Kurtenbach et al., Mao et al., Platt et al., Sawar et al., Su et al., Zhang et al., all Zhou et al.

Response: References have been checked and updated.

In addition: Carr et al.: page 336b is missing.

Response: References have been updated.

Kleffmann et al., 2003: Lörzer. Mao et al.: Chen, S.,?Zhou et al., 2011: Nature Geosci.

Response: References have been updated. For Zhou et al., 2011, Nat. Geosci. is the abbreviation of Nature Geoscience. No changes are made for this reference.