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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.

Anonymous Referee #2

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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.

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 explained 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 uncertainties 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. . .).

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 induce 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 recommended.

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.

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.

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.

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).

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).

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.

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.

Page 27784, equation (2)

Shouldn't it be: Irradiance = Irradiance(max.) x J(NO2)ˆ3/J(NO2)noonˆ3 ?

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.

Page 27785, equation (4):

Numbers too high, see general comment.

Page 27787, line 6, Fig. 2:

A complete diurnal emission profile is recommended to better identify also the afternoon rush hour.

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 overestimated 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 op-

timized (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.

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.

Page 27790, line 6:

Nice to see the daytime maximum of HONO/NO2 now also for a DOAS study!

Page 27791, end of para. 3.2

Alternative explanation: the missing HONO source on high buildings, see general comment.

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. . .

Page 27793, line 16:

Value is still too high, see 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.

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).

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. . .

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.

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?

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.

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.

Page 27798, line 17-19:

Should be: “The daytime averaged total. . .” Number is also integrated over the time. . .

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)?

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 surface 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.

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.

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.

In addition:

Carr et al.: page 336b is missing.

Kleffmann et al., 2003: Lörzer.

Mao et al.: Chen, S.,

Zhou et al., 2011: Nature Geosci.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 27775, 2012.