

Interactive comment on “High resolution vertical distribution and sources of HONO and NO₂ in the nocturnal boundary layer in urban Beijing, China” by Fanhao Meng et al.

Jörg Kleffmann

kleffman@uni-wuppertal.de

Received and published: 11 September 2019

The gradient study presented in Meng et al. is a nice piece of work showing night-time gradient data on a meteorological tower up to 250 m altitude similar to our former study (Kleffmann et al., 2003). Here a measurement container is lifted on the side wiring of the tower, far away from the open steel construction of the tower, thus minimizing potential wall effects, which is a nice idea. I strongly encourage the authors to extent these measurements including other important species for the future (see below). I have a few points which may be considered for the revised manuscript:

1) Direct HONO emissions (section 3.3):

The authors determined the HONO/NO_x emission ratio from the minimum HONO/NO_x ratio, which by definition will only result in an upper limit value, since always some secondary HONO is included in ambient measurement data. If emission ratios should be derived from field data, the authors should look for sharp peaks during night-time and should evaluate only the elevations of HONO and NO_x over the background levels (DHONO/DNO_x). In this case the risk overestimating direct emissions is minimized – but still even this peak data presents an upper limit caused by potential secondary HONO formation during transport from the emission to the measurement site (will be short for sharp concentration peaks). I expect that the HONO/NO_x emission ratio derived by the peak method will be considerably lower, closer to direct emission data (see test stands and tunnel data: <1%). The use of correct HONO emission data is important for the whole study, since emission corrected HONO data (considerable ca. 50% contribution, typically emissions have 10-20 % contribution) is used later for the evaluation of the other HONO sources.

2) HONO formation on aerosol surfaces (section 3.4.2).

The authors used heterogeneous uptake data for NO₂ derived in the laboratory to calculate potential HONO formation during night-time. However some studies cited/considered focus on the daytime production of HONO by photosensitized conversion (George et al., Sremmler et al.), leading to overestimation of the night-time conversion. Here references to other dark studies are recommended and it should be mentioned that the used value of 10^{-5} represents really the upper limit night-time kinetics (typically 10^{-6} is used in the dark). In addition, the authors should explain that they considered a 100 % yield for the NO₂ conversion (see factor $\frac{1}{4}$ in eq. (1)), which is also the upper limit, e.g. when using the typically considered night-time reaction R1: $2\text{NO}_2 + \text{H}_2\text{O} \Rightarrow \text{HONO} + \text{HNO}_3$ (see the first reference used in line 370) for which the maximum yield is 50 %. So please define that a redox reaction ($\text{NO}_2 + \text{X} \Rightarrow \text{HONO}$) is considered here. But all this will even further decrease the low contribution of particle surfaces to the night-time HONO production, which is in line with my own point of view.

[Printer-friendly version](#)[Discussion paper](#)

3) Nocturnal HONO production on the ground (section 3.4.3):

Instead of using the “two-point” equation (4), simply plot the night-time HONO/NO₂ ratio as a function of the time. In this case the slope determined by linear regression will statistically better describe the efficient first order NO₂⇒HONO conversion rate constant. Since this is a rate coefficient, it should be better termed by e.g. “k(het)” and not by the term “C” (C: concentration?), which I often found in recent Chinese HONO papers? Since HONO(corr.) will be significantly higher (see point 1) also the efficient conversion rate coefficient will increase.

In this section the authors also determine a net HONO yield from the ground surface conversion of NO₂ of the order of 10 % by using deposition velocities for HONO and NO₂. The value for HONO is to my opinion too low and will be more of the order of 2 cm/s (see cited studies and others). In addition please specify the value used for NO₂. The HONO yield determined is quite high and our recent gradient study (Laufs et al., Atmos. Chem. Phys., 17, 6907–6923, 2017) could be also cited, where we determined lower values in the range of 0.02-0.044 by a more direct approach in good agreement with the gradient study by Stutz et al., 2002 (0.03). In addition you will find there also data for the deposition velocity of HONO, confirming a higher value, at least at the low temperatures of the present study.

4. Concept used:

The authors tried to distinguish between heterogeneous night-time formation of HONO on particle surfaces and on the ground, which is an important question with respect to the decades long discussion on the sources of HONO in the atmosphere. Here first, I am missing a more focused introduction of the basic problem. There are ground level studies, which found a nice correlation of HONO/NO₂ with the particle surface area and which propose HONO formation on particles. On the other hand there are gradient studies of HONO (and NO₂) which typically determine a negative gradient, pointing to the ground as most important surface. However, none of these studies can answer

[Printer-friendly version](#)[Discussion paper](#)

the question! The correlation with particles could be also explained by the variation of the vertical mixing and the fact that both, HONO and particles are emitted/formed near the ground. Here pioneering studies by A. Febo found nice correlation of HONO with Radon during night-time and there is clearly no chemical link between both species. . . On the other hand the gradients could be also explained by formation on particle surfaces, if there is also a negative gradient in the particle surface area density (S/V). So what we need are gradient measurements over a few hundred meters (like the present study) but including besides HONO and its precursors (most probably NO₂) also the surface area density (see our former study Kleffmann et al., 2003). Only if there is no gradient in the particles, a negative gradient of the HONO/NO₂ ratio will show HONO formation on the ground. Thus, second, I strongly recommend that the authors use this nice tower set-up and include in future campaigns also fast particles and NO measurements!

The later is important since the titration reaction of NO+O₃ may mask the observation leading e.g. to artificial gradients of the HONO/NO₂ ratio not resulting by any HONO processes, but simply by a changing NO₂/NO_x ratio. For example, the decreasing HONO/NO₂ ratio shown in Figure S4 (see first two gradients near the ground) is not plausible since the HONO/NO_x ratio is expected to increase during the night. Most probably NO was converted into NO₂ leading to lower HONO/NO₂ ratio.

Minor points:

There are numerous errors in the references, please check, examples: Line 60: Vogel et al.; missing blanks between the references (throughout the whole manuscript). Line 68: Bröske et al., etc.

Line 76: the photocatalytic conversion of NO₂ on TiO₂ (“mineral dust”) is not a redox reaction.

Line 77-82, R2: This reaction is not a photosensitized conversion.

[Printer-friendly version](#)[Discussion paper](#)

Lines 84-88: In the cited studies neither all used a DOAS, nor was the DOAS installed on an elevator.

Line 93-94: In our gradient study in Chile the measurement frequency was very high, only the vertical resolution was low (should be “or”).

Line 106-110: Please add our recent flux study Laufs et al., 2017 (see above).

Lines 381-384, Fig.11: I do not understand that statement. The figure shows only the column average HONO concentration is near (81%) to the ground level. That could be also explained by a particle source?

Figures 7+8: The concentrations in the residual layer typically represent daytime levels (in the absence of a volume source of HONO). Here HONO levels of 1-2 ppb are observed, which should be discussed. Such high HONO levels at 250 m altitude are really exceptional!

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-613>, 2019.

Printer-friendly version

Discussion paper

