Review of “Quantification of the unknowns HONO daytime source and its relation to NO_2”, Sörgel et al. (2011) ACPD

General Comments

This manuscript presents an analysis of HONO concentrations observed above a near-coastal forest in SW Spain during the DOMINO campaign in early winter of 2008. All of the requisite quantities were directly measured for calculation of photostationary HONO levels, allowing a detailed analysis of the HONO budget at this site. As generally seems to be the case in these types of studies, measured daytime HONO concentrations far exceed those expected from known gas-phase and heterogeneous sources, implying a large missing source. The authors show that several recently-proposed sources are unable to close the HONO budget. It is suggested that the missing source is due to some process involving NO_2 and light, though to me this conclusion is not evident from the available data. The paper is generally well-written and, by virtue of presenting new results alongside a thorough budget analysis, is worthy of publication in ACP. My comments are primarily aimed at clarifying the discussion of the HONO budget, as it seems to transition back and forth between the various budget terms and can be difficult to follow at times.

Specific Comments

P4, L33: What is meant by “zero OH cycle”?

P5, L16: I know of two other studies dealing with HNO_3 photolysis on plant surfaces, one of which was published after this manuscript (Raivonen et al., 2006; Zhou et al., 2011). Zhou et al. (2011) suggest a HONO source of 140 – 200 ppt/h above a mixed deciduous forest, which is on the right order of magnitude for the missing HONO source in the present study. The authors site (Rohrer et al., 2005) as evidence against this mechanism; however, that study did not deal with plant surfaces, which are very different from teflon and glass and inherently contain many “organic photosensitizers.” This source should be considered in the later analysis.

P5, L22: This sentence is somewhat out of place relative to the rest of the discussion, as the remainder of this paragraph deals with NO_2*. I suggest either moving or deleting it.

P7, L9: Some additional information about this forest would be helpful for comparisons with other studies (e.g. height and leaf area index).

P7, L23: What is the uncertainty in the LOPAP observations? I believe this is stated later, but it would be appropriate to mention it here.

P7, L31: I suggest combining this with the previous paragraph. Was this inlet co-located with the HONO inlet?

P8, L15: This phrasing is somewhat awkward; I suggest re-wording to clarify.

P9, L25: This sentence should be switched with the one above it (it is strange to go from k7 to k6 and then back to k7). This statement seems to infer that the above-discussed rates constants are at the high-pressure limit, which should be stated explicitly before discussing the values. What is the low-pressure limit rate constant?

P10, L1: please provide a reference (paper or personal communication) for these OH interferences. Is it possible to put an upper limit on these? 20%? Factor of 2? It is probably most appropriate to discuss uncertainties in OH in Section 2.

P10, L10: How is this albedo used to adjust j(HONO)? Do you just increase these values by 5%?

P10, L14: This uncertainly should be mentioned in Section 2.

P10, L19: Why is that data taken from the 1m measurement for 1 day? Was it not available from the 10m instrument?

P10, L23: This is somewhat surprising to me, given that the missing source is likely related to the surface, though the measurements in the cited paper do support this. Are there any other measurements of HONO gradients in forests to support this generalization?

P10, L25: This sentence does not make sense. Instead, I suggest saying something like "On average, $[HONO]_{PSS}$ comprises xx ± xx% (mean ± 1σ) of measured HONO concentrations."

P11, L1: We can infer that HONO and NO co-vary, but not that one is dependent on the other. Very likely, this is because both are related to $j(NO_2)$ and NO_2 concentrations.

P11, L6: Higher $HONO/NO_x$ certainly indicates that most of the observed HONO is due to processing of oxidized nitrogen rather than direct emission; however, this does not imply that "light-induced conversion of NO_2" is the source. As the main point of this paragraph is to argue that direct emissions are not important, I would change or delete this sentence. Also, this paragraph does not really seem to fit with the discussion of the PSS, thus I suggest moving it to Sect. 3.3 (see below).

P11, L13: I would suggest starting a new section here for "Known Heterogeneous Production" or something similar.

P11, L30: I suggest moving the discussion of how these conversion frequencies are calculated to this section (see also below comments).

P13, L24: Presumably, T_v represents entrainment of free tropospheric "background" air, which will have fairly low HONO concentrations. Given that the HONO lifetime is typically 15 – 30 minutes during the day and the timescale for mixing of the boundary layer is likely on this order, it is probably safe to assume it is a small contribution. This seems like a better argument than simply assuming it is similar to L_{dep}. Alternatively, you could estimate this via a parameterization such as that suggested by (Dillon et al., 2002):

T_v = -k(dilution)*[HONO – HONO(background)]

Assuming k(dilution) = 0.23 /h, HONO = 25 ppt (for noon) and HONO(background) = 0 give a dilution term of 0.001 ppt/s, which is indeed quite small.

P13, L28: Is it more correct to scale the deposition velocity by the measurement height rather than the BL height? I present this as a question because I myself am not sure. Since HONO was measured relatively close to the forest (at z/h = 10m/6m = 1.67, according to Sect. 2), one might expect surface sources and sinks to be more important for mixing ratios here relative to the boundary layer average. This would be reflected in concentration gradients, and the authors state that measurements were available at 1m as well. So, I guess really my question is: do the authors feel that their measured concentrations are representative of the BL average?

P14, L3-11: I suggest combining these paragraphs and also moving the discussion of HONO/NO_x to here. Did the authors observed any noticeable variations of HONO with wind direction that might help identify direct emission sources? For example, is HONO/NO_x lower when air is coming from urban or industrial regions?

P14, L9: "The contribution of directly emitted HONO to $P_{unknown}$" is misleading, as this makes it sound like you are wrapping P_{emis} into $P_{unknown}$. I think it is more correct to label it as the contribution to the HONO budget.

P14, L21-24: Given that you discuss this process in detail earlier, I suggest this be moved to the previous section. I have two additional points here:

1) Since nighttime data is not really shown in any of the figures (aside from Fig. 1), it would be instructive to see a figure showing typical nocturnal HONO profiles.
2) Is it safe to assume that heterogeneous formation is the dominant nighttime process? For example, if deposition were important but not accounted for, this would bias your estimate of P_{het} low.

P15, L1: Rigorously, the error in dC/dt is equal to roughly twice the uncertainty in any single 5-minute measurement.

P15, L30: It strikes me as odd that you would not simply include all values of dHONO/dt. If they were indeed small, then this should not affect you budget calculation. Rejecting points below some threshold biases this term high.

P16, L5: What is meant by “correlation scheme”? Do you mean that more of the data falls onto the trend line with j(NO_2)? If so, the fact that the correlation improves here does not necessarily imply that the missing source is driven by NO_2. Here is an alternative (though long) explanation: 1) the points with high dC/dt are those most affected when normalizing by NO_2; 2) dC/dt is most variable during times of rapid change in concentrations (e.g. advection events); 3) HONO and NO_2 tend to co-vary; 4) L_{photo}, which depends on HONO, is generally the largest term balancing $P_{unknown}$, and P_{het}, which depends on NO_2, is the largest source term. Thus, normalizing by NO_2 could also be thought of as “normalizing out” the effects of advection on HONO budget terms.

P16, L8: Please see my comment for P14, L9.

P17, L20 – 22: Why not just scale the photon flux with j(NO_2), as was done for j(HONO)?

P18, L10: What is the value for k_{air}?

P18, L18: The use of so many percentages makes this sentence quite confusing. If the point is to show that NO_2* is small, just give a mean value or percentage for comparison with $P_{unknown}$.

P18: Is it possible to calculate, or even estimate the potential magnitude of, any of the other potential HONO sources from the available data, e.g. photolysis of nitrate or heterogeneous light-driven NO_2 reactions?

P19: Are HCHO measurements available to include in the calculation of HOx sources? I would be curious to know how it compares to HONO.

P20, L17: This statement may be too strong. Figure 4 shows slight correlation of the unknown source with j(NO2), but the slope is so low that the correlation looks weak at best. To me this suggests that the unknown source is possibly light-dependent, but not necessarily that it is related to NO_2. You could instead say that the data is *consistent with* light-dependent heterogeneous chemistry (possibly involving NO2 as suggested by lab experiments).

P29, L1: Varying between light and dark shades would make the lower bars easier to discern. Also, you might consider putting the loss terms on the negative y-axis, if possible.

Technical Comments

P6, L5: unfocused

P7, L7: change “has been” to “is”

P12, L26: where

P14, L8: were

P17, L17: unknown

Cited Literature

Dillon, M. B., Lamanna, M. S., Schade, G. W., Goldstein, A., and Cohen, R. C.: Chemical evolution of the Sacramento urban plume: Transport and oxidation, J. Geophys. Res., 107, 4045, 10.1029/2001JD000969, 2002.

Raivonen, M., Bonn, B., Sanz, M. J., Vesala, T., Kulmala, M., and Hari, P.: UV-induced NOy emissions from Scots pine: Could they originate from photolysis of deposited HNO3? Atmos. Environ., 40, 6201-6213, 2006.

Rohrer, F., Bohn, B., Brauers, T., Bruning, D., Johnen, F. J., Wahner, A., and Kleffmann, J.: Characterisation of the photolytic HONO-source in the atmosphere simulation chamber SAPHIR, Atmos. Chem. Phys., 5, 2189-2201, 2005.

Zhou, X., Zhang, N., TerAvest, M., Tang, D., Hou, J., Bertman, S., Alaghmand, M., Shepson, P. B., Carroll, M. A., Griffith, S., Dusanter, S., and Stevens, P. S.: Nitric acid photolysis on forest canopy surfaces as a source for tropospheric nitrous acid, Nature Geoscience, 10.1038/NGEO1164, 2011.