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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Comparison of HONO budgets for two measurement heights at a field station within the boreal forest (SMEAR II – HUMPPA-COPEC 2010)" *by* R. Oswald et al.

Anonymous Referee #2

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General comments:

This paper presents measurements of HONO and budgets for its daytime production and loss at two measurement heights during the SMEAR II campaign, a site in the boreal forest in Hyytiala. Like several other recent field studies, results show that the daytime budget for HONO is not balanced, with no clearly identified source able to explain the presence of measurable HONO, a species that undergoes rapid photolytic loss. The authors consider and attempt to quantify several potential HONO sources that could address this imbalance. These include the gas phase reaction of OH + NO, the heterogeneous reaction of NO2 with water leading to disproportionation to

HONO + HNO3, photolysis of nitrophenols, photosensitized heterogeneous uptake of NO2 to soils, emission of HONO from soil and photolysis of surface absorbed HNO3. The work is comprehensive, since it nicely considers all of these sources. However, the authors also show that none of these sources can explain the observations, and that the apparent HONO source is correlated most convincingly with its photolytic loss rather than with any other single parameter possibly related to the above sources.

The presentation and discussion of the HONO photochemistry is well done. However, the authors fail to consider or allow the potentially most obvious explanation of these observations, which would be a small interference on the Lopap instrument that is unrelated to HONO itself, or from uncertainty in the zero level of the instrument. Such an interference or zero uncertainty would produce an apparent budget that would correlate perfectly with the photolytic loss for HONO. The authors should state clearly why they believe that the HONO measurements are reliable enough at the several tens of parts per trillion level. I recommend publication of this manuscript only with the addition of such a section or with some additional detail added to the experimental section, since a low-level interference or offset would clearly provide the simplest explanation of the observations.

The paper also does not consider the implications of the measurements for either the HOx or the NOx budgets. How large a contribution do the observed HONO levels make to either? The recent Li et al. paper in Science (2014) suggests that HONO observations cannot be reconciled with HOx or NOx budgets unless the HONO source is itself derived from something that consumes both HOx and NOx. Can the authors make quantitative comparisons to these budgets and state how this constraint might affect each of the source terms they consider?

Specific comments:

Page 7827, line 2: Phrase "less important" is confusing here, since reactions R2 and R3 are not in competition. Clearer would be "the flux (or mass) through this reaction is

smaller," or something to that effect.

Page 7828, equation (3). For completeness, best to specify units. Also, is the upper limit given here due to just the absorption cross section of nitrophenols relative to NO2, or due to the absorption cross section and a quantum yield for HONO?

Page 7831, experimental section. The experimental section is very brief and relies upon a reference to an earlier paper to describe the HONO measurements. In that earlier paper, the two LOPAP instruments were compared using identical 50cm-long inlets. Are the same inlets used here? If not, this paper should note the inlet length and residence time. Also, the paper should discuss the instrument diagnostics that were performed. Were there any efforts to calibrate or zero the instruments at the field site? Power disruptions are used to explain why simultaneous measurements were available only 30% of the campaign. How long did it take to restart an instrument after a power disruption? Since daytime HONO levels are much higher than can be understood, the authors must do more to justify that their measurements are free from artifacts at $\sim$20 ppt level. It appears that HONO is always well above zero (Fig 1). How well is the instrumental background understood?

Also, how was J(HONO) measured?

Page 7831, line 25: What does "reasonable agreement" mean? Please give a quantitative comparison of the two OH instruments.

Page 7832, Results section: More discussion of the NO2 levels is needed. They are shown in Fig1, and one day with low NO2 levels is mentioned. But many studies report the relationship between HONO and NO2, and it would be helpful here to discuss the NO2 levels and the relationship to HONO. Also, NO2 conversion to HONO on activated surfaces are proposed as a possible HONO source. Could this occur in the instruments or inlets?

Page 7834: dHONO/dt is not defined. What is the time step here? It appears to be

the $\sim$1 hour time step between averaged observations in figure 5. But photolytic loss of HONO is quite a bit faster than this time step, so in reality the better form of this equation is to simply set dHONO/dt to zero and just solve for the difference between sources and sinks? It seems in reality this is what the authors have done. The need for explicit inclusion of dHONO/dt for slow observations is not clear.

Page 7835, last paragraph. The HONO observations presented here show at best only a modest vertical gradient. It seems unreasonable to apply a 50-60% contribution of vertical transport to HONO loss? Perhaps the argument of this paragraph could be clarified.

Page 7837, lines 14-21: A humic acid soil source would likely lead to a gradient in HONO, with larger values at 1 m than 24 m, correct? Are the modest gradients and their diurnal variation consistent with or contrary to this source?

Section 3.3.3, HNO3 photolysis: Is the use of the HNO3 surface loading from Zhou et al. likely to be applicable to the SMEAR environment? A short comparison of the sites with some justification is warranted. As in the comment above, would surface HNO3 lead to an observed gradient in HONO? Can the height resolved measurements and their diurnal variation provide any insight?

Figures:

Fig 1 is difficult to read. Some of the panels have two red traces, and I can't know which trace goes to which label. Please use 3 colors for 3 traces, and much larger axis labels.

Both concentrations and mixing ratios are used to describe abundance of a single compound, which makes it hard to compare figures. Please choose just one unit for each compound.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 7823, 2014.