

## ***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.***

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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 Hyttiala. 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 NO<sub>2</sub> with water leading

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to disproportionation to HONO + HNO<sub>3</sub>, photolysis of nitrophenols, photosensitized heterogeneous uptake of NO<sub>2</sub> to soils, emission of HONO from soil and photolysis of surface absorbed HNO<sub>3</sub>. 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 HO<sub>x</sub> or the NO<sub>x</sub> 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 HO<sub>x</sub> or NO<sub>x</sub> budgets unless the HONO source is itself derived from something that consumes both HO<sub>x</sub> and NO<sub>x</sub>. Can the authors make quantitative comparisons to these budgets and state how this constraint might affect each of the source terms they consider? “

We thank referee #2 for the detailed evaluation of our paper and the valuable comments that will help to further improve the manuscript.

We agree with the referee that the accuracy of the HONO measurements is crucial for determining the budget. The experimental section has been extended to discuss

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the reliability of the LOPAP at the lower ppt range (see detailed comments below). We are confident that these values are not an instrument artefact as HONO daytime values in the lower ppt range were also observed by other techniques (see manuscript p 7841, L1). The study from Li et al. in Science (2014) was not yet published when we submitted this paper. We will briefly discuss the implications of this "new HONO source" for the budget at our site in the revised version of the paper. However, a detailed investigation and comparison of HOx and NOx budgets is out of the scope for this study (for details see Hens et al., 2013).

#### Specific comments

"1. 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."

We clarified this sentence to: "...has less influence on HONO cycling than (R2) even with...as the turnover is low and constitutes..."

"2. 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 NO<sub>2</sub>, or due to the absorption cross section and a quantum yield for HONO?"

We specified the units. The text reads now as follows: "...it is possible to estimate the photolysis frequency (in s<sup>-1</sup>) by an upper limit..." The upper limit approach is based on measured photolysis rates that were converted to photolysis frequencies (Bejan et al., 2006). They are not based on absorption cross sections and quantum yields. The factor of  $2.5 \cdot 10^{-3}$  arises from the ratio of  $J(o\text{-NP} \Rightarrow \text{HONO})/J(\text{NO}_2)$  measured by Bejan et al. (2006) and the relation to  $J(\text{HONO})$  from a factor of 0.175 of  $J(\text{HONO})/J(\text{NO}_2)$  as derived by Trebs et al. (2009). We clarified the text accordingly.

"3. 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

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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 20 ppt level. It appears that HONO is always well above zero (Fig 1). How well is the instrumental background understood? Also, how was  $J(\text{HONO})$  measured?"

No inlet lines were used. Also in the study of Sörgel et al. (2011b) no inlet lines have been used for the intercomparison. We clarified the text accordingly by introducing: "Artefacts due to wall reactions are minimized in the LOPAP by using an external sampling unit where the derivatization takes place, instead of using inlet lines. The LOPAP uses two stripping coils in series. Hence, potential interferences are accounted for by quantitative sampling of HONO in the first coil by a fast and specific reaction (Heland et al., 2001; Kleffmann et al., 2002). All interferences are assumed to react in the same way in both coils and, therefore, the HONO signal can be corrected. The zero level of the instrument was checked automatically several times (every 4 hours for 30 min.) per day using purified air. Consequently, any diurnal fluctuation of the background signal is subtracted from the HONO signal. Potential interferences of the LOPAP instrument have been discussed in several studies including those cited in the manuscript (Heland et al., 2001; Kleffmann et al., 2002). There is only one study (Kleffmann and Wiesen, 2008) that studied interferences for HONO measurements with the LOPAP in the low ppt range and proved its reliability. Furthermore, Sörgel et al. (2011a) measured values around the detection limit ( $\sim 2$  ppt) in clean marine background air, thus in clean ambient air no background HONO has been observed. In this study, values reached the detection limit after a rain event (see manuscript line 15, page 7833). Furthermore, daytime values in the lower ppt range but well above the PSS were measured by dif-

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ferent techniques (see manuscript page 7841).  $J(\text{HONO})$  was calculated according to Trebs et al. (2009) from  $J(\text{NO}_2)$  measurements by a filter radiometer.

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

For more detail on OH LIF and OH CIMS please refer to Hens et al. (2013).

"5. Page 7832, Results section: More discussion of the  $\text{NO}_2$  levels is needed. They are shown in Fig1, and one day with low  $\text{NO}_2$  levels is mentioned. But many studies report the relationship between HONO and  $\text{NO}_2$ , and it would be helpful here to discuss the  $\text{NO}_2$  levels and the relationship to HONO. Also,  $\text{NO}_2$  conversion to HONO on activated surfaces are proposed as a possible HONO source. Could this occur in the instruments or inlets?"

As described above, no inlet lines were used. A short  $\sim 1.5$  cm radiation shielded glass inlet is the only instrument surface to which the sampling air is exposed to before HONO is stripped in the first coil. It is not exposed to direct sunlight and, therefore, fast photochemical reactions can be ruled out. The slower heterogeneous reactions of  $\text{NO}_2$  can be ruled out as the residence time is in the milli-second range. The  $\text{NO}_2$  interference in the stripping coil has been minimized by using a highly acidic (1 mol l<sup>-1</sup> HCl) sampling solution and it was shown, that this minimized interference is efficiently corrected for by the two channel design (Heland et al., 2001; Kleffmann et al., 2002). If HONO values would arise from  $\text{NO}_2$  interference they should be directly correlated to  $\text{NO}_2$ , which was not the case. Instead of discussing the  $\text{NO}_2$  levels in relation to HONO we calculated HONO formation from (dark) heterogeneous  $\text{NO}_2$  conversion during the night (Phet, Fig.5) according to the generally accepted approach of Aliche et al. (2002). This source did not play a role for daytime HONO formation. To clarify this we added some discussion on Phet to the results section. Furthermore, in section 3.3.1 we discuss the light induced  $\text{NO}_2$  conversion as potential HONO source and provide some information about  $\text{NO}_2$  values.

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"6. Page 7834:  $d\text{HONO}/dt$  is not defined. What is the time step here? It appears to be the 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  $d\text{HONO}/dt$  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  $d\text{HONO}/dt$  for slow observations is not clear."

Indeed,  $d\text{HONO}/dt$  is defined in eq. 7. Its value equals zero only if the sources and sinks are equal. As HONO values change during the course of the day there must be a (local) imbalance of the sources and sinks and, thus,  $d\text{HONO}/dt$  has to be taken into account otherwise sources or sinks would be over/underestimated. The referee is right that HONO lifetime during midday is much lower than the averaging interval (given by other data), but to take into account the "real loss" by photolysis during daytime we have to account for a change in the HONO concentration over that time (i.e.  $d\text{HONO}/dt$ ).

"7. 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."

In case a ground source and photolytic loss exists within the boundary layer, the argument has to be reversed. Without considerable upward transport of HONO (surface loss), substantial gradients would exist. This means a small gradient indicates fast vertical transport (c.f. (Sörgel et al., 2011b)). Even a light dependent volume source would result in visible gradients without vertical mixing due to the shading of the canopy. As already pointed out in the reply to referee 1, we believe that a qualitative discussion of this topic without further measurements is highly speculative and we prefer not to include it in the revised version.

"8. 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

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and their diurnal variation consistent with or contrary to this source? Section 3.3.3, HNO<sub>3</sub> photolysis: Is the use of the HNO<sub>3</sub> 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 HNO<sub>3</sub> lead to an observed gradient in HONO? Can the height resolved measurements and their diurnal variation provide any insight?"

Unfortunately, only gradients without fluxes do not provide detailed information into the vertical source or sink distribution. Hence, from the gradients alone we cannot favor one or the other source. Certainly, there would be more humic acids at the ground, but there is also less radiation available (see Fig. 1), which is essential to accelerate this reaction to levels comparable to daytime HONO formation (Stemmler et al., 2006). We believe that the values of Zhou et al. (2011) can serve as a best guess as the SMEAR II site as well as the PROPHET site where Zhou et al. (2011) measured are rural forested sites. Furthermore, Zhou et al. (2011) report their values to be close to one monolayer coverage, thus we do not expect much higher values for the SMEAR II site that are effective for photochemistry. In the revised version we will provide a more detailed intercomparison of the sites in the text. Additionally, the height resolved values do not provide much insight as during the most intensive photochemistry vertical transport is also maximal (ff. (Sörgel et al., 2011a)), which (in a well-mixed situation) on the other hand is a prerequisite to apply the budget method.

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."

As suggested by the referee in cases of two red colored traces in Figure 1 we changed one trace to green color. Also the axis labels were enlarged. We used the unit ppt for NO and HONO in Figure 1 for an easy comparison of values with other publications.

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The change to molec. cm<sup>-3</sup> in the following figures is due to the general use of this unit for the calculation of reaction kinetics and use of reaction rate constants. For best comparison with other publications there is no other choice than changing the unit.

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