

Referee 1:

We appreciate the reviewer's helpful comments on the manuscript. Thank you very much for your time and effort!

Comment:

1. P.21111, L.22, should “(NO₂(ads)+H(ads)→HONO(ads))” be “(NO₂(ads)+H₂O(ads)→HONO(ads))”? Also in two places on the same page (L.19-20 and L. 26), I would suggest changing the phrase “not of atmospheric relevance” to “not of atmospheric importance” or something like that. These processes are certainly relevant to atmospheric HONO formation, but may not very important in the real atmosphere.

1.) NO₂ (ads) + H(ads) → HONO(ads) is the elementary step of HONO formation proposed by Gustafsson et al. (2008), following the dissociative chemisorption of water adsorbed on mineral surfaces to H(ads) and OH(ads). To differentiate between a potentially interesting HONO formation pathway and its importance to the real atmosphere is a good suggestion, and we changed the phrases accordingly.

2. P. 21114-21115, it would be great to include a little more information regarding the site (major nearby cities and roads which might influence the measurements at the site) and the chemical and meteorological conditions during this study. Perhaps including a figure with time series of chemical/meteorological parameters (e.g., NO, NO₂, O₃, HONO, temperature, RH, wind speed and direction, J(NO₂), boundary layer height, etc.) would be good.

2.) A detailed site description was not included, as the cited literature (e.g. Matzner et al. 2004) gives an extensive overview. Since we measured in a mountainous region, local wind direction does not easily allow for interpretations of source origins, and local streamlines are complex. During the fair weather period (most of the represented data) the local wind direction was from south-west and south-east. To the east there are no bigger cities within 70 km. The motorway (A9) is about 9 km to the west, running from north to south. The cities of Kulmbach (~ 30000 inhabitants) and Bayreuth (73000 inhabitants) are 30 km west and south-west respectively. An extensive description of the experiment and the meteorological conditions can be found in the experiment documentation by Serafimovich et al. (2008) which is now referenced in the manuscript. A general report about the whole experiment is in preparation (Foken et al., 2011). Fig.3 was changed and now, in addition to RH and $j(\text{HONO})$, contains above canopy measurements of wind direction, friction velocity (u^*), NO, NO₂, Ozone, HONO and temperature. The friction velocity (u^*) is a better measure for turbulent exchange than wind speed alone.

3. P.21117-21118, Section 3.1, the large deviation in the intercomparison of two LOPAP instruments during the wet period is a little worrisome, despite the good agreement during the dry period. The authors gave a few possible reasons, but in my opinion none of them is convincing. What were HONO levels during the wet periods? It is better to include time series of both HONO measurements in Figure 1 (maybe add an upper panel) to see the absolute differences in HONO level.

3.) Indeed, we do not present a single "convincing" explanation for the differences (up to 80 ppt) but discuss possible reasons. From Fig. 1 it is clear that contrary to the Gaussian error distribution centred at zero during the dry period, during the periods with reduced visibility there is a systematic difference ($LOPAP_{MPIC} > LOPAP_{UBT}$) which must have something to do with one of the instruments. Unfortunately, we were not able to identify the exact reason. HONO values during the wet period from 9/28 to 9/29 were quite low, around 20-50 ppt. As suggested, we added both HONO measurements in Fig. 1 as an upper panel.

4. Figure 1, x axis: "01-Sep", "02-Sep", and "03-Sep" should be "01-Oct", "02-Oct", and "03-Oct". Also, before the noon of Sep. 29, there was significant difference between two instruments which seems related to low visibility. After the evening of Oct. 2, the visibility decreased again. However, the relative difference was not very large compared to the wet periods before. Any explanations for this?

4.) We corrected the erroneous axis-labelling. We have no convincing explanation for the lower relative errors on Oct. 2. At the beginning of this event HONO mixing ratios are higher (thus relative errors smaller) than in the previous events, but then drop down to comparable values with no increase in relative errors.

5. Figure 2, add NO_x time series to show relatively constant NO_x level.

5.) We added the NO_x time series in Figure 2.

6. In Figure 4, I am surprised to see the poor correlation between NO_2 and HONO. Have the authors tried to look at the correlation during the dry periods only? I wonder if the data points from the wet periods are causing the scatter.

6.) Restricting the correlation only to the dry period discussed in the manuscript (20-25th) makes things even worse ($r^2=0.013$ with a negative slope instead of $r^2=0.039$). Thus, data points from the wet periods are not likely to cause the poor correlation alone. Further details are discussed in the response to Reviewer 2.

7. In Figure 5, briefly explain the meaning of C, Cs, Ds, Dc and Wa so that the figure is self-explained without going back to the text. Also on P.21124, more description is needed regarding how to get the red boxes and what measurements are included in the red boxes in Fig. 5. I only found one sentence: "As an indicator for the effectiveness of vertical mixing, the detection of coherent structures was used," which is not very clear to me and not sufficient.

7.) We appreciate this suggestion and added the requested information to the manuscript.

8. In Figure 6, the relatively large HONO difference at two heights between 21:00 and midnight is kind of surprising to me. More discussion is needed in the text (P.21115). The authors attribute this to the "advection of HONO-enriched air masses above the forest canopy" or the release of adsorbed HONO from the wet canopy. These are not sound and need more evidence to explain the observations. Also, any explanation for the sudden increase (from 5-10 to 15-25) in the HONO lifetime ratio (red bars) at around 14:00?

8.) As stated in the original manuscript, the main contribution to the large positive differences (change around 21:00) originates from the last two days (of the dry period) as mixing ratios were the highest. On the 23rd, this increase can be attributed to an air mass change (see point 10 and section 3.4 in the original manuscript) On the 24th, wind direction changes but other than on the 23rd other trace gases exhibit no significant change. In addition to these peak values, HONO and HONO/NO_x values are predominantly higher above canopy from 21:00 to sunrise. If we discuss this phenomenon locally (no advection), we have to explain why the canopy source is more efficient in late night to morning. We see a relation to RH but can only speculate about the reasons which might be caused by a mechanism similar to that of Trick (2004). On the other hand, at night the HONO lifetime is only limited by deposition and thus quite long. Therefore, advection is also a possible reason. To really distinguish between advection and local release, more measurements and an adequate model approach would be required. The sudden increase of lifetime ratios in the afternoon at around 14:00 is due to shading of the sensor by the canopy. Although single values may be influenced by the shading of a single tree (even a branch), the average diurnal course (including the increase at about 14:00) is representative for this forest stand (comparison to in-canopy global radiation measurements ~ 60 m south east) and is related to the canopy structure.

9. P.21126, L.23-24, from Fig. 7, it seems to me that both HONO and RH (from the counter plot) follow similar trends at the two heights and I would expect similar correlation between RH and HONO concentration within the canopy. Please verify the significant difference in the correlation at the two heights.

9.) Although the structure in RH and HONO seems to correlate very well, the direct correlation of these quantities is often poor. For the period from midnight to sunrise (0:00 to 6:30 on 23rd Nov.) described in the paper, $r^2 = 0.78$ (N= 40) for the correlation of RH and HONO above canopy, whereas below canopy $r^2 = 0.07$ (N= 37) for RH at ground level (0 m) and $r^2 = 0.02$ for RH measured at 2 m. From 6:30 to 8:30, there is no correlation at all as HONO is decreasing due to photolysis and RH is constant or even increasing (vertical line in x-y-plot). From 8:30 to 12:00, both are decreasing ($r^2 = 0.5$ at 24 m, $r^2 = 0.63$ (RH at 0 m) and $r^2 = 0.66$ (for RH at 2 m), with smaller variation in HONO (94-65 ppt) whereas RH is strongly decreasing (85-61 % in 24 m). After the event at 21:00, at both heights HONO and RH are anticorrelated ($r^2 = 0.9$, N= 13, RH range 76-85 % at 24.5m and for RH ground (0m) $r^2 = 0.94$, N=13, RH range 88-93 %). We do not want to imply that RH does not play a role in HONO formation/deposition and release, but want to state that this possible mechanism is too complex to extract it from both time series.

10. In Figure 7, a sudden increase in HONO concentration measured above canopy around 21:00 needs more explanation. The authors state: "This event is considered to be dominated by an air mass change and not by local HONO production or release". Any evidence from wind direction switch and/or wind speed change?

10.) There are no clear signals in wind speed and direction regarding the event at 21:00. Wind speed is almost continuously increasing from 19:00 (1 m s⁻¹) to 23:00 (3 m s⁻¹). At 21:00 wind direction only changes by 15°. In contrast, almost all quantities measured (except NO) change tremendously. NO₂ increases by 200 % (1.5 - 4.5 ppb) whereas ozone drops by 30 % (20 ppb as described in the paper). As can be seen in Fig. 7, RH and HONO also sharply increase. Also, water vapour mixing ratios (not

shown) increase sharply. All these changes cannot be explained by local chemistry alone. We have clarified our statement in the manuscript.

11. In Reference, Sander, 1999 is missing.

11.) We included Sander (1999) in the manuscript.

References:

Serafimovich, A., Siebicke, L., Staudt, K., Lüers, J., Biermann, T., Schier, S., Mayer, J.-C., Foken, T.
ExchanGE processes in mountainous Regions (EGER) Documentation of the Intensive Observation Period
(IOP1) September, 6th to October, 7th 2007: Arbeitsergebnisse Nr. 36; Bayreuth, Germany, 2008; Print ISSN
1614-8916; Internet ISSN 1614-8924