Reply to Referee 1:

We would like to thank anonymous referee 1 for his/her detailed and helpful comments, helping us to improve the manuscript.

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

> *By "zero OH cycle" we meant a scheme of chemical reactions, which in equilibrium consume as much OH as they produce. We changed the phrase to: “no net OH formation”.*

P5, L16: I know of two other studies dealing with HNO3 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.

> *We clarified the passage about nitrate/HNO_3 photolysis, as to our opinion it does not differ from the suggestions made by the referee (see original manuscript). We have already discussed that organic photosensitizer may enhance nitrate/HNO3 photolysis (as speculated by Kleffman, 2007 and Finlayson-Pitts, 2009), and have also cited very recent papers by Zhu et al. (2008 and 2010) about enhanced absorption cross sections of HNO_3 with respect to gas phase HNO_3. The study of Zhou et al. 2011 provides new interesting data and has been included in the discussion. We also cite the study of Raivonen et al., (2006) as indirect evidence for HNO_3 photolysis as a HONO source.*
>
> *The current study was focused on the HONO sources which could be directly calculated from the available data. Therefore we avoided to speculate about other sources for which we lack important information for their quantification. As both referees claimed that these sources should be considered, we included rough estimates of these sources based on the numbers given in the respective publications (see below comment).*

P5, L22: This sentence is somewhat out of place relative to the rest of the discussion, as the remainder of this paragraph deals with NO2*. I suggest either moving or deleting it.

> *To clarify this section, the mentioned sentence itself was made a new paragraph as it describes a completely different source of HONO. Additionally, the equation (R8) was moved into the paragraph discussing this reaction instead of being placed between the different paragraphs.*

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

> *The requested information has been added to the manuscript.*

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.

> *The uncertainty is 12 %. This value was given in the results section, but according to several comments of both referees we moved all information about the instrumental uncertainties to the experimental part (Section 2).*

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

> *The inlets were co-located. The paragraphs have been combined.*

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

> *We changed this sentence to:" We derived a factor for scaling modeled j(NO_2) to measured j(NO_2). This factor was then applied for scaling modeled j(O^1D)."*

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?

> *It is a good suggestion to move the sentence in order to clarify this paragraph. Then it might become clearer that the rate constants for k_7 from JPL and IUPAC where calculated for atmospheric pressure from the high and the low-pressure limit rate constants according to the formulas and values given in the cited literature. The value of Bohn and Zetzsch was measured directly at atmospheric pressure and has been overlooked in the evaluations.*

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.

> *The measured OH values are an upper limit. Interferences probably reach a factor of 2 under certain conditions (Harder, personal communication, 2011). The discussion has been moved to section 2.*

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

> *Yes, the values were increased by 5 %.*

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

> *As mentioned above, all uncertainties of the instruments are now available 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?

> *Since no data from the 10 m instrument was available due to instrument failure on December 2nd, data was taken from the 1 m instrument for that day. This is now clarified in the revised manuscript.*

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?

> *To our knowledge up to know no such measurements (for daytime) are available. Sörgel et al. (2011) do not exclude a ground source. The study just showed that in periods with extensive vertical mixing gradients are too small to be resolved by LOPAP instruments. This is supported by the study of Zhang et al. (2009) who found hardly any gradient throughout the boundary layer for well mixed conditions.*

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."

> *We clarified the sentence. As the values are not normally (Gaussian) distributed we preferred to give the median and the 25th and 75th percentiles.*

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(NO2) and NO2 concentrations.

> *This sentence was misleading as the comparison with OH was missing. The dependency was meant in a way, that most of the variation in $[HONO]_{PSS}$ was due to NO ([NO] r^2 =0.78, [OH] r^2= 0.006 and j(HONO) r^2 = 0.01). The statement has been clarified accordingly. For the measured HONO mixing ratios, coefficients of determination with NO and NO_2 were just mentioned without inferring dependencies. The coefficient of determination for HONO and NO_2 is higher than that of HONO and NO (see original manuscript) which is in line with the referee's statement about an indirect correlation depending on NO_2 and j(NO_2).*

P11, L6: Higher HONO/NOx 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 NO2" 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)

> *The referee is right. The light induced NO_2 conversion is not the only possible explanation and thus our statement was misleading. It should rather be stated that the observed behavior would be explainable by light induced conversion but that other sources cannot be excluded.*
>
> *The paragraph has been moved to section 3.3 as the main discussion of direct emissions is located there.*

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

> *Section 3.2 has been restructured into 3.2.1 "Calculating the photo stationary state/ gas phase" and 3.2.2 "Including "known" heterogeneous formation into PSS calculations". This should provide more clarity to the reader.*

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

> *In agreement with the above comment we moved all calculations and parameterizations of the "dark heterogeneous" source to the new section 3.2.2.*

P13, L24: Presumably, Tv 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 Ldep. Alternatively, you could estimate this via a parameterization such as that suggested by (Dillon et al., 2002):

Tv = -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.

> *Thank you for providing this useful hint. We included the provided parameterization into the manuscript.*

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?

> *Yes, but as stated in the manuscript, only for well mixed conditions (see also above comment). As already discussed in the original manuscript the relative contribution of deposition might be higher as S/V (scaling height!) decreases. The discussion has been clarified accordingly.*

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

> *We followed the referee's suggestion and combined both paragraphs and moved the discussion of HONO/NO_x from Section 3.2 to here. Although highest HONO values were indeed observed in the urban/industrial sector (Huelva), HONO/NOx values show no obvious difference for all continental sectors. Thus we find no clear indication for the contribution of direct emissions.*

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

> *This is right. As Punkown is calculated as the residual of the HONO budget it was intended to say that we cannot quantify the effect of neglecting direct emissions in the budget on Punknown. We can only assume that around noon they are of minor importance (see original manuscript).The sentence has been clarified accordingly.*

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 Phet low.

> *Regarding point 1): Due to the focus on daytime chemistry we intended to provide the most detailed view of the data on daytime. According to a comment of referee 2 we plotted HONO in Fig. 1 on a log scale.*
>
> *Regarding point 2): Currently there is no doubt about the heterogeneous formation being the dominant nighttime formation term. The referee is right that as Phet is rather a pseudo steady state of heterogeneous formation and deposition (as discussed in section 3.2 of the original manuscript) the "real" Phet is biased low. This adds to the discussion in section 3.2 (original manuscript) about the uncertainties applying Phet to daytime conditions. The paragraph has therefore been moved to this section in accordance with the referees' suggestion.*

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

> *This is right. As a consequence more points will be rejected. See discussion below.*

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.

> *Although changes in mixing ratios are small, the relative contribution of dHONO/dt to the budget calculations is substantial (see Fig. 3 original manuscript) even for the rejected points. This might bias (the mean contribution of) this term high. On the other hand, it is hard to justify adding or subtracting a substantial contribution to the budget calculations which might simply be caused by the instrument.*

P16, L5: What is meant by "correlation scheme"? Do you mean that more of the data falls onto the trend line with j(NO2)? If so, the fact that the correlation improves here does not necessarily imply that the missing source is driven by NO2. Here is an alternative (though long) explanation: 1) the points with high dC/dt are those most affected when normalizing by NO2; 2) dC/dt is most variable during times of rapid change in concentrations (e.g. advection events); 3) HONO and NO2 tend to co-vary; 4) Lphoto, which depends on HONO, is generally the largest term balancing Punknown, and Phet, which depends on NO2, is the largest source term. Thus, normalizing by NO2 could also be thought of as "normalizing out" the effects of advection on HONO budget terms.

It was meant that all data points lie on or below an upper limit which is increasing linearly with j(NO_2). We are aware that a correlation (or improved correlation) alone is not a proof. Therefore we consider the referees´ arguments and included a case study in this section which illustrates the effect of this normalization applying different scenarios (e.g. local formation, advection, etc.).

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

The statement was changed to: "contribution to the HONO budget" instead of "contribution to Punknown".

P17, L20 – 22: Why not just scale the photon flux with j(NO2), as was done for j(HONO)?

The relation of j(NO_2) and j(HONO) has been intensively studied (see cited literature) whereas photon flux and j(NO_2) may behave differently. With the given upper limit photon flux this source normally contributed less than 1 % of the unknown HONO source. As this contribution is already low a better parameterization makes it just lower.

P18, L10: What is the value for kair?

We took a value of $3 \cdot 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. The value (and citations) has been added to the manuscript.

P18, L18: The use of so many percentages makes this sentence quite confusing. If the point is to show that NO2* is small, just give a mean value or percentage for comparison with Punknown.

We clarified the sentence. As the values are not normally (Gaussian) distributed we preferred to give the median and the 25th and 75th percentiles.

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 NO2 reactions?

The calculation of the source strength of the surface sources is very complex and requires more information about turbulent transport. Also, important input parameters (amount of organic sensitizers or of HNO_3 at the surface) are not available. Thus, a real calculation is out of the scope of this study. As both referees claimed that these sources should be considered, we included rough estimates of these sources based on the numbers given in the respective publications (Stemmler et al., 2006 and Zhou et al, 2011).

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

HCHO photolysis is an indirect source of OH (via HO_2). Its contribution to OH was about half that of $O(^1D)$ during the DOMINO campaign (Regelin, personal communication, 2011).Thus the answer is: less than half the contribution of 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 NO2. You could instead say that the data is consistent with light-dependent heterogeneous chemistry (possibly involving NO2 as suggested by lab experiments).

> *The correlation in Fig. 4 is really weak, but we included a linear fit to the data (only clear days) of Fig. 5 (see reply to referee 2) which shows a better correlation. Nevertheless we changed the statement according the referees suggestion.*

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.

> *In accordance with the comment of referee 2 we changed Figure 3 and added colors. We also alternated light and dark shades.*

Technical Comments:

P6, L5: unfocused
P7, L7: change “has been” to “is”
P12, L26: where
P14, L8: were
P17, L17: unknown

> *The changes have been applied to the manuscript.*

Cited Literature

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