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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Quantification of the unknown HONO daytime source and its relation to NO_2" *by* M. Sörgel et al.

Anonymous Referee #2

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The manuscript by Sörgel et al. describes measurements of HONO, NO_X, OH, J(NO_2), and other parameters made in southwestern Spain in Fall 2008. The observations are interpreted to study the daytime chemistry of HONO, and to quantify the unattributed source strength of HONO. Two proposed daytime HONO formation mechanisms are also investigated quantitatively. The main result of the manuscript is that two of the proposed sources of daytime HONO, conversion of NO_2 on soot and the photoexitation of NO_2 followed by the reaction of NO_2^* with water, do not seem to play a major role for the daytime HONO budget. By considering various chemical processes, as well as deposition and non-photolytic heterogeneous conversion, the study quantifies the unknown daytime HONO source to -700-1800 ppt/h during the entire experiment, and 105 +/- 39 ppt/h around noon on sunny days. Assuming that the conversion of NO_2 is the most likely process to explain daytime HONO the authors

also derive a conversion rate of $\sim$14%/h around noontime. The OH formation through HONO photolysis is also discussed.

This manuscript presents an interesting dataset and provides a well thought through quantification of the daytime HONO source. Two of the proposed sources of daytime HONO are applied to the dataset in detail, but a number of other proposed sources, such as the photo-enhanced conversion of NO_2 on the ground and the canopy, are not discussed extensively. It would help the manuscript if the possible impact of other proposed daytime HONO sources would be included.

The manuscript discusses the contribution of HONO photolysis to OH levels, but the discussion is too incomplete to be compelling. For example, the contribution of aldehyde photolysis and O_3 + alkene reactions to HOx formation is missing. The contribution of NO + HO_2 (which was probably measured by the HO_x instrument) could be included in the discussion as well. Without a better discussion of the OH budget I would propose to considerably shorten this part of the manuscript and to remove Table 1.

In summary, this manuscript is potentially very interesting and could provide new and interesting insights in daytime HONO chemistry. I support its publication in ACP, but only after some major revisions. The following lists my specific comments:

Page 15124 / Section 2: While I can understand not wanting to repeat the details of each instrument in this manuscript, it would very helpful for the reader to get a better idea of the possible systematic and random uncertainties of the instruments and the data that went into the interpretation in Section 3. If the authors do not want to write much text, a table with this information could be added.

Page 15125, lines 8-14: What was the residence time in the tubing? Would the

O_3 + NO reaction in the tube shift the NO/NO_2 pseudo steady state?

Page 15128, line 26: As NO enters the calculation of $[HONO]_{PSS}$, isn't it obvious that $[HONO]_{PSS}$ shows a correlation with NO? I am not sure that I follow the author's argument here. I am also unclear what the significance of a correlation of HONO with NO and NO_2 is. Shouldn't the HONO formation rate be correlated with NO_2, rather than HONO itself? Please clarify this section.

Page 15129, lines 18 – 21: This statement is only correct if NO_X is predominantly in the form of NO_2 (as it seems to be the case in most of the nights here). In the absence of ozone, for example, addition of NO_X in the form of NO at night could, according to our current understanding, decrease the $HONO/NO_X$ ratio without any actual impact on HONO chemistry. Why not use $HONO/NO_2$ in this discussion to avoid misunderstandings. Adding $HONO/NO_2$ in Figure 1 and 2 may also be helpful in understanding the NO_2 to HONO conversion.

Page 15130, line 25 ff: A recent ACP paper by Wong et al., 2011, provides a detailed description on the impact of nocturnal vertical mixing on HONO, as well as new data on the nocturnal NO_2 to HONO conversion.

Page 15132: The discussion of advection and HONO from industrial sources should be expanded. The authors state that a large industrial area was located 15km upwind from the site. While the time from this source to the site of $<$2hours is too long to play a role during the day, it may have impacted nocturnal and morning HONO. How well is the $HONO/NO_X$ emission ratio of this source known?

Page 15134, lines 7-14 and Figure 4: Please provide a more detailed statistical analysis of these correlation plots. Add a linear fit line to Figures 4a,b, as it is very difficult to see if there is indeed a correlation between HONO production and $J(NO_2)$.

Page 15134, line 24: Please clarify what a "correlation scheme" is.

Page 15135 / Section 3.4: As already discussed above, this section should be expanded to consider other possible daytime sources. For example, a recent manuscript by Zhou et al, 2011, proposed the photolysis of HNO_3 on the canopy as a source of daytime HONO. Other publications, have proposed the photo-enhanced conversion on humic acid like substances on the surface and the aerosol. Some of these mechanisms are discussed in the introduction but are not considered sufficiently in the data interpretation.

Page 15135, lines 4 – 21: This text seems out of place here and should be moved to section 3.5, or removed completely if a better OH budget calculation cannot be presented.

Page 15137/ Section 3.5: As mentioned above, this section together with Table 1 is a half-hearted attempt to provide an OH budget calculation. The authors should decide whether they want to extend this discussion to consider other OH sources, such as aldehyde photolysis, O_3 + VOC, and HO_2 +NO, or shorten this section and remove Table 1 to solely show the comparison of OH formation from ozone and HONO photolysis.

Figure 1: It is basically impossible to see daytime HONO in this figure. Please plot HONO and $[HONO]_{PSS}$ on a log scale to show both nighttime and daytime periods with sufficient resolution.

Figure 2: Please use colors in this figure. The gray scales are very difficult to distinguish.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 15119, 2011.