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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A comparison of measured HONO uptake and release with calculated source strengths in a heterogeneous forest environment" *by* M. Sörgel et. al.

Anonymous Referee #1

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General Comments. The discussion article by Sörgel et al. presents data from a study of HONO fluxes at two different rural field sites. At each site, meteorological and actinic radiation data were used in conjunction with HONO measurements that were made at two different heights above ground level. The data as a whole was used to infer information about net HONO deposition and emission rates to and from ground surfaces, respectively. The study is well thought out and executed and the data analysis is thorough and informative. A particular strength of the paper lies in the authors' attempts to reconcile observed HONO fluxes with proposed daytime sources (e.g., reaction of NO2 by photochemically excited humic acid, nitric acid photolysis,

soil emissions) and sinks (e.g., gas phase photolysis and dry deposition). The only weakness in the composition was that it lacked a section in the introduction or abstract that convinced the readership of why this study was novel and significant. This point is clear to me, but it needs to be made also to the reader who is not as familiar with this area of research. As it is written, the new aspects of the work are buried throughout the text and only pointed out in passing. In addition, some points are raised below that I hope will improve the clarity of the manuscript.

Specific Comments (page #, line #):

2121, 21: It is sufficient to just write NO2 dimer, or N2O4 instead of including both.

2127, 11-21: The authors refer to NOx measurements at different heights above ground, listing average mixing ratios for the campaign period, but only show the actual data at 1.6 m (Figures 2 and 3). For completeness, it would useful to include the data at the other measurement heights in the supplement.

2131, 15: I recommend the following addition to the text: ". . .sources and sinks coexist over small spatial scales,. . ."

2131, 18-20: The authors state, "The prevailing HONO deposition at the forest floor might also explain the poor correlations of HONO and NO2 found during the EGER IOP-1 campaign at the same site. . ." Some readers may not be familiar with EGER IOP-1. In addition, I felt that this last sentence of section 3.3.1. required more elaboration. Are the authors saying that because the net transport of HONO is dominated by deposition, this has the effect of masking the variables that would provide clues as to which HONO sources are important? Or are they trying to make a different point about the EGER IOP-1 campaign?

2132, 20: The authors mention that the contribution of the ground source to total HONO production rate was 80% in the Wong et al. (2013) study, which is much higher than the few % observed in the current study. However, the Wong et al. study was con-

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ducted in a polluted urban area (Houston), so HONO emissions could be impacted by numerous other factors, while the present study was conducted in a rural setting. I feel the authors should discuss this very important difference and speculate on additional location-specific considerations.

2132, 24: The authors end the paragraph with: "this issue remains unclear." Please clarify what the "issue" is with a more specific statement, or frame the issue more clearly earlier in the paragraph.

2133, 15: The soil pH values for the sampling sites are listed in the supplement, but it would help if the average soil pH or range of soil pH values are included in the text here.

2135, 8: The authors might want to specify a "flat" smooth surface here.

2135, 10: Again, NO2 mixing ratios at 10 cm above the ground are mentioned, but they are not provided anywhere in the document. I only see the NO2 mixing ratios at 1.6 m presented in the figures. Since these data are used, I would include them somewhere in the manuscript. Either in the supplement or as another figure.

2135, 10-25: The authors use the parameterization outlined by Stemmler et al. 2007 to calculate the HONO flux expected from the reaction of NO2 with photo-excited humic acid surfaces. They do this for their measured NO2 concentrations at the clearing on a day where presumably NO2 levels were below 2 pbb. Due to the mathematical relationship between rate of formation and spectra irradiance in the parameterization, one would expect that the HONO flux rapidly reaches a maximum and remains independent of light intensity in the lower NO2 concentration range. The calculations in Figure 4 are useful and the comparison in Figure 6 suggests that the diurnal dependence of HONO flux may only be due in part to the NO2+humic acid mechanism.

However, I do not understand the statement, "If this saturation behavior prevails on natural surfaces, the unknown HONO source should be well-correlated with NO2 only

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at mixing ratios below 1 ppb." From the modeled results in Figure 4 and the parameterization equations used, it seems to me that for a given light intensity there is a strong dependence on NO2 at all NO2 mixing ratios, not just those below 1 ppb.

As described on p. 2128, the authors calculated net HONO fluxes from selected parts of their campaign. I am not sure if there is enough data to do such a comparison, but have the authors derived any correlations between those HONO fluxes and light intensity or NO2 levels? Is there a dependence of the HONO source on J(NO2), irradiance, or NO2 levels that could help them decide whether the NO2-humic acid model fits the observed diurnal profile?

2136, 14-15: the multiplication signs for the numbers (in scientific notation) did not come out in my copy of the manuscript. Please check.

2137: what happens when one does not assume any enhancement in the absorption cross section or quantum yields for nitric acid?

2138, 8-9: I do not understand why HONO formation via the NO2+[humic acid*] reaction would be slow if there was rapid formation of NO2 from nitric acid photolysis. Can the authors clarify?

2138, 13: See Scharko et al. 2014 (doi: 10.1021/es503088x), which presents a discussion of how NO2 hydrolysis could be potentially significant if NO2 is formed photochemically in aqueous solutions, as opposed to if NO2 reacts heterogeneously. In addition, this article points out that non-chromophoric organic matter may act to enhanced HONO yields due to OH radical scavenging ability.

Figure 2: Consider using a different color for the wind speed label, u*. It does not stand out against the grey background.

Figure 6. I note that the fluxes derived by the aerodynamic gradient method all occur between 11:30-15:00. Are these the only flux values for that particular day that were positive (i.e., represent a net emission of HONO from ground)? Also, the timing is

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interesting, as this is the time of day when VandenBoer et al. Nature Geosci. 2015 suggest that the acid displacement mechanism would be most important Perhaps this should be addressed somewhere in the text?

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 2119, 2015.