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Comment

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.

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REF: 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 pho-

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tochemically 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.

A: We thank reviewer 1 for his valuable comments helping to improve the manuscript. We rephrased some parts in the abstract and within the main text to state clearer the novelty and significance of main parts of the work.

REF: Specific Comments (page #, line #):

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

A: We changed the text accordingly.

REF: 2127, 11-21: The authors refer to NO_x 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.

A: We agree with the referees' suggestion. We included the respective graph to the supplement. See also below comment.

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

A: We changed the sentence accordingly.

REF: 2131, 18-20: The authors state, “The prevailing HONO deposition at the for-

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est floor might also explain the poor correlations of HONO and NO₂ found during the EGERIOP-1 campaign at the same site. . .” Some readers may not be familiar with EGERIOP-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?

A: The referee is right that the reader might not be able to understand what the point here is. We wanted to point out that in this previous campaign in 2007 the obtained results were already pointing to a dominating role of nighttime deposition, which with the existing measurements could not be proved. “The weak correlation of HONO to NO_x does not necessarily mean that NO₂ is not a precursor for HONO. We simply do not see a correlation, which is similar to results from another rural forest site (Zhou et al., 2002). This indicates that other processes like deposition or re-emission are also important“(Sörgel et al., 2011). As a consequence the new measurements prove that the prior interpretation was right and that the dominating role of nighttime deposition is a common feature at that site. Nevertheless, to avoid confusion and not to distract the reader we discard this point from the manuscript.

REF: 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 conducted 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.

A: As none of the other studies used a chemistry-transport model to infer the ground contribution we did not discuss the differences in detail. Nevertheless, the referee is right that site specific differences should be discussed as well and are a potential

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reason for the observed differences. We included the requested information. First of all we have to apologize for providing a wrong number here. Actually it was meant to write over 60 % as Czader et al. (2012) calculated up to 65 % contribution (this study was conducted in Houston as well). The study of Wong et al. (2013) reports somewhat lower values of about 50 %. We corrected the information. Nevertheless, both numbers are considerable larger (at least a factor of 2) than the roughly 25 % calculated by Zhang et al. (2009) and Li et al. (2014), based on measured profiles throughout the boundary layer.

REF: 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.

A: The “issue” meant the discussion of ground surface source versus volume source. We clarified this point and provided more information about the different approaches (see also above comment). As each of the approaches has shortcomings we don't think that there is already a clear picture.

REF: 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.

A: We included the respective pH-values.

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

A: Although, there is a slope of about 3° in south west direction, in the direction of the main wind (west) the slope is less pronounced ($\sim 1^\circ$) (Siebicke, 2010). In the vicinity of the measurement ($\sim 3\text{--}4$ m) the surface had no bigger irregularities (differences in elevation < 10 cm) and was covered by moss which smoothed the surface. This type of ground surface was extended in the main wind direction and just occasionally there were holes (~ 20 cm) and dead wood (5–30 cm) within the fetch but at distances > 5

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m. We included the information in the manuscript.

REF: 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.

A: We agree with the referees' suggestion. We included the respective graph in the supplement (see above comment).

REF: 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 ppb. 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 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.

A: A misunderstanding occurred within this sentence. It was meant that in this case (NO₂ below 1 ppb) HONO is only correlated to NO₂ and not to both NO₂ and light intensity. We changed the sentence accordingly.

REF: 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

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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?

A: Unfortunately there is not enough data for such kind of correlation study. Furthermore, regarding the fluxes it was only possible to calculate them for rather stationary HONO levels (see section 3.2 of the manuscript) that mostly occurred in the afternoon (see below comment).

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

A: We will check the appearance in the final copy.

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

A: The reaction won't be a significant contribution to the HONO budget.

REF: 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?

A: The interesting point here is, if HONO is produced via NO₂ reactions or directly from HNO₃ photolysis. If NO₂ is the precursor, even the enhanced (~ factor 2000 with respect to gas phase) HNO₃ photolysis fails to compete with ambient NO₂ values. The number of NO₂ molecules formed at the surface through HNO₃ photolysis (~ 2000 absorption crosssection and quantum yield 1) is equal to the number of molecules hitting the surface by gas kinetic collisions at just a few ppt of ambient NO₂.

REF: 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

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enhanced HONO yields due to OH radical scavenging ability.

A: We included the suggested reference in the discussion.

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

A: We used black for the labeling to increase the contrast.

REF: 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 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?

A: As can be seen in Fig. 2, except for a rainy day, mixing ratio differences are all negative throughout the day on the clearing. This indicates that emissions are occurring throughout the day. Due to the limitations of the method we could only calculate 17 flux values for 3 days. Six of them are presented in fig.6 for the 12th of June. Almost all calculated daytime flux values are between 11:00 and 15:00. The reason is that with our method, that measures each height of the profile consecutively, we need rather stationary HONO concentrations which only occur during that time of the day. In the early morning HONO values are declining fast and in the late afternoon they begin to rise again. Therefore, it is rather a method bias than a result of fluxes driven by the acid displacement. Besides the low number of flux values the bias towards midday is one of the reasons we did no correlation analysis (see above comment). Instead we decided to compare the source strengths directly as we can compare them point by point. Therefore, we did not discuss this relation between flux appearance and potentially stronger acid displacement. Additionally, we discussed (section 3.3.1) the acid displacement for the forest floor data as we have at least one week of continuous measurements (showing no emissions) available.

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References:

Czader, B. H., Rappenglück, B., Percell, P., Byun, D. W., Ngan, F., and Kim, S.: Modeling nitrous acid and its impact on ozone and hydroxyl radical during the Texas Air Quality Study 2006, *Atmos. Chem. Phys.*, 12, 6939–6951, doi:10.5194/acp-12-6939-2012, 2012.

Li, X., Rohrer, F., Hofzumahaus, H., Brauers, T., Häseler, R., Bohn, B., Broch, S., Fuchs, H., Gomm, S., Holland, F., Jäger, J., Kaiser, J., Keutsch, F. N., Lohse, I., Lu, K., Tillmann, R., Wegener, R., Wolfe, G. M., F. Mentel, T. F., Kiendler-Scharr, A., and Wahner, A.: Missing gasphase source of HONO inferred from zeppelin measurements in the troposphere, *Science*, 344, 292–296, doi:10.1126/science.1248999, 2014.

Siebicke, L.: Advection at a forest site an updated approach, Ph.D. thesis, University Bayreuth, Germany, 113 pp., 2010.

Sörgel, M., Trebs, I., Serafimovich, A., Moravek, A., Held, A., and Zetzsch, C.: Simultaneous HONO measurements in and above a forest canopy: influence of turbulent exchange on mixing ratio differences, *Atmos. Chem. Phys.*, 11, 841–855, doi:10.5194/acp-11-841-2011, 2011.

Wong, K. W., Tsai, C., Lefer, B., Grossberg, N., and Stutz, J.: Modeling of daytime HONO vertical gradients during SHARP 2009, *Atmos. Chem. Phys.*, 13, 3587–3601, doi:10.5194/acp-13-3587-2013, 2013.

Zhang, N., Zhou, X., Shepson, P. B., Gao, H., Alaghmand, M., and Stirm, B.: Aircraft measurement of HONO vertical profiles over a forested region, *Geophys. Res. Lett.*, 36, L15820, doi:10.1029/2009GL038999, 2009.

Zhou, X., Civerolo, K., Dai, H., Huang, G., Schwab, J., and Demerjian, K.: Summertime nitrous acid chemistry in the atmospheric boundary layer at a rural site in New York State, *J. Geophys. Res.*, 107(D21), 4590, doi:10.1029/2001JD001539, 2002.

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