

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.

M. Sörgel et. al.

m.soergel@mpic.de

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REF: This study reports vertical mixing ratio profiles of nitrous acid (HONO) measured over a forest floor and a nearby clearing. In the forest, deposition dominated the net flux day and night, while in the clearing, deposition occurred during the night and emission during the day. The measured fluxes were compared to available information about potential HONO sources. Biogenic emissions seem not to be sufficient at this site. The light induced conversion of nitrogen dioxide to HONO turned out to explain only a smaller fraction of the observed daytime emission flux, due to significant light intensity saturation reported. Photolysis of adsorbed nitrate or nitric acid would either

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underestimate or overestimate measured fluxes, depending on the mechanism and parameterization used. The budget of HONO continues to be a debated topic in atmospheric chemistry due to its role as a photolytic OH source. Its sources and sinks are not sufficiently understood, and the present study is a valuable contribution to this topic. The measurements seem to be performed carefully, the analysis appears sound, and the discussion is thoughtful and detailed. The manuscript is well structured and quite well written. I recommend publication after addressing a few minor comments.

A: We thank M. Ammann for his valuable comments helping to improve the manuscript.

REF: Page 2122, line 5: reference to Gutzwiller et al., the quoted study is about diesel exhaust emissions; may be the authors rather wanted to cite Gutzwiller, L., George, C., Rössler, E., and Ammann, M.: Reaction kinetics of NO₂ with resorcinol and 2,7-naphthalenediol in the aqueous phase at different pH, Journal Of Physical Chemistry A, 106, 12045-12050, 2002. This study directly reported reduction of NO₂ by organics.

A: The referee is right that the mentioned reference is better suited. The reference has been changed accordingly.

REF: Page 2123, line 24ff: Discussion of mechanisms involving NO₂^{*}: Better explain what the limitation is: production rate of NO₂^{*} or the reaction rate of NO₂^{*} + H₂O. This is important, since for the HNO₃ photolysis pathway NO₂^{*} production rates maybe higher than those from excitation of NO₂ in the gas phase. This issue is coming back in the discussion of the HNO₃ photolysis pathway at the end of section 3.4.3

A: Actually, the rate limiting step is the relatively slow rate of reaction of NO₂^{*} + H₂O=> HONO and OH. The formation of NO₂^{*} should not be limiting as j values for excitation are about a factor of 5 higher than for photo dissociation (Crowley and Carl 1996). The majority of NO₂^{*} molecules is deactivated by collision with N₂, O₂ and H₂O. Therefore, as discussed in the manuscript, the formation of HONO and OH by this reaction critically depends on the relative rate of deactivation and reactive quenching which might be different for a surface reaction. We updated the discussion in the manuscript

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accordingly.

REF: Page 2123: Some new studies related to the exchange of HONO with ground surfaces and their components by Van den Boer et al. (2014) and Donaldson et al. (2014) may be included in this part of the introduction.

A: Both studies were discussed elsewhere in the manuscript. The referee is right that they should be included already in the introduction where the surface exchange of HONO is described.

REF: Page 2126, line 22: . . . if water is condensing (rather than 'humidity')

A: We changed the sentence accordingly.

REF: Page 2129: maybe the Su et al. (2011) should also be discussed in this context, since it did not make a proof about the origin of nitrite, biogenic or through NO₂ deposition. In addition, the soil pH of the present site should be mentioned and discussed already here.

A: The referee makes an important point here. The partitioning described by Su et al. (2011) is a reversible process and Ren et al. (2011) already argued that the high soil pH at the Blodgett Forest site was one of the reasons for the very low observed HONO fluxes. Contrary, our site has a very low pH (~3), but low HONO emissions (or better dominating deposition) as well. Recently, Donaldson et al. (2014) argued that surface pH of the soil minerals is a better measure for HONO uptake and release than bulk pH. Their study was motivated by the discrepancy between the expected pH dependency of HONO release (Su et al., 2011) and the observed maximum of HONO emissions for neutral to alkaline (bulk) pH soils (Oswald et al., 2013). Donaldson et al. (2014) showed that acidity of soil minerals can be indeed higher than suggested by the bulk pH but the driving force behind emissions in the study of Oswald et al. (2013) was microbial activity that is hindered at low pH. Instead of including this discussion here, we would prefer extending the discussion of these contrasting views of physicochemical

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and biological factors in section 3.4.1 (see also comment below). So far all these studies refer to bare soil which in our case is not representative. Therefore, we believe plant stomatal uptake (Schimang et al., 2006), that potentially is non reversible, or uptake to leave cuticula and dead wood to be more important at our site, as discussed in section 3.3.1 and elsewhere in the text.

REF: Section 3.4.1: what would be the contribution of NO₂ deposition to nitrite, if one would assume a reasonable uptake coefficient on the ground surface for this process?

A: We have no direct measure of the nitrite pool derived by various sources, e.g. the microbiological. We can provide a rough estimate* for the pools caused by HONO deposition by using the average integrated nighttime net-deposition and for that resulting from NO₂ reacting to HONO with a typical uptake coefficient and compare that to measured nitrite in the soil. Nevertheless, we assume uptake to plant surfaces and stomata to be more important but this cannot be satisfactorily quantified with the current measurements and parameterizations. *back of the envelope calculations: Deposition fluxes of HONO were observed between 22:00 and 6:00 CET (28800 seconds). The average net deposition flux was 0.006 nmol m⁻² s⁻¹. Therefore, the integrated flux is about 173 nmol m⁻². Average NO₂ mixing ratios are around 2 ppb. Assuming a reasonable reactive uptake coefficient for the NO₂ to HONO (NO₂-) conversion of 10⁻⁶, that all formed HONO stays as nitrite at the soil surface and the same 8 hours of duration for forming the reservoir yields 202 nmol m⁻². This is about the same magnitude as direct HONO deposition. Measured nitrite in the soil was 0.8 mg Kg⁻¹ N. Therefore, assuming the uppermost 2 cm take part in the exchange the total reservoir is 1.2 x 10⁵ nmol m⁻². Therefore, the contributions of both HONO deposition and NO₂ reaction do not substantially (< 1 %) contribute to the nitrite reservoir. As discussed microbial activity was low due to low pH but we assume that biological formation is still the largest fraction of the nitrite reservoir.

REF: Last paragraph of section 3.4.2: discussion of actinic flux saturation. Would the NO₂ to HONO conversion be substantially higher during the day if the low irradiance

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linear behavior would be extrapolated linearly? As Bartels-Rausch et al. (2010) point out, the origin of the saturating behavior could also result from adsorption limitation of the adsorbed NO₂ precursor. Since NO₂ concentrations are low, adsorption saturation would not be a limitation in the present case.

A: Assuming a linear increase of the HONO flux with irradiance would result in roughly a factor of nine higher HONO flux at maximum irradiance for a given NO₂ concentration. Furthermore, if NO₂ is not limiting one could extrapolate the linear increase in the morning in Fig. 4 b to maximum values of irradiance (that correspond to max. values in $j(\text{NO}_2)$). The referee is right that the adsorption limitation is not an issue here as it only becomes obvious at comparably high (> 50 ppb) levels of NO₂ (Stemmler et al., 2006; Stemmler et al., 2007). In both studies Stemmler and coworkers argue that the saturation behavior regarding the actinic flux might be explained by the formation of photo oxidants that limit the lifetime of the “photo-produced reductive species (Ared)”. This Ared is the intermediate formed by irradiating the humic acid that subsequently reacts with NO₂ to yield HONO. Therefore, deactivation of Ared competes with the reaction of NO₂ at higher light intensities. This also explains why the saturation behavior is less obvious at high NO₂ levels. We included this discussion in the manuscript.

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