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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurements of ambient HONO concentrations and vertical HONO flux above a northern Michigan forest canopy" *by* N. Zhang et al.

Anonymous Referee #1

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This paper by Zhang et al. provides a more complete discussion of relaxed eddy accumulation measurements of HONO fluxes at the PROPHET site in Michagan, which were presented elsewhere previously. The apparent upward HONO fluxes are an intriguing result. However, the excessive use of speculation about mechanisms and processes rather than quantitative reasoning detracts from the overall impact of the paper.

Pg 7277, line 6 What is evidence of HONO being quantitatively removed by the denuder? EPA 1999 is cited for this, but was denuder performance verified by challenges in the field? Some potential tests would be supplying varying levels of HONO to the

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scrubber and confirming no change in signal, putting two scrubbers in series to see if there is a difference. Is PAN really passed through the scrubber?

7280 line 11, for the Temperature, dew point, precipitation, relative humidity and weather conditions, please specify the location where measurements were made

7284 line 17 The evidence supporting a supposed difference in canopy and soil pH as a rationale for differences in HONO emission is inadequate. Soil pH is dependent on parent material geology and soil development processes. The surface in actual contact with air is likely litter and organic material rather than parent soil. Precipitation chemistry is unlikely to be a useful indicator for the pH relevant to HONO partitioning on the surface. The effective canopy pH would be controlled in part by the chemical composition of aqueous films within the stomatal openings of the vegetation and accumulated dust and aerosol on the foliar surfaces. It would be helpful to present this section more quantitatively. At the pKa HONO and NO2- are equal. You can compute the pH where either HONO or NO2- will dominate. Compare this to actual estimates of surface pH. pH increases above the pH where most of HONO is already dissociated won't change the partitioning further.

7286 line3, What is the basis for the estimate of a 350 ppt/hr HONO source to support 70 ppt concentration level? Is this just the required production to balance photolysis and other reaction losses? Line 10, Are there data for OH and NO to constrain the estimate that 43% was from volume HONO production mechanisms, such as gaseous NO-OH reactions, or heterogeneous reaction. Statements like this need to quantitatively backed up not simply speculation

Page 7287, 1. It is an interesting finding that apparent HONO flux is not dependent on NOx level. For making statements about homogeneous HONO sources, please support the statement that they are important by computing a rate based on OH and HONO (observations or typical values). It would be preferable to consider a slope and its standard error instead of an r2 value. 0.1 is hardly meaningful. Is the slope

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significantly different from 0 and positive?. Especially for the relationship in Figure 7, compute the slope and its standard error, Except for 3-4 points with larger HONO flux above 2 ppb NOx the relationship between HONO flux and NOx at night looks horizontal, and is not convincing that NOx reactions support HONO fluxes.

7287, line 4. On what evidence is the statement supported that HONO in the airmass was probably generated by heterogeneous NOx reactions on aerosol surfaces? This needs some quantitative support, not just speculation.

Conclusion 4 does not appear to be supported by any of the observations in this paper. This study shows there is an apparent net upwards flux of HONO but does not directly address any of the reaction mechanisms that account for that HONO.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 7273, 2012.