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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.

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The present paper attempts to evaluate HONO fluxes measured using the relaxed eddy accumulation method. The manuscript lacks a rigorous quality assessment of the measurements involving a thorough analysis of systematic and random errors. As a consequence, it is unclear whether the determined fluxes are a result of measurement artifacts and analyzer imprecision or if they are "true" fluxes.

1 Analyzer precision

In order to perform reliable REA measurements a very high precision of the measured concentration difference (Δc) between updraft and downdraft is required, particularly when fluxes are very low (mean 0.1 nmol m^{-2} s^{-1} in this study). It was demonstrated for e.g., aerodynamic gradient measurements that wet chemical analyzers may have uncertainties of a few percent (Wolff et al., 2010). This is especially relevant when two dedicated measurement systems are used as it is the case in this study. It was shown using a similar technique that the error of two HONO measurement systems can be above 10% (Soergel et al., 2011) under prevailing low mixing ratios. Additionally, the occasionally measured HONO deposition fluxes under rainy and foggy conditions may be affected by HONO being trapped at tube walls under high humidity conditions. The authors state, that each analyzing unit has at least an overall error of 5% and that the total flux error is 15%. It is not mentioned in the paper, how these error estimates were determined and which implications they have for the interpretation of the results. For instance, the concentration difference of 8% (average) in Figure 6 from which the fluxes where calculated could also be the result of a systematic difference between the sampling units. The diurnal variation of the HONO flux is then simply a result of the diurnal cycle of σ_w. The authors do not elaborate if the analytical system meets the requirements to resolve true vertical HONO exchange fluxes or if the determined fluxes are within the noise of the measurement system. The errors of updraft and downdraft sampling unit have to be combined to derive the overall system precision. This can only be achieved by evaluating the side-by-side measurements of the two measurement systems in the field (using the same time resolution as for the REA) and by evaluating the systematic and random uncertainties. The authors should present the side-by-side measurements made over the entire concentrations range that was used to calculate fluxes (and with the same length of the inlet tubing) and perform rigorous uncertainty estimation. The error of 2% for a mixing ratio range of 50 ppt to 5 ppb might be much higher for the prevailing low HONO mixing ratios at the site (10-189 ppt, mean 49 ppt).

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2 Flow conditions in the sampling tubes

Were the flow, temperature and pressure monitored in the inlet line? Apparently, the flow in the inlet line was near-laminar (Re $\sim$ 2600 at 6 l/min; 20°C, 1013hPa), which may result in a significant frequency attenuation. This was shown e.g., for water vapor by Ammann et al. (2006). The turbulent fluctuations at the intake may be diminished and this may cause a smearing effect on the fast fluctuating signal. Was this effect evaluated? How were potential pressure fluctuations in the system due to switching between sampling units and zero air measurement assessed?

3 Effect of inlet tubing on HONO

HONO is well known to form on any kind of surface in the presence of NO_2 and water or other pollutants. In addition, it may stick to surfaces, in particular when long inlet lines are used (2.2m in this case). These processes can be a function of temperature. The flow in the inlet line was near-laminar, which favors wall effects on HONO concentrations. Have the authors assessed the performance of the inlet for HONO measurements?

4 Delay time

How was the delay time of 200 ms determined? There might be extra time lags due to online data processing and the time response of the splitter valves. What are the expected variations of the delay time and the associated errors of the determined flux?

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5 Determination of β-factor

The authors state that the application of a deadband results in a lower β-factor (<0.6). However, they do not mention the value of the actual β-factor applied for the REA. Was it taken from the literature or was it calculated using a proxy-scalar (e.g., temperature)? The application of β=0.6 may introduce errors in the fluxes if a deadband was applied.

6 Additional comments

Page 7277, line 7: HONO may evaporate from aerosol nitrite.

Page 7278, lines 14-16: Does that mean in total data from only about 1 min were used for the flux calculation for each sampling interval? This should be clarified. What was the fraction of the data not used for the flux calculation due to calm periods and how long was the actual sampling time on average for each reservoir?

Page 7282, line 7: Which coordinate rotation method was used, planar fit or double rotation?

Page 7282, line 14: The values 0.1-20s should be explained (mean, median?). This has important implications for the relevance of the lag time determination error on the precision of the measurements.

Page 7282, line 20: Was the sampling unit temperature controlled? The sampling efficiency is temperature dependent (Henry's law).

What kind of splitter valves was used? Was the effect of the inner valve material on sampled HONO concentrations evaluated?

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From the drawings in Figures 1 and 2 it is not clear, how the system was working. The illustration of the inlet system combining zero air and REA measurements should be improved.

A sampling cycle of 20min may be too short because flux contributions of lower frequencies may not be captured.

Figure 4: the difference between updraft and downdraft always remains nearly the same (middle panel). The flux varies only with σ_w (see comment above).

The interpretation of the results is largely a repetition of the findings by Zhou et al. (2011). Instead of only considering the canopy as a major HONO source, the potential importance of HONO emission by soils as recently reported by Su et al. (2011) should be included in the discussion. Soergel et al. (2011) showed that during periods when forest is subject to intensive turbulent exchange with the air layer above, HONO formed in the soil (or at the ground surface) can be readily transported to the photo-chemically more active air layer above.

7 Literature

Ammann, C., Brunner, A., Spirig, C., and Neftel, A.: Technical note: Water vapour concentration and flux measurements with PTR-MS, Atmospheric Chemistry and Physics, 6, 4643-4651, 2006.

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