Interactive comment on “Observations of reactive nitrogen oxide fluxes by eddy covariance above two mid-latitude North American mixed hardwood forests” by J. A. Geddes and J. G. Murphy

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We thank the reviewer for their careful consideration of our manuscript. Our responses to the reviewer comments are below (original comments in small indented text).

Page 27896, line 18 missing "to"

Done.

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page 27898, line 12, to support the use of night-time NO measure as a zero check the text should note what the typical O3 values were. Night time NO would not go to zero if O3 was very low.

We have added the following to the manuscript:

"During HFWR, the half-hour mean O3 concentrations at midnight were 27 ppb. On average, O3 reached a minimum of 23 ppb around 07:30. These concentrations are sufficiently high that NO would likely have been titrated overnight."

page 27902 I think you may not need to consider the O3 correction for fluxes. In the case of gold converter ozone is destroyed in the converter and there is no back reaction. I don’t know what the Mo converter does to O3, you ought to check and then ignore this if the O3 is consumed

page 27903 -line3 True the potential error is only 5-10 always affects the mid-day fluxes. After reconsidering whether O3 passes through the Mo converter is the conclusion about overall uncertainty still valid?

Thanks to the reviewer for pointing this out. Upon discussion with our manufacturer we do agree it is likely that O3 could be destroyed in the Mo converter as in other converter designs. This has been confirmed by our lab results.

We have clarified that the flux interference of the back reaction is only considered for observations of NO and NO2. In the case of the NOy fluxes, we have emphasized the caveat that the water correction term may result in a systematic artificial deposition component during the day time on the order of that illustrated in Figure 3.

page 27903, line 12, the approach of using covariances far from the true lag ought to cite prior use in other studies. Where I’ve seen this used before covariances are computed at multiple lags in a range that is far from the peak, and the statistics for that covariance provide the estimate of uncertainty.
We understand the reviewer's suggestion. In our case, we were interested in trying and comparing a variety of approaches. As we discuss, we did compute the covariances at multiple lags (albeit only at 20s and 60s). Although we found consistent results from the two time lages, our approach of calculating the covariance at a single lag but combining the results from the whole campaign was motivated by the desire to avoid issues of signal leakage across a time lag which may be important in fluxes of NOy, and to best characterize the error as a function of the observed fluxes across the entire campaign. We are not aware of other studies that use this approach, but since we believe it reflects an appropriate alternative to characterizing flux error, we hope that having it documented here will stimulate discussion. If the reviewer has significant reservations about whether our approach can capture error accurately, we are open to hearing criticisms.

page 27903, line 17, you say this covariance should be close to zero, is it?

The average of the covariance at a lag time of 60s was -0.01 ± 1.67 ppt m/s at HFWR, and 0.11 ± 2.74 ppt m/s. We have added this detail in the manuscript to show that indeed, this suggests the error calculated with this approach is random.

page 27909, periods with rapidly changing concentrations should be evaluated for the magnitude of storage term.

The reviewer makes an excellent point. We have added the following text to the manuscript:

"During this period, very steep changes in the atmospheric concentrations are observed. Under such conditions, it is unlikely that the storage term can be ignored in calculating the flux, making the eddy covariance observations alone unrepresentative of true flux. In the absence of vertical profile observations, the storage term can be estimated to a first order by the equation:
\[ F_s = \frac{dC}{dt} h \]  

where \( F_s \) is the storage term, \( \frac{dC}{dt} \) is the change in mixing ratio over time \( dt \), and \( h \) is the measurement height. For example, the decrease in NOy concentrations from 07:30am to 11:00am on the morning of October 7 leads to an average storage flux term of around -30 ppt m/s. This term is roughly equal to the positive eddy covariance flux measured. The interpretation of the flux measurements during this time is therefore problematic without measurements of NOy at multiple heights to accurately determine the storage term. For this reason, NOy flux observations during this time are excluded from the discussion of the rest of the campaign that follows.

While we believe it is safe to say the apparent fluxes are opposite, it is difficult to say whether at any individual half hour, the magnitude of the fluxes were equal or not, due to the large uncertainty in individual measurements. We have added the following statistical summary to the observations section:

"The diurnal plots are shown in Fig. 10. Generally, mean night time observations were close to zero and impossible to detect, while during the day time, mean fluxes outside the random variability could be detected. Upward fluxes of NO2 peaked at mid-morning (median of +4.8 ppt m/s and +2.6 ppt m/s at PROPHET and HFWR, respectively) and downward fluxes of NO peaked at the same time (median of -4.0 ppt m/s and -2.1 ppt m/s at PROPHET and HFWR, respectively). Daytime fluxes of NO and NO2 largely..."
cancel each other out. Between 11:00 and 15:00, the average NO and NO2 fluxes were -1.3 ± 1.0 and +1.5 ± 1.4 ppt m/s at HFWR. At PROPHET, the average NO and NO2 fluxes between 11:00 and 15:00 were -0.8 ± 0.8 and +1.5 ± 1.0 ppt m/s. Therefore, on average, these fluxes appeared to be statistically indistinguishable from being equal and opposite."

Note, we do not suppose there is an uptake mechanism of NO at the leaf- or soil-atmosphere interface. Rather, we interpret this likely as an artefact of the vertical profile shapes of NO and NO2 that is resulting from variable photochemical conditions above and below the canopy.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 27891, 2013.