

Interactive
Comment

***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**

J. A. Geddes and J. G. Murphy

jeff.geddes@mail.utoronto.ca

Received and published: 31 January 2014

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.

C11768

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper





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 5-10always 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 NO_y, 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:

C11770

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

$$F_S = \frac{dC}{dt} h \quad (1)$$

where F_S is the storage term, dC/dt is the change in mixing ratio over time dt , and h is the measurement height. For example, the decrease in NO_y 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 NO_y at multiple heights to accurately determine the storage term. For this reason, NO_y flux observations during this time are excluded from the discussion of the rest of the campaign that follows."

page 27911 line 7 Are the apparent NO_2 and NO fluxes distinguishable from being equal and opposite? There is a mechanism for NO_2 emission, but NO uptake has not been considered likely. In the case of no net flux of NO_x the NO and NO_2 would counteract each other. This is mentioned in the discussion section, but here in the results it would help to include some statistical tests and evaluate whether the differences between NO and NO_2 flux are outside the confidence limits.

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 NO_2 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 NO_2 largely

C11771

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

cancel each other out. Between 11:00 and 15:00, the average NO and NO₂ fluxes were -1.3 ± 1.0 and $+1.5 \pm 1.4$ 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 $+1.5 \pm 1.0$ 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.

ACPD

13, C11768–C11772,
2014

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

C11772

