**Atmospheric
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Discussions

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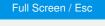
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We thank the reviewer for their careful consideration of our manuscript. Our response to their comments are below (original comment in small indented text).

General Comments:

> Regarding the terms "deposition" and "emission": Many times throughout the manuscript, these terms are used to describe downward and upward fluxes, respectively (starting with line 14 of the abstract). These terms imply actual interac-

tions with the surface, that is, physical sinks (deposition) or sources (emission). We know, however, that chemistry can also influence the fluxes of reactive species, notably NOx. Since flux observations represent the net effect of physical and chemical processes, the reviewer recommends that these be referred to as "downward" and "upward." Moreover, the authors might explicitly state that total NOy is conserved (i.e. chemistry just converts one form of NOy into another), thus downward NOy fluxes really do represent deposition.

We agree with the reviewer that the proper distinction must be made between the terms "deposition" and "emission" and the observations which were of "downward" and "upward" fluxes. We have gone through the manuscript and replaced the former terms with the latter wherever we found it appropriate. We have also made the point more explicitly that we are assuming total NOy is a conserved species and that therefore observations of downward NOy fluxes do represent deposition when this term is used. The following was added to the introduction:

"A further consequence of the above is that it is difficult to elucidate actual emission and deposition of individual reactive nitrogen oxides at the surface-atmosphere interface from above-canopy observations. Here, we make use of the assumption that NOy is a chemically conserved species, implying therefore that observed downward fluxes are true net deposition. However, for individual species such as NO and NO2 (and possibly even their sum, NOx), the observed fluxes are referred to either as "downward" or "upward" fluxes. How these relate to emission and deposition at the surface-atmosphere interface requires careful consideration."

Specific Comments:

p.27894, l.20: It has also been suggested that deposited nitrate may be re-emitted as HONO (Zhou, 2011).

We have added this particular point and citation to the introduction.

> p.27897, l.16: what is the total uncertainty in mixing ratios?

We have summarized the total error for NO, NO2, and NOy mixing ratios based on adding random errors quadratically, and noting systematic error separately:

"Adding the random errors in quadrature, the total error in NO and NO2 at HFWR and PROPHET were $\pm11\%$ and $\pm22\%$, and $\pm7\%$ and $\pm12\%$ respectively. The total error for NOy at HFWR and PROPHET was $\pm11\%$ and $\pm7\%$ respectively, with a systematic underestimate of up to +10% as a result of the conversion efficiency."

> p.27898, l.14: "incorrectly accounts for artefacts if the interferences have a diurnal profile." There is some evidence that ozonolysis of biogenic alkenes (e.g. monoterpenes) can produce photons and thus lead to a positive artifact in CL-based NOy measurements (Bloss, 2012; unfortunately this reference is a poster and not a paper). Such interferences, if present, would be most severe above a forest in the summer; moreover, these may not be adequately accounted for by the employed background determination methods. Can the authors provide any evidence that this was not an issue? For example, does the background signal ("dark counts") exhibit a diurnal cycle? It is somewhat concerning that the uncertainty in the NO background at HFWR (50 pptv, using the 1-sigma variability) is 30
>
> p. 27902: following the earlier comment, it is possible that biogenic alkenes could produce a positive artifact in NOy fluxes (in a manner similar to fast fluctuations in ozone and water). The authors should consider if they have the data available to estimate (or rule out) such an artifact. If not, it is at least worth acknowledging as a potential problem for future efforts.

We have added the point that our instrument uses a glass red filter to block wavelengths < 610 nm in order to avoid interferences as a result of alkene ozonolysis resulting in excited ketones for example, but are not able to rule out intereferences from biogenic

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alkenes above 610 nm as reported in the Bloss poster. Nor do we have observations of biogenic hydrocarbon species at HFWR or PROPHET during our field campaign. We are able to say that the dark counts (our background signal) respond largely to the PMT temperatures, which fluctuate over the long term (a period of weeks) and in response to our air conditioning systems (a period of hours). These fluctuations are low and easy to account for between background tests.

We have also added the relevant point about potential interferences in the flux observations should there be some interferences from biogenic alkenes, and that future work investigating this is desirable:

"It is well-known that ozone can react with olefin species to produce excited ketones that may chemiluminesce and could conceivably interfere with NO measurements. However, since species such as formaldehyde and glyoxal have an emission peak below 600 nm (Finlayson et al., 1974; Hills and Zimmerman, 1990) we minimize these inteferences by using a glass red filter blocking wavelengths less than 610 nm. We are unable to account for potential interferences that occur at longer wavelengths."

"Finally, we note an additional potential interference as a result of the chemiluminescence from ozonolysis of hydrocarbon species at wavelengths longer than 610 nm. We are unable to 5 account for this interference, although it may be worth investigation in future work."

p.27898, l.17: what was the location of the generator relative to the tower?

We have noted the location of the generator:

"At HFWR, a generator located 100 m northeast (usually downwind) was required to power the instruments."

p.27898, l.27: was ozone measured at the same height as NOy?

We have clarified that ozone measurements were collocated at the same height.

> p. 27900, l.9: what percentage of data is lost due to failing stationarity?

We have added the following to the manuscript:

"During HFWR, 33% and 21% of the NOy and NOx flux observations respectively were removed due to failing this stationarity test. During PROPHET, 46% and 33% of the NOy and NOx flux observations were removed respectively."

> p. 27903, l.19: Rather than binning fluxes, it would seem simpler to normalize each error estimate by the corresponding flux measurement. Alternatively, one might just fit a line through the error estimates (Fig. 4, bottom) to get an error function. By eye, this looks to be 15% + 0.5 ppt m/s.

This is an interesting point which occurred to us as well. We have added this approach to our description of error:

"We note that the results of this error analysis show a strongly linear relationship between estimated error and measured covariance. Using the intercept and slope from ordinary best-fit lines of this data would suggest that an alternative formulation of the 1σ error could be expressed as 0.4 ppt m/s $\pm16\%$ and 0.4 ppt m/s $\pm11\%$ for the downward and upward fluxes at HFWR respectively, and 0.8 ppt m/s $\pm13\%$ and 0.3 ppt m/s $\pm31\%$ for downward and upward fluxes at PROPHET respectively."

> p. 27903, l.21: what is meant by "atmospheric effects?"

We have clarified that we were referring to wind speed and direction.

> p. 27904, l.1: how do you know the "true covariance" if you are measuring zero air?

We have added the quotation marks around "true" in this context, which refers to the notation in the previous paragraph, where we clarify that we are calling the calculated covariance at the lag at which the covariance between the scalar of interest and vertical wind is maximized the "true" covariance. The zero air signal was taken from one half hour sample and applied to the uncertainty calculations for whole campaign.

> p. 27905, l.8: The reviewer believes that the application of the transfer function is incorrect. It would seem more logical to apply this transfer function to the measured cospectrum, as it is meant to "correct" for attenuation. The corrected cospectrum should then be compared to the ideal cospectrum. Looking at Figure 5, this would likely bring w'NOy' into better agreement with w'Ts' at the high frequency end. Also, the most appropriate citation is Massman (1991).

In response to comments made by another reviewer, we have changed this section discussing the cospectra (for details please see our response to Reviewer 2). The main point we are expressing is that the transfer functions show us the signal should be dampened at a certain frequency (which is also consistent with our understanding of the time response of the instrument). However, since we are not observing the dampening (and indeed in some cases observe an increase in cospectral power), we believe the transfer function approach will not appropriately correct the flux observations. In the end, since we do not apply the transfer function approach, we refer the reviewer to the updates in our manuscript (section 2.3.3). We have also added the citation to Massman (1991).

> p. 27909, l.20: This is a fascinating result. Is it possible to estimate the gross vs. net uptake? In other words, can you estimate how much a model might over-predict N-deposition in such cases if it did not include re-emission?

In response to other reviewers, we have clarified that our observations during this particular time are problematic and difficult to discuss due to storage terms (when mixing

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ratios are changing rapidly within the averaging time), which are being ignored. As a result, we have limited any interpretation of these results. We have added the following 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:

$$F_S = \frac{dC}{dt} h \tag{1}$$

where Fs 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 NOy concentrations from 0730 to 1100 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, the NOy flux observations during this time are excluded from the discussion of the rest of the campaign that follows."

> p. 27909, l.24: Such linearity (which is stated but not shown) seems odd given the different diel cycles of concentration and fluxes. Moreover, deposition velocities should also exhibit a diel cycle as they depend on boundary layer height, stomata, and other sun-driven processes. As such, I am not sure whether reporting an "average" deposition velocity is fair.

We agree with the reviewer that our reporting of deposition velocity is simplistic. Instead, we have opted to summarize the deposition velocities in terms of midday and

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night-time averages. This has been changed in the abstract, and we have also replaced our original wording with the following in the observation section:

"NOy fluxes roughly correlated with NOy mixing ratios. Deposition velocities (vdep) are calculated as the observed flux divided by the observed mixing ratio, and are generally reported in units of cm/s. Note that this observed quantity is actually the net result of both upward and downward fluxes, and is therefore also known alternatively as the "exchange velocity". At any given time, this parameter is expected to be controlled by atmospheric conditions and, for example, the ratio of NOx/NOy. As expected, vdep exhibited a diurnal pattern, with higher values during the day (corresponding to more turbulent atmospheric conditions), and lower values at night (corresponding to more stable conditions generally), however they were highly variable. Average midday (12:00 to 16:00) values of vdep at HFWR and PROPHET were 0.20 ± 0.25 cm/s and 0.67 ± 1.24 cm/s respectively. Average night time (00:00 to 04:00) values of vdep were 0.09 ± 0.23 cm/s and 0.08 ± 0.16 cm/s respectively."

> p. 27917: While $ng\,(N)\,m^{-2}\,s^{-1}$ are the traditional units for NO emission, for comparison with observed N deposition it might be better to put these in the same units as observed fluxes (ppt m/s).

We agree that there are unfortunately several traditional conventions for describing these types of observations. In order to try and be as widely applicable as possible, we have already included the conversion necessary, where we state that 0.5 - 3 $ng\,(N)\,m^{-2}\,s^{-1}$ would correspond to a 0.8 - 5 ppt m/s flux.

> p. 27917, l.13: As you state, your estimate ignores chemical/canopy losses. However, fluxes of NO and NO2 nearly cancel; thus, the net NOx flux is near 0. Thus, emitted NO is either converted to higher NOy species (HNO3, PNs, ANs) or lost to deposition. These would have different influences on the observed NOy flux.

We have added the following clarification to our text:

"Since the observations suggest the net NOx flux is near zero, these emissions are either lost to deposition as NO2, or converted to higher NOy species (HNO3, PANs, RONO2). In the former case this would make no net contribution to the observed NOy flux; in the latter case this would influence the observed NOy flux by contributing an upward flux component."

Technical Comments:

p. 27896, l.9: move sentence to end of first paragraph in this section.

p. 27900, l.15: QAQC not defined. Since this term is not used again, just write it out.

p. 27902, l.18: "0.41 ppt m s-1 and"

p. 27903, l.6: delete "on"

p. 27906, l.14: "the integrated area"

p. 27909, l.4: L is the Monin-Obhukov length. z/L is the "stability parameter."

p. 27914, l.23: perhaps you mean "diurnally-integrated"?

p. 27916, l.21: net result of emission, deposition and chemistry.

Figure 3: Also include a line for the sum of all interferences.

Figure 5: More information is warranted for the caption. For starters, what are (a) and (b)?

Figure 8: Not sure if z/L and u* are necessary, as these are barely referenced in the text. You might consider removing these and instead putting vertical lines on the flux plots to denote unstable conditions (z/L < 0).

Figure 10: Recommend putting "NO" and "NO2" in big letters on the lower and upper portions of the graph to expedite interpretation.

Figure 11: More info needed in caption. What are limits for boxes and whiskers?

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We have addressed all of these technical comments accordingly. With regards to Figure 8, while we agree that z/L and u* are not discussed very much in the manuscript, we believe it will be of enough general interest to the audience that it merits inclusion in the figure to help guide interpretation.

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

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