Review of "Observations of reactive nitrogen oxide fluxes by eddy covariance above two mid-latitude North American mixed hardwood forests", Geddes and Murphy, ACP (2013)

25 November, 2013

Summary

This paper presents observations of the abundance and surface fluxes of NO, NO2 and NOy above two deciduous forests in North America. Content includes 1) a detailed evaluation of uncertainties and errors in fluxes, and 2) discussion of results with a focus on their implications for the budget of atmospheric N deposition. Despite the importance of N deposition and the large uncertainties associated with this process, very few reliable direct observations of NOy fluxes have been reported. This paper is suitable for publication in ACP after consideration of the following.

General Comments

1) 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 interactions 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.

Specific Comments

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

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

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% of the typical daytime maximum.

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

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

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

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.

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.

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

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

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).

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?

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.

p. 27917: While ng(N)/m^2/s 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).

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.

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?

References

Bloss, W., et al., NOx analyser interference from alkenes, EGU General Assembly 2012, Geophysical Research Abstracts Vol. 14, EGU2012-6330.

Massman, W., The Attenuation of Concentration Fluctuations in Turbulent Flow Through a Tube, *J. Geophys. Res.,* 96(D8), 15269–15273, 1991.

Zhou, X., et al., Nitric acid photolysis on forest canopy surfaces as a source for tropospheric nitrous acid, *Nature Geoscience*, 4, 440-443, 2011.