Atmos. Chem. Phys. Discuss., 12, C1892–C1894, 2012
www.atmos-chem-phys-discuss.net/12/C1892/2012/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Observations of atmosphere-biosphere exchange of total and speciated peroxynitrates: nitrogen fluxes and biogenic sources of peroxynitrates" *by* K.-E. Min et al.

Anonymous Referee #1

Received and published: 27 April 2012

This paper presents an intriguing analysis demonstrating an apparent upward flux of unknown nitrogen species that behave like a peroxynitrate from a coniferous forest in the Sierra foothills of California. There is good evidence indicating the extra peroxynitrate is formed by reaction with biogenic hydrocarbons in the canopy and it can contribute to an upward flux. This is followed by discussion of potential implications.

I note two areas of specific comment where the manuscript could be improved and clarified, however it should be noted that revising the treatment of uncertainty will not alter the conclusions. Line 23 pg 6212 We also applied a frictional velocity filter keeping

only that data with a range of frictional velocities between 0.1ms−1 and 1.5ms−1 Is this window of u* taken directly from Foken or evaluated for this particular site? A constant u* criteria for all sites is unlikely to be appropriate for any site but the one it was computed for. In the case of depositional fluxes the reasons for excluding low u* fluxes are probably not relevant. Emission fluxes are suspect when turbulence is weak because emitted gases may be escaping by horizontal advection and inability to quantify storage over the spatial scale of a flux footprint. However, depositing species are not accumulating or being dispersed by horizontal advection so a measured low flux is likely real. These intervals could be kept in the analysis, and likely would only serve to make the fluxes during night-time interval more tightly clustered around zero. As long as the data are treated by computing overall diel averages and the actual number of data points at each hour considered, it should be fine to eliminate the suspect data intervals as they have been..

Line 11 pg 6213 The statement “we calculate 17% systematic uncertainty (9% without errors from the concentration estimation) in FÎPNs and 10% random uncertainty in half hour average FÎPNs” .needs some further elaboration. What do you mean by systematic uncertainty? If there are some systematic terms like inlet damping and sensor separation they should be applied to the data, not just counted as an uncertainty. These are almost certainly not constant, but depend on the turbulence characteristics. Secondly, the approach to compute a concentration uncertainty does not apply directly to computing a flux uncertainty, so the values you report here are probably not appropriate. Errors in absolute concentration cancel when you subtract the mean, though error in the gain remains. As discussed in Saleska et al Isotopes in Environmental & Health Studies; Jun2006, Vol. 42 Issue 2, p115-133, the instrumental uncertainty at time intervals for flux calculation are what matter, and Allan variance plots are useful for identifying the signal averaging properties appropriate for a particular instrument. One approach to quantifying the contribution of random noise to flux uncertainty is to compute the covariances at several lag times far from the true lag that aligns the concentration and wind data, then the variance of those covariances gives an estimate

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of the variability in computed fluxes due to random covariance – effectively this is an estimate of the flux detection limit. The flux uncertainty could be noted on Figure 5. Be sure to consider if the flux uncertainty is smaller than the standard deviation of repeated observations, which will be different. Overall, the flux uncertainty treatment in the manuscript could be revised.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 6205, 2012.