Response to Reviewers
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Special Issue: Biosphere Effects on Aerosols and Photochemistry Experiment: BEARPEX
Title: Observations of atmosphere-biosphere exchange of total and speciated peroxynitrates: nitrogen fluxes and biogenic sources of peroxynitrates

We would like to thank both reviewers for their constructive and thoughtful comments. We also recognize that relevant comments on our methods were described in the ACPD paper by Phillips et al. (2012) and our revised manuscript will include analysis of their comments as well.

<u>**Response to Reviewer #1 (Responses in Bold)**</u>

1)   Line 23 pg 6212 "We also applied a frictional velocity filter keeping only that data with a range of frictional velocities between 0.1 m/s and 1.5 m/s." Is this window of u* taken directly from Foken or evaluated for this particular site? 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.

We have added text to the revised manuscript to clarify our reasoning. We tested a window of u* that had a range from 0.05 - 0.2 m/s at the lower end and found our conclusions insensitive to the choice. We agree with the reviewer that the sensitivity of emission and deposition fluxes to advection and weak turbulence is different. We emphasize that we don't a priori know the relative balance of those two terms to the net flux. And thus make what we believe are conservative choices for the u* window.

2)   Line 11 pg 6213 The statement "we calculate 17% systematic uncertainty (9% without errors from the concentration estimation) in ΣPNs and 10% random uncertainty in half hour average ΣPNs." 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.

We added text and a table to clarify our meaning. By systematic we refer to errors that would be corrected by a single multiplicative or additive constant applied to the entire data set (although possibly a different constant for the two instruments) such as uncertainties in instrument calibration. We also include in that category the imperfect correction of inlet damping and sensor separation. We note that the two data sets would have nearly identical additional correction applied.

3)   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 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.

We added a discussion along the lines suggested by the referee.

Response to Reviewer #2 (Responses in Bold)

1)   My main criticism regards the fact that even if the biggest differences between total_PNs and APN (denoted in the paper XPN) arise mainly during nighttime, the Authors did not point out this result in terms of analysis developed to explain the reasons for the observed XPN. For example: 1) page 6216 (lines 24-25) to derive the XPN flux is used the average daytime concentration of NO2, 2) page 6217 (lines 5-6) the derived HO_2 is compared with the mean daytime HO2. These analysis need more description considering that during daytime XPN is much lower than during nighttime. Why the reactions of sesquiterpenes with NO_3 are not considered to explain the observed XPN during nighttime?

The reviewer is correct that the largest concentration differences between the two instruments occur in the dark. In this paper, our focus was on the fluxes and as turbulence is low at night, these concentration differences don't contribute significantly to atmosphere-biosphere exchange. In response to this comment, we have added text to the revised paper speculating that the differences are associated with NO_3 chemistry which is not active in the daytime because of the open canopy.

2)   The intercomparison between total_PNs and APNs measurements (Page 6211 and Fig. 2) is limited to daytime observations. Since the differences between total_PNs and APNs concentrations arise mainly during nighttime, it would be worth seeing the intercomparison between the TD_LIF and TD_CIMS for nighttime observations as well. A similar comment for the altitude chosen to make the instruments intercomparison: since XPN is different for each height, why did the authors decide to intercompare the two systems only using observations at 18 m. A description of the agreement between the two instruments at different heights would be worth.

Although we only plot one measurement vs. the other for a single time of day, Figure 3 does represent a comparison of the two measurements at all heights and all times of day. We believe that any error in calibration is independent of time of day or height and thus find it sufficient to compare at one time and height. We note that at 10AM the concentrations measured by the two instruments at all heights are nearly identical. These comparisons lead us to believe that the relative calibration of the two independently calibrated instruments is accurate to better than 5% and probably to better than 2% as described in the text. We have revised this section in response to this comment and to reviewer #1's comment on the uncertainty analysis.

3)   Page 6214, lines 17-22: Are there observations and/or reference that support the hypothesis that the contribution of N_2O_5 to the XPN is negligible in the observational site?

Observation at this site from our group using Berkeley NO_3/N_2O_5 LIF instrument during the summer of 2005 showed the sum of the NO_3 and N_2O_5 to be 4±1.5 ppt at 14m at night and below

detection limit during daytime, (Minejima, PhD Thesis 2008). In 2009, NO_x was ~50 % lower allowing us to estimate that the sum of NO_3 and N_2O_5 is below 4ppt at night and remains near zero during the day. Calculations suggest that the lifetime of NO_3 with respect to BVOC is too short (< 300 seconds at night) for appreciable formation of N_2O_5 although production of NO_3 may be rapid enough to support the observed XPNs at night.
We added text explaining our reasoning to the revised manuscript.

4)　　　Page 6218, lines 16-20: To reconcile the results of this work with those of a previous campaign (Farmer et al., 2006) one of the hypothesis is that the biogenic source of PN precursors at the BEARPEX site have decreased over the last decade. Are there any evidences that this Authors' speculation is plausible?

We have added text indicating the magnitude of changes in NO_x, and O_3 the interval between the two studies and discussing the corresponding effects on OH and secondary organic molecules such as aldehydes.

 References
Farmer, D. K., Wooldridge, P. J., and Cohen, R. C.: Application of thermal-dissociation laser induced fluorescence (TD-LIF) to measurement of HNO_3, Σalkyl nitrates, Σperoxy nitrates, and NO_2 fluxes using eddy covariance, Atmos. Chem .Phys., 6, 3471-3486, 2006.
Minejima, C.: Nitrogen oxide chemistry at night: Novel instrumentation applied to field measurement in California, PhD thesis, University of California at Berkeley, 2008.