

Interactive comment on “Eddy covariance fluxes of acyl peroxy nitrates (PAN, PPN, and MPAN) above a Ponderosa pine forest” by G. M. Wolfe et al.

G. M. Wolfe et al.

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We thank the referee for taking the time to review and provide critical feedback on our manuscript. Our responses to the referee's questions and comments are outlined below.

Reviewer: "The authors state that the summer of 2007 was unusual for this site. Does the statement in the abstract (expounded upon in last section) "PAN deposition is approximately 4 - 19% of that due to dry deposition of nitric acid at this site" stand as a general conclusion or might the fraction vary under more typical photochemical conditions?"

Response: The referee is correct that we note several times throughout that paper

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that temperatures were a few degrees lower in 2007 relative to previous summers, which would lead to less biogenic emissions and thus less photochemical production of APNs and ozone, which is also reflected in the measurements. Day et al. (2008) recently demonstrated that higher temperatures at BFRS lead to more HNO₃ and less APNs; thus, we might expect this fraction to be smaller under more typical (i.e. warmer) conditions. We have added a sentence to this effect at the end of Sect. 4.7.

Day, D. A., Wooldridge, P. J., and Cohen, R. C.: Observations of the effects of temperature on atmospheric HNO₃, sumANs, sumPNs, and NO_x: Evidence for a temperature dependent HO_x source, *Atmos. Chem. Phys.*, 8, 1867-1879, 2008.

Reviewer: "Might the authors share the details of their estimate for APN losses due to thermal decomposition in the inlet lines? Did they ever conduct calibrations by placing the calibration gas at the air inlet?"

Response: TD losses in the inlet lines is estimated by first using the internal volume and volumetric flow rates to calculate a plug-flow residence time in the lines. Then, the average temperature is used to calculate the PAN TD lifetime. Division of the former by the latter gives a rough estimate of the PAN TD loss in the inlet lines. We have added a phrase clarifying this technique in the methods section.

We did indeed perform some calibrations by adding PAN to the far end of the inlet, both in the lab and in the field, and evidence suggested no detectable loss of PAN in the inlets. We have added a sentence mentioning these tests in the text.

Reviewer: "Are there references that should accompany the text at the start of section 2.5 or does it refer to this work only?"

Response: The appropriate references for these effects are listed throughout Sect. 2.5 as they appear in the discussion.

Reviewer: "Page 17507 lines 5 - 11. I would be more comfortable with the actual correction being applied to the data (according to actual turbulence values). Without

knowing what the uncertainty in tW is, it's difficult to know if it would be appropriate to apply the daytime average correction to the daytime data and the nighttime average correction to the nighttime data. In either case, it seems "cleaner" to correct the data rather than adding to the total uncertainty. I am aware that this is how isoprene flux data are treated - if this is not the case for APN fluxes, then it may make comparisons with other results more difficult. Perhaps the authors might comment on the consequences of this choice as regards data comparisons and data interpretation."

Response: Farmer et al. (2006) calculate this factor but do not apply it to their data. Turnipseed et al. (2006) do apply this correction, but their method of computing it is slightly different from ours. Thus, it is not clear as to whether this should be treated as a correction or an error for APN flux data. In any case, the correction is small (~5%) relative to the total error in the fluxes (40 - 50%), so it should not affect data comparison or interpretation. As it is difficult to know the exact value for a single flux point, it seems most appropriate to leave it as part of the error.

Reviewer: "Page 17521 lines 20-23: how great of an underestimation might this cause?"

Response: It is difficult to quantify this underestimate without measurements at the surface. On p.17525, we state that "we can explain ~90% of the gross downward PAN flux with thermochemical gradients if we assume that air temperature increases by 20C and $[NO]/[NO_2]$ doubles between 3.0m and 0.01m above the surface." This equates to a total TG flux of ~3 pptv m/s, which is three times larger than our average estimate (Fig. 9); however, this is an extreme upper limit. We have added a note here stating that the underestimate may be a factor of two to three and referencing Sect. 4.6.

Reviewer: "The word "outward" is used in 4 times in this paper. An explanation of the authors thinking here would be useful. (both upward and horizontal flux out ? only horizontal flux out?)"

Response: In the text, we use "outward" and "upward" interchangeably, but the re-

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viewer makes a valid point. To avoid confusion, we have changed all instances of "outward" to "upward."

Reviewer: "Page 17575 line 25: is this assumption reasonable? Add support?"

Response: Previous unpublished measurements from BFRS have shown that the surface can be 10 - 20C hotter than the air at 1.5m (A.H. Goldstein, personal communication, 2008), and a modeling study by Gao et al. (1991) that only considered the NO-NO₂-O₃ system showed a doubling of the NO/NO₂ ratio between the top of the canopy and 1.5 m. Thus, this assumption is an extreme upper limit. We have stated this and added the above references in the text.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 17495, 2008.

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