Atmos. Chem. Phys. Discuss., 7, S7919–S7921, 2007
www.atmos-chem-phys-discuss.net/7/S7919/2007/

Atmospheric
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Discussions

Interactive comment on “Observations of HNO_3, ΣAN, ΣPN and NO_2 fluxes:evidence for rapid HO_x chemistry within a pine forest canopy” *by* D. K. Farmer and R. C. Cohen

D. K. Farmer and R. C. Cohen

Received and published: 22 December 2007

Reply to Ref #3

We thank the referee for their comments, and agree that, while there are possible sources of error and approximations in the analysis presented, which we acknowledge and provide constraints on, the results and concepts we suggest are contentious, and should provide incentive for further measurements.

In critique, Referee 3 writes: I have two primary issues with the overall argument. First, the residence time of 400 seconds for OH seems quite long and based on a fairly weak argument. Second, the results they present are in stark contrast to the recently published (Turnipseed et al. 2006, JGR-Atmospheres) estimates of PAN deposition measured over a similar canopy (Loblolly pine) in North Carolina.

The referee feels that the 400 second residence time is long, a point echoed by other reviewers. In the revised manuscript, we will emphasize the point already made in the manuscript that our analysis is sensitive to the product of OH and residence time, and that different methods used give residence times ranging from 70 to 420 seconds. Canopy residence times are notoriously poorly constrained in the absence of Rn-222 measurements. Calculations are available for a turbulent timescale, which is a few seconds for Blodgett Forest; however, this timescale is for turbulent momentum exchange is not unambiguous, nor identical to the chemical timescale. While a histogram of residence times might provide the most realistic description, we use a range constrained by different calculation methods and pick a realistic residence time for the system to continue calculations. We hope that the problem highlighted in our manuscript and the referee comments encourages further research in understanding and modeling turbulence effects on chemical residence times.

Second, we acknowledge that these results are in strong contrast with observations of PAN by Turnipseed et al. Several possibilities that are outlined in the manuscript and also discussed in our reply to the comments by Karl could explain this discrepancy. Our measurement includes the sum of all peroxy and peroxy acyl nitrates, and our flux signal may be dominated by a different type of PN than observed by Turnipseed et al., even if the concentrations were dominated by the same PN. Alternately, the VOC emissions are likely different in the Duke Forest than at Blodgett Forest, resulting in lower HOx. Further, the LAI and canopy structure at Duke Forest is markedly different from Blodgett Forest. The open canopy structure and low LAI at Blodgett allows for the possibility for sticky molecules to escape the canopy airspace without depositing, whereas the broadleaf trees at Duke Forest may make deposition a more likely fate. Finally, the gradient that drives the flux depends on both within-canopy chemistry and above-canopy chemistry, and thus on absolute values of NOx, PAN and aldehydes within and above the canopy, none of which is identical at the two sites.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 7087, 2007.

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