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Atmospheric
Chemistry
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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

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We thank the reviewer for his/her careful reading of our manuscript.

The reviewer suggests: “The calculated profiles rely on a constant flux approximation, using essentially a big leaf approach. The discussed species have a shorter chemical time scale than the turbulent time scale in the virtual box. The flux is not constant with height and the source and sink are at different locations. A basic requirement of the used methodology is thus violated. A more advanced approach using a 1-d chemical model should be used.”

We fully agree with the reviewer’s suggestion that there are things to be learned from a more sophisticated model than presented in this paper. We hope that the referee

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is not implying that the results we present in this paper are not sufficiently interested and unique to warrant publication. In our opinion, before attempting to build a more sophisticated model, it is important to have a zero order description that is capable of simultaneously explaining all 4 of the different nitrogen oxide fluxes simultaneously. This zero order explanation points out the minimum essential physics and chemistry that a more sophisticated approach needs to include in order to describe the observations.

We note that we have used this zero order model to identify some of the specific parameters which are unknowns and which would have to be examined in a more detailed modeling study. Most notably, these include product yields for $RONO_2$ oxidation. Further our zero-order model includes conservation constraints for the inter-conversion of NO_{yi}species that imply other specific experimental tests—such as the size of the NO flux and the presence of a HONO or some other non-standard NO_x flux. These represent predictions that can be evaluated in future experiments.

The reviewer raises the question of what the appropriate time and spatial scales are for VOC ozonolysis reactions: “I rather think that a layer of ca. 2m around the canopy top where the reactive VOC occurs would be appropriate reducing considerably the residence time. The 400 s residence time do correspond to a mean Eddy diffusivity of 0.34 m2s-1, a value that seems much too low, especially regarding the mostly hot and sunny weather at this site with its open tree structure and the high surface temperature enhancing convection. Comparable eddy diffusivity profiles through denser canopy e.g. brasil rain forest or a deciduous canopy in Europe are clearly higher.”

In the paper, we attempted to make the point that our analysis of the measurements constrains the product of OH and canopy residence time. We discuss OH based on a range of 70 to 420 seconds, choosing 420 s as a residence time for further calculations. Since both this reviewer and reviewer 3 find the references to 420 seconds distracting, we will include the full range at each point where we mention OH in the revised manuscript.

We agree with the reviewer that measuring NO and gradients of the NO_{yi} species will be an important test of the concepts outlined in this paper. Such measurements are planned for a future experiment, BEARPEX (Biosphere Effects on AeRosols and Photochemistry Experiment, https://webfiles.berkeley.edu/~bearpex/). However, we note the predicted gradients are quite small, making their observation challenging.

Further, the reviewer comments "The concept of the interpretation relays on the reasonable assumption that all different chemical species are transported in a similar way in and out of the canopy. If so, also the spectral distribution of the different fluxes must show the same behaviors. This can be tested by the cumulative frequency distribution, the ogives. The authors make a small remarks that they found systematic differences in the four channels, I strongly suggest that this analysis is included in the paper."

The reviewer notes our brief comment that the ogives for the 4 different nitrogen oxides are not identical (Figure 1). Although there is some discussion of use of ogives to relate fluxes of conserved tracers to source locations, we are not aware of any precedent for quantitative interpretation of the ogives and certainly there is no precedent for quantitative interpretation of the ogives in a situation where there is chemcial flux divergence. If our zero-order model is correct, then the ogives will include effects of deposition and of chemical production. These two terms are different for the different species and are not necessarily contributing equally to the flux at all frequencies. For example, for HNO_3we calculate a gradient due to deposition of -27 ppt and chemical production of +35 ppt. These numbers are approximately 5% and 8% of the 500 ppt concentration and they result in a net increase of HNO_3 of about 1%, or +4ppt within the canopy. For comparison, the ΣPN gradient due to deposition is about $^1/_2$ the magnitude of that due to HNO_3 and the chemical production 2/3 the magnitude corresponding to 2% and 3% of the 750 ppt above canopy ΣPNs. Further, the ΣPN production depends on reaction of aldehydes with OH and then subsequent addition of NO_2 whereas HNO_3 production occurs in a single step. Thus we might expect that the source term for chemical production of PNs and HNO_3 will have a slightly different spectral distribution because the production and removal terms occur at different heights for each chemical species and not necessarily at the same height for the different species. Thus as a result of these different factors, the ogives which represent both the effects of the sinks and the sources will change sign from upward to downward at different frequencies.

None of this is to say that our analysis should be considered the last word. However, we do not believe that differences in the ogives can be used to support or contradict our hypothesis with much confidence at this point in time. In our opinion, a direct calculation using large eddy-simulation to predict the spectral distribution of the chemical fluxes will be required to interpret the ogives. However, we hope that the analysis presented here will inspire further discussion of how to use the information in the ogives and we welcome ideas and will gladly share our data with interested colleagues.

The reviewer requests more information on experimental details. We have already discussed the flux measurements in detail in a separate manuscript and do not believe that we could add sufficient detail here to examine experimental issues that were not discussed in the previous manuscript. However, we attach here separate lagged covariance plots for each species. We are not sure what the reviewer means by chromatographic effects. If the question is related to smearing in the sample lines that would occur with laminar flow. We showed in the methods paper that smearing was a negligible. We would be happy to provide further clarification if the reviewer explains what is meant here.

Finally, we believe the ideas presented in this paper showing that a gradient in OH coupled with sufficient residence time would produce a chemical source of HNO_3 and ΣPNs large enough to compete with deposition but would likely not do so for ΣANs. We show the effects of this chemistry should have observable consequences for the NO_x flux. In our opinion, the hypothesis we present is interesting even if at some later date, we learn that our measurements of the fluxes are in error. We don't believe this

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to be the case and we do not know of any errors that are capable of affecting the sign of our fluxes.

Specific comments:

We will address the technical comments in the final manuscript (add LAI, wind direction, etc.).

Our 15% estimate is of the systematic error. We have averaged over the entire month of August the error bars in Figure 1 represent the variance in the fluxes over the month.

We are not persuaded that there is any problem with PSS calculations. See for example Thornton et al. .(Thornton, Wooldridge et al. 2002). However, errors of the sort invoked by Volz-Thomas et al. will affect the details of our calculation but will not alter the basic conclusions in any way.

Thornton, J., P. Wooldridge, et al. (2002). "Ozone production rates as a function of NOx abundances and HOx production rates in the Nashville urban plume." Journal of Geophysical Research **107**(D12).

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

Figure 1. Ogive plot (cumulative contribution to flux as a function of frequency) of TD-LIF data for all day-time half hours from 1-10 August 2004. As the ogive plateaus at high frequencies for all species, the TD-LIF is fast enough (5 Hz) to capture all relevant flux-carrying eddies.

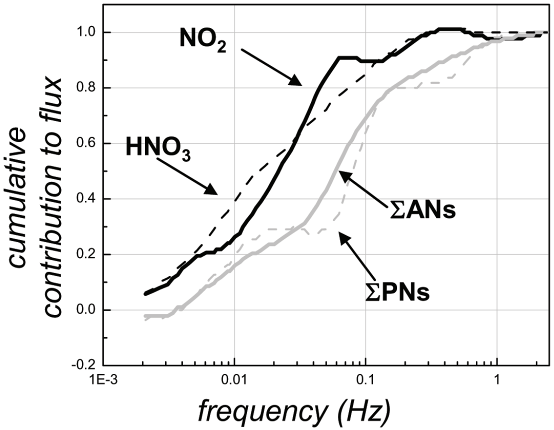

Figure 1: