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Atmospheric Chemistry and Physics 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

Anonymous Referee #2

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This is the second paper by Farmer et al. on their TD-LIF flux measurements of oxidized N species from the Blodgett forest. This paper focuses on the interpretation of the results that already have been presented in the technical paper.

In this paper the consequences of the measured flux values are shown and lead to completely counter-intuitive results. The authors have chosen simple approaches that are well described. Essentially they calculate from their measured fluxes and concentrations at the measuring height concentration profiles into the canopy layer. They rely on a constant flux approach using three similar approaches scaled with measured profiles of conservative parameters (CO2 and water fluxes). They further assume that

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HNO3 has a negligible surface resistance, i.e. each molecule touching a surface stays there. To explain the observed upward flux e.g. of HNO3 they have to invoke a volume source in the canopy layer that is overcompensating the deposition flux. An analogue procedure is then made for the other lumped species. Chemical processes are then calculated in a simple box approach.

The resulting OH radical concentrations are very high and are inversely related to the assumed residence time in the virtual box in the canopy. Such high radical concentrations can only be produced as consequence of a reaction of ozone with very reactive VOC's emitted by the pine trees. Only indirect evidence that such compounds are emitted at the predicted rate exists at the moment.

The authors reach a more or less consistent interpretation of the measured flux data, but have to use questionable assumptions.

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.

To get OH radical concentration in a reasonable range the authors assume a residence time of 400s, derived from the calculated deposition velocity of HNO3 for winter conditions scaled with u* using a the simple relation from Maartens. As the authors mentioned themselves turbulence in summer is much higher and scaling with u* will most likely overestimate the residence time. They also assume the measuring height of 14 meters for the residence time, 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 tem-

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perature enhancing convection. Comparable eddy diffusivity profiles through denser canopy e.g. brasil rain forest or a deciduous canopy in Europe are clearly higher.

As the authors said themselves the results are surprising and call for a test with direct measurements of profiles of OH radicals. An important additional measure would be NO fluxes and concentration profiles of the different species through the canopy. 220Rn and 222Rn measurements can yield direct information on residence times. But I am perfectly aware that suggesting more measurements is generally not a helpful advice, because larger field campaigns can most of the time not be repeated. But more can be done to convince skeptical reviewers that the flux data are reflecting true fluxes. 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. In addition I would like to see for at least a typical summer case the covariance functions of the four channels. What is the variability of the covariance function I relation to the peak height where the flux value is taken?

I encourage the authors to add a more critical discussion of the quality of the flux data and try to convince the reader that no artifacts e.g. chromatographic effects in the oven are causing part of the measured fluxes.

Some specific comments:

Paragraph 2 (page 6): LAI or typical tree density should be added.

(page 7): A figure with mean wind velocity and wind direction would help.

(page 9): Instrumental noise affects fluxes by $<$ 15%. E.g. the third channel corresponding to ΣAN's must show net fluxes very close to zero, I expect that the

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relative error exceeds 15%. Precision of fluxes should not only be derived from instrumental behavior, but also from the noise in the covariance function.

Paragraph 4 (page 17): Applying photo stationary state to calculate from measured NO2 concentration the NO concentration is somewhat risky. There are evidences from larger field studies that there are inherent contradiction between measurements of the NO/NO2 ratio and the PSS approach (see e.g. Volz-Thomas et al. J.Geophys. Res. 108(D4), 2003.

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