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Atmospheric
Chemistry
and Physics
Discussions

# *Interactive comment on* “Observations of $HNO_3$, $\Sigma$AN, $\Sigma$PN 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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Reply to Foken.

1. Re: night-time data: Foken wrote: "I think for the eddy covariance method some more information is necessary in addition to the reference to Farmer et al. (2006). Their method seems not to be state of the art (Lee et al., 2004) because of the reference to McMillen (1988). The data selection for night time, calm and other situations should be repeated or explained - or is the paper restricted to conditions at noon "

We fail to see why a reference to an older paper would prevent our new technique from being state of the art. Our methodology is described in detail in (Farmer, Wooldridge et al. 2006). As we clearly say in the text, all of the calculations described in this paper are restricted to noon, making a detailed review of night-time data selection a distraction. All eddy covariance data published from this instrument has been restricted to times when the stationarity criterion has been met for both turbulent and chemical components.

2. Re: Temperature measurements. Foken wrote: "p. 7094, line 15-16: If you use the temperature measurements from the sonic anemometer (sonic temperature) you measure the buoyancy flux and not the sensible heat flux (Liu et al., 2001; Schotanus et al., 1983). The calculation of the stratification has an error up to 20 %."

Calculations of sensible heat were compared to CO2, H2O and temperature flux-gradient profiles. We agree that use of the virtual temperature may provide an additional source of error in those comparisons, and will mention that in the revised manuscript. As our paper is largely concerned with the sign of the fluxes and the order of magnitude of the derived OH, possible errors of order 20% do not affect any of the conclusions.

3. Re: Bowen Ratio Terminology: Foken wrote: "p 7097, line 11ff: The method described is extremely unclear. You do not use the Bowen ratio method but the modified Bowen ration method (Businger, 1986). The method works only if both fluxes are similar. This is valid for the carbon dioxide and water fluxes in the case of well transpirating canopies, but for most of the fluxes is not (Ruppert et al., 2006). Furthermore, both scalars must be inert gases. This is probably also not the case."

We will re-phrase the terminology in our methods to refer to the modified Bowen Ratio method. We acknowledge that there are potential sources of error from the difference in controlling mechanisms between trace gases of different reactivities. However, as described in our paper and in responses to the other reviewers, the potential errors have been acknowledged and accounted for as rigorously as is feasible. We do specifically mention the issue of possible differences in vertical profile, however we do not believe there is any evidence in the literature that such differences can change the sign of a flux.

4. Re: CO2 profile: Foken wrote: "p. 7097, line 25 ff: If I understand the paper correctly, you have carbon dioxide measurements up to 10.5 m and have extrapolated these up to 14.3 m. Furthermore, you have concentration measurements at 14.3 m for different chemical species and assumed a similar gradient as the carbon dioxide concentrations to calculate the concentrations of the chemical species for 7 m. Firstly, was the scalar similarity controlled and the fluxes identically, otherwise the gradients differ for different fluxes and scalars, which must be furthermore inert gases. Secondly, how can you extrapolate a profile in the roughness sublayer (canopy height 7 m), as the available approaches are not very accurate."

The CO2 profile above the canopy fits an exponential curve ($<$1% error comparing observed to calculated CO2), allowing us to extrapolate a few meters above the highest measurement height with confidence. As described in the paper, the CO2 flux-profile relationships were compared to H2O flux-profile relationships, and the errors are quantified to estimate potential contribution of poor micrometeorology to the range of error in our analysis.

5. Re: Incorrect von Karman constant. Foken wrote: "Furthermore, you use the universal function of the Kansas experiment (Businger et al., 1971), but with the wrong von-Kármán constant. Nowadays a different function is used (Högström, 1988)."

Hogstrom (Hogstrom 1996) points out that the von Karman constant has been reported to vary between 0.32 and 0.65, and that most data appear to fall between 0.39 and 0.41. Our use of k=0.4 seems a justified approximation.

6. Re: Ramp structures and time scales Foken wrote: "p. 7098, line 16ff: The use of the surface renewal method is very questionable: firstly, the determination of the gradient (see above) and secondly the transition time. Normally typical ramp structures (Finnigan, 2000) are used (Snyder et al., 1996). This time is much shorter than your resistance time of 400 s. p. 7100, line 12: For forests, coherent structures are very typ-

ical (Collineau & Brunet, 1993a; Collineau & Brunet, 1993b; Finnigan, 2000; Thomas & Foken, 2005; Thomas & Foken, 2007). The typical time scale is about 30 s. Therefore the mixing occurs muchfaster than you calculated. Resistance times of about 400 s correspond to smaller circulation systems like between forest and clear cuts (Zhang et al., 2007). More important than the separation between winter and summer time are the time of the day and the coupling situation between the atmosphere and the canopy to interpret the data (Göckede et al., 2007; Thomas & Foken, 2007). Finally, I think that the investigated fluxes of chemical species need, because of changing micrometeorological and reactive conditions, that means the Damkoehler number, a much higher time resolution and the averaged data presented in the Tables are less helpful."

Turbulence time scales and the limitation of using ramp structures to derive a canopy residence time are described in detail in our response to Meixner and Referee #2. We expect the ramp structure timescale to be shorter than the residence time as it does not equate a complete flushing of the canopy, and is thus a lower bound on the residence time. While Foken suggests using the Damkoehler number to consider chemical effects, it is not clear that this approach would add any new or more accurate information, as the turbulent timescale is not equivalent to the chemical lifetime (e-folding time). While previous studies (Vila-Guerau de Arellano, Duynkerke et al. 1993) have considered the NO-O3-NO2 triad further research will be required to understand how to apply this theory to a more complex chemical system including multiple HOx-NOx interactions.

References

Farmer, D. K., P. J. Wooldridge, et al. (2006). "Application of thermal-dissociation laser induced fluorescence (TD-LIF) to measurement of HNO3, Salkyl nitrates, Speroxy nitrates, and NO2 fluxes using eddy covariance." Submitted, ACPD. Hogstrom, U. (1996). "Review of some basic characteristics of the atmospheric surface layer." Boundary-Layer Meteorology 78(3-4): 215-246. Vila-Guerau de Arellano, J., P. G. Duynkerke, et al. (1993). "The divergence of the turbulent diffusion flux in the surface layer due to chemical reactions: the NO-O3-NO2 system." Tellus 45B: 23-33.

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