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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

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We greatly appreciate the time Prof. Meixner has taken to review our manuscript and provide such detailed comments. The comments are centered around 1) the canopy residence time, 2) photostationary steady state of NOx, and 3) limitations of measurements made in the roughness sub-layer and assumptions made in our flux-profile calculations. We address these in turn:

1) Canopy residence time

Prof. Meixner wrote: "I agree also with the particular argument of both, referee #1 and referee #2, namely that the residence time used by the authors (400s) is much to long, the corresponding eddy diffusivity (0.34 ms-1) is much to low, and that the deduction

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of that values are based on a fairly (to my opinion: very) weak argument."

The residence time of air within a forest canopy is a poorly understood quantity. In the context of our analysis, and as described in our manuscript, the residence time refers to the average amount of time a molecule spends in the forest canopy between the ground and our sensor and is able to participate in chemical reactions. In the manuscript, we present two lines of reasoning that address this comment. First, as we point out in our manuscript, the scaling argument we use to calculate residence times are subject to significant errors and uncertainties, however, we show that these scaling arguments do provide a self-consistent description of H_2O, CO_2, heat and nitrogen oxide fluxes.

Second, we present 70 seconds and the resulting very high OH concentration - as a possible residence time (see line 25, page 7104) and we clearly state in several places in the manuscript that our analysis is most sensitive to the product of OH and residence time, not to either individually. We will rewrite the section on timescale calculations to be more explicit as to the limitations of potential turbulence timescale/canopy residence time calculations. That said, we agree that defining and observing chemical residence times remains an open question. Calculations for a turbulence time-scale exist, as do measurements from ramp structures (addressed in our manuscript), but it is unclear as to whether these time-scales refer to the e-folding time for a molecule residing in the canopy (as the term timescale usually refers to in chemical kinetics). In the case of ramp structure timescale calculations, the derived timescale is likely a lower limit estimate of residence time; the frequency of such sweeps does not guarantee complete (or 1/e) exchange of mass in the canopy on that time scale.

2) Prof. Meixner wrote: "I consider the application of photostationary state calculations to get (not measured) NO concentrations from measured NO_2 concentrations definitely as risky (if not wrong). It is widely accepted common sense among those groups which are performing simultaneous NO-NO_2-O_3 flux measurements (even outside of California) that close to (emitting and/or absorbing) surfaces the photostationary equilibrium

is never fulfilled."

Prof. Meixner suggests that using the NOx photochemical steady state calculations are an incorrect method of calculating NO from NO2 data because the two species should not be in photostationary steady state. We have shown previously that above the canopy NO and NO2 are in photostationary state (Dillon. PhD Thesis). We explicitly acknowledge possible deviations from PSS in the text; however, at a 70 second residence time, the NO-NO2-O3 triad should be approaching steady state since the PSS time scale is ˜100 seconds. If we are correct about the peroxy radical concentrations, then the approach to steady-state for soil NO emissions will be even faster.

3) Prof. Meixner wrote: "since more than 15 years it is state-of-the-art knowledge in micrometeorology, that immediately over tall canopies there exists the so-called roughness layer (a sub-layer of the surface layer), where Monin-Obukhov similarity laws fail. In this layer, for a given flux, the corresponding (scalar) gradient is about half (or even less than half) of that which would be calculated over a smooth surface. application of the modified Bowen ratio method deserves also a very careful check of the necessary assumptions. These particularly address the demanding requirement of the co-location of sources and sinks of the considered trace gases. Assuming a-priori co-location without any (plausible or real) proof makes the application of the modified Bowen ratio method at least doubtful. Furthermore, as attractive this method may be, its application in the roughness layer requires additionally, that the above mentioned correction functions for the M-O-stability functions can be regarded as identical between the individual trace gases (see Foken, 2003).

We agree with Prof. Meixner that there are significant difficulties and limitations when applying flux-profile relationships. However, in the absence of a significantly better constrained model that includes the complex interplay of HOx-NOx chemistry we describe, we are limited to making and acknowledging approximations. As a test of the approximations, we compared gradients and fluxes of CO2, H2O and temperature. As noted in the paper, temperature, water and CO2 gradients at and above 7m show the expected profile, consistent with similarity theory, suggesting that, for the heights and ecosystem used in this study, that these approximations are reasonable. Given this fact, we believe it reasonable to extend this approximation to the N-compounds.

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