

***Interactive comment on “Observations of HNO<sub>3</sub>,  
ΣAN, ΣPN and NO<sub>2</sub> fluxes:evidence for rapid HO<sub>x</sub>  
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 Karl.

We appreciate the constructive discussion initiated in this comment. The basic question is what sort of VOC emission rate and oxidation mechanism can combine to produce high OH concentrations.

Karl writes that "Taking Helmig et al. emission measurements the expected OH density produced from alkene-O<sub>3</sub> type reactions at Blodgett would be on the order of 1-5 x 10<sup>(5)</sup> molecules/cm<sup>3</sup> in the canopy In order to explain upward fluxes of HNO<sub>3</sub> and PAN an OH density of 0.2 to 1 x10<sup>(8)</sup> molecules/cm<sup>3</sup> is suggested."

We did not mean to imply that the sesquiterpenes reported by Helmig et al. were sufficient to fully explain the observed fluxes and the OH we derive. As Holzinger et al. (2005) clearly demonstrated, the flux of oxidized VOC from Blodgett Forest is significantly larger than the observed monoterpene fluxes. These fluxes cannot completely be explained by the Helmig et al. observations of speciated sesquiterpenes, since those fluxes are smaller than the monoterpene fluxes. Still, the presence of multiple double bonds in some sesquiterpenes leaves open the possibility that their reactivity with O<sub>3</sub> may be a significant source of OH - one we felt it was important to highlight.

The observed methylbutenol (MBO):monoterpene emission ratio above the canopy at Blodgett Forest is 15:1 (Holzinger et al. 2005). Helmig et al. report a MT:SQT emission ratio for ponderosa pine of between 7 and 14:1 for temperatures of 25-30C. Assuming zero losses of MBO in the canopy (based on a lifetime of MBO with respect to 60 ppb of O<sub>3</sub> equal to 26 hours and with respect to 107 OH of 24 minutes), the above canopy MBO flux can be equated with the total ecosystem flux. We make the same assumptions for the monoterpenes and calculate the source strength for OH as follows: we use OH yields for the ozonolysis reactions of MBO of 0.19 (Alvarado et al., Atmospheric Environment, 1998) and MBO-ozonolysis rate constant of  $8.3 \times 10^{-18}$  molec<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup> (Carrasco et al. J. of Atm.Chem., 2007); monoterpene ozonolysis rates and OH yields vary by an order of magnitude; for example, the yield\*rate constant products are  $6.7 \times 10^{-17}$  and  $5.3 \times 10^{-18}$  molec<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup> for alpha and beta-pinene, respectively. OH yields for SQT-O<sub>3</sub> reactions range from 0.06 for beta-caryophyllene to 0.22 for alpha-humulene and 0.67 for alpha-cedrene, and reaction rates are 1160, 1170, and  $2.8 \times 10^{-17}$  molec<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup>, respectively (Shu and Atkinson, Int.J.Chem.Kin. 1994). For the most part, these numbers make the sesquiterpenes sources of OH that are quite strong. OH in the forest canopy will consist of primary OH generated directly by reactions of O<sub>3</sub> with VOC and O(1D) with water and recycled OH produced by reaction of HO<sub>2</sub> with RO<sub>2</sub>.

We calculate the OH source integrated over the canopy height from the oxidation of

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

these BVOC by O<sub>3</sub> using the MBO (8ppb) and monoterpene (0.5ppb) concentrations (reported by Holzinger et al. 2005) and assuming that the sesquiterpene emissions result in reaction with O<sub>3</sub> instantly. Assuming the emissions and reactions are well mixed from the surface to 7.3 m agl gives a production rate for OH ranging from  $4.1 \times 10^5$  to  $9.11 \times 10^6$  molecules/cm<sup>3</sup>/s where the range is largely driven by variation in OH yield and uncertainty in emission ratios. At the high end of the range SQT represent 91% of the VOC ozonolysis OH source. Converting the high end of this source strength to a concentration using an 8.4 s<sup>-1</sup> OH lifetime and a HO<sub>x</sub> chain length of 1 results in a concentration of  $1.2 \times 10^6$  OH/cm<sup>3</sup>.

There are several reasons to believe this is an underestimate:

- 1) recycling of primary HO<sub>x</sub> by reactions of HO<sub>2</sub> and RO<sub>2</sub> with each other and with NO are likely a major source of OH, amplifying the primary source by a factor of order 10.
- 2) there are multiple double bonds in the SQT and the calculation above only includes the oxidation of the initial bond
- 3) there may be significant emissions of oxygenated SQT, analogous to the oxygenated monoterpene methyl chavicol, that are not reported in Helmig et al. and not included in the above calculation
- 4) Holzinger et al. observe larger fluxes of oxygenated products above the canopy than monoterpene emissions indicating the presence of emissions that are not accounted for in current models.

We agree that direct measurements of high OH in canopies do not yet exist. Prior to this paper, there have been discussions of evidence for high production rates (Paulson et al. 1999, Faloon et al. 2001) and high loss rates (Di Carlo et al. 2004). To our knowledge this paper is the first to describe a direct observable consequence of high OH - that is we show that high OH is capable of changing the sign of HNO<sub>3</sub>, PN and NO<sub>x</sub> fluxes. Calculations have also shown that OH can affect fluxes of isoprene and its oxidation products - but these calculations have all been assuming/calculating that within canopy OH is lower than above.

We note that we provide a direct calculation of OH above the canopy in the paper

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

based on the assumption that HNO<sub>3</sub> and NO<sub>2</sub> are in steady state above the canopy. Our estimate is 5 x 10<sup>6</sup> molec cm<sup>-3</sup>.

While we agree that flux divergence measurements would be potentially interesting, we do not think an observational/theoretical basis for interpreting such measurements within a canopy is sufficiently mature. However, we are planning an experiment to measure the concentration gradients through the canopy (<https://webfiles.berkeley.edu/~bearpex/>).

Finally, we note that comparison of fluxes to other ecosystems should not be made simply on the basis of similar basal emissions. As Helmig et al. (2007) demonstrated, loblolly and ponderosa pines may have different sesquiterpene:monoterpene emission ratios. Temperature and water are known to have strong effects on basal emission rates (Holzke et al. 2006). Stand age may also affect emissions. And the effect of within canopy chemistry will depend directly on the above canopy concentrations. For example, we measure the mixing ratio of total\_PNs above the canopy to be 750 ppt, deposition is calculated to produce a negative gradient of 13 ppt and the rather rapid chemistry we infer represents a source of 21 ppt, overcoming this negative gradient to produce a positive gradient of 8 ppt. These two terms are in close balance, if the above canopy concentration were double or the deposition were twice as fast the sign of the flux would be reversed. Such variations are within the range of prior reports of deposition velocities and concentrations for total\_PNs.

---

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper