

***Interactive comment on “Observations of HNO₃,
ΣAN, ΣPN and NO₂ fluxes:evidence for rapid HO_x
chemistry within a pine forest canopy” by
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The authors cite Helmig et al. (ES&T, 2007) who report a reactive terpene (e.g. b-caryophyllene) to monoterpene emission ratio on the order of 10-20% for Ponderosa Pine. This is in stark contrast to the extremely large reactive terpene flux hypothesized at the Blodgett Ponderosa Pine Forest (e.g. up to 30 times higher than the ‘a-or b-pinene like’ monoterpene emission fluxes (Kurpius and Goldstein, GRL, 2003, Holzinger et al, JGR, 2005)). Taking Helmig et al.’s emission measurements the expected OH density produced from alkene-O₃ type reactions at Blodgett would be on the order of 1-5 x 10⁽⁵⁾ molecules/cm³ in the canopy (e.g. MBO:MT:SQT ~ 100:10:1,

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O₃=50 ppbv, YOH=20%). While branch enclosure measurements (Helmig et al., 2007) could underestimate reactive VOC emissions due to the limited number of samples and a general bias because typically only understory species are investigated, only indirect evidence (e.g. Kurpius and Goldstein, GRL, 2003, Goldstein et al., GRL, 2004, Holzinger et al., ACP, 2005 and di Carlo et al., Science, 2004) suggests extremely high reactive terpenoid emission rates at forests so far (e.g. Blodgett and UMBS forest). In order to explain upward fluxes of HNO₃ and PAN an OH density of 0.2 to 1 x 10⁸ molecules/cm³ is suggested. Evidence of extremely high OH concentrations in canopies has not been confirmed and remains circumstantial. Di Carlo et al. (2004) reported a missing OH sink above a deciduous forest in Michigan; they suspected missing reactive hydrocarbons emitted from the forest (comparable in magnitude to what is suggested for Blodgett) as a reason. The same group (Faloona et al., JGR, 2001) reported daytime OH densities on the order of 2-4 x 10⁶ molecules/cm³ at canopy top at the site in Michigan during an earlier study. Based on a study by Dreyfus et al. (JGR, 2002) mixing ratios of isoprene advected to Blodgett forest can be comparable to the site in Michigan (Faloona et al., 2001). In addition MBO contributes a significant amount to the OH loss at Blodgett forest (e.g. Dreyfus et al., JGR, 2002), suggesting that OH loss due to the dominant biogenic VOCs are of comparable magnitude and might be even higher at Blodgett forest. The above comparison implies that the in-canopy OH density would have to be up to 2 orders of magnitude higher than the above-canopy OH density (e.g. 2x10⁶ vs 1x10⁸ molecules/cm³) if similar magnitudes of reactive hydrocarbons producing OH at both sites were present as currently suggested (di Carlo et al., 2004, Kurpius and Goldstein, 2003, Holzinger et al., 2005). If the Blodgett observations of HNO₃ (and PAN) emission fluxes as well as ozone deposition fluxes are due to strong chemical production/destruction in the canopy, flux divergence measurements should reveal any production/loss terms due to gasphase chemistry at this site. These measurements could also shed light on upward fluxes of HNO₃ and PAN reported in this and an earlier paper. Above a comparable ecosystem (Loblolly Pine) Turnipseed et al. (JGR, 2006) saw clear deposition fluxes of PAN, PPN

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and MPAN based on direct eddy covariance measurements.

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