

## ***Interactive comment on “Forest-atmosphere exchange of ozone: sensitivity to very reactive biogenic VOC emissions and implications for in-canopy photochemistry” by G. M. Wolfe et al.***

**Anonymous Referee #2**

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General Comments. This is a fairly speculative manuscript that is primarily focused on understanding what is termed “non-stomatal” deposition of ozone (i.e. the deposition of ozone that cannot be explained by stomatal uptake). I whole-heartedly agree with the authors that this is a process (or, in actuality, a set of processes) that is not well understood and is often treated as a “black box”. The authors correctly point out the inherent difficulties in understanding the nonstomatal term: (1) the high uncertainty in the measurement (usually a difference of 2 measures) and (2) many of the postulated mechanisms can have similar dependencies to environmental driving forces (e.g., temperature, light). Prior work at this site (by these authors) has suggested that fast reactions of biogenic compounds with ozone in the canopy may be affecting both the

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observed O<sub>3</sub> deposition and overall photochemistry. The focus here is then to engage in a detailed modeling exercise to show these possible effects.

The authors are successful in demonstrating that very reactive VOC can affect observed ozone flux measurements and that the current results here tend to agree with their previous estimates based on direct ozone flux measurements or possible oxidized-VOC observations. However, just proving that VRVOC can explain the observed discrepancies in ozone deposition is not that ground-breaking. Certainly even the authors show that addition of VRVOC does not solve all issues of within canopy photochemistry (the OH recycling and the balance between OH and RO<sub>2</sub> as examples). It is also likely the total nonstomatal flux is described by some combination of different mechanisms and not totally VRVOC reactions. Although rather speculative in nature, what this study does is to point some key issues and chemical observations that can be targeted for future studies. In that sense, it is my opinion that this is useful manuscript for the scientific community and should be published with some consideration to the comments below.

Specific Comments: Page 6-7. If the eddy diffusivity ( $K(z)$ ) scaled differently somehow within the canopy as opposed to that above? Certainly the wind profile is quite different within the canopy.

Page 11, lines 12-17. I would use the term: “highly-energized hydroperoxide” etc. to describe the energetic Criegee intermediates. The term “hot” is a bit colloquial and you are already using “hot” to describe your experimental time periods. The term above is a bit more specific.

Page 16, last paragraph and Figure 2. The authors suggest that one may be able to distinguish between direct surface deposition and chemical “deposition” by observing flux divergence on a tall tower. However, at heights above  $z/h = 3$ , one must then begin to consider footprint and advection issues. Ecosystem, landscape and topographical changes can induce advection (note that the model assumes no advection!), which can

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then lead to observed flux divergences, even in chemically-conserved scalars. Furthermore, if there are any changes in species composition as the footprint becomes increasingly larger, then one must consider that the biogenic VOC emission mixture will be changing with height as well. At some point, you will also enter the mixed-layer, where surface-layer scaling no longer applies and entrainment from above the boundary layer can affect measured fluxes. I am a bit skeptical that increasing measurement height to see flux divergence will be the answer. It is, admittedly, a rather difficult problem.

Figure 3 and 4. Is  $V_d$  mostly just stomatal uptake in these figures? Or does it include some parameterization for cuticular (or other surface) loss?

Page 28. Elevated formaldehyde. It has been shown from branch enclosures that HCHO can be directed emitted by Ponderosa pine (see Villanueva-Fierro et al., 2004, Atmos. Environ. 38, 249-260). This does not seem to be included in the current model or in the previous study of Choi et al (2010) as a possible source of HCHO. This could, at least in part, explain higher HCHO concentrations as opposed to emission of highly reactive VOC. It would be interesting to see how much HCHO is observed in the model when incorporating the emission values of Villanueva-Fierro et al.

Page 30, lines 9-10. I think that your results “suggest” that accurate partitioning of ozone fluxes could be tied to BVOC emissions. You are still postulating an un-named and heretofore unobserved species that can influence the fluxes (at least emission rates of VRVOC from enclosures are not sufficient). This hypothesis is in line with some of the chemical observations, but it is not a certainty.

Page 30, lines 11-13. I am also not sure that the wording on this conclusion is completely accurate. The chemistry that perturbs the flux is fast relative to the turbulent mixing time. However, it is a very low concentration (and reactive) reagent that is perturbing the concentration gradient (and thus flux) of a higher concentration reagent (O<sub>3</sub>). Although the bulk lifetime of ozone is long – emission and subsequent fast chem-

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istry perturbs the atmospheric fluctuations and concentration profile near the surface.

Page 31, line 7. Although I do not dispute the need for more “controlled laboratory experiments...”, I think that controlled experiments in the field are also warranted. Aspects such as wind disturbance of needles, microbial communities on leaves, etc. which could be important factors controlling surface features (or BVOC emission from surfaces) cannot always be duplicated well in lab settings. It would also be useful to suggest what types of laboratory experiments would be warranted. Certainly, as the authors point out, there have been branch and leaf-level enclosure studies which have not found large enough emission rates of very reactive BVOC to explain the nonstomatal ozone deposition issue. Overall – it still appears to be very difficult to obtain direct observational evidence in order to discern between different depositional mechanisms. But I would agree that controlled, small-scale ozone reactivity experiments may be a good first step.

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