

Author Response to Anonymous Referee #1

We thank the referee for reviewing our manuscript and providing important feedback. Our responses to questions and suggestions are outlined below.

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.

Yes. This is described in detail in the model description papers, but we agree that it is appropriate to mention here. We have added the following text:

“Within and immediately above the canopy, $K(z)$ is parameterized as a function of friction velocity (u^*) with a small correction to account for “near-field” effects of individual canopy elements on turbulence (Raupach, 1989). In-canopy friction velocity is determined by attenuating the measured above-canopy u^* via an exponential function of the cumulative leaf area index (Yi, 2008). Typical values of $K(z)$ at $z/h = 0.01$ and 1 are 2.2×10^3 and $2.9 \times 10^4 \text{ cm}^2 \text{ s}^{-1}$, respectively. Above $z/h = 1.25$, $K(z)$ is based on the values used by Gao et al. (1993).”

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.

This has been changed.

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 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 mixedlayer, 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.

We agree that this is a difficult problem, and the design of such an experiment must certainly consider all of the details mentioned by the Referee. Our goal here was merely to note that the model suggests that a divergence measurement may provide a means for experimental validation of the chemical flux hypothesis. In referring to a “tall tower,” we meant more to suggest that a larger forest, which may have stronger BVOC emissions and also a longer transport timescale through the surface layer, would be an ideal location to conduct such an experiment. We have altered the wording to reflect this thought.

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

For these figures, only stomatal deposition is included (due to our assertion that non-stomatal deposition is very uncertain). We have altered the text in Sec. 3.4 and the figure captions to clarify this.

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.

Villanueva-Fierro et al. (2004) report a formaldehyde emission of 500 ± 400 ng/g/h. Using the upper limit of this estimate (900 ng/g/h) in CAFE causes canopy-top HCHO concentrations to increase from 4.2 to 4.8 ppbv; thus, our model suggests that this is not sufficient to explain the high HCHO levels observed in 2007. We have added a statement to this effect.

A more recent study by DiGangi et al. (2011) observed much lower HCHO emissions of 15 ± 7 ng/g/h from Ponderosa Pine, though in the same study it is also noted that observed eddy covariance HCHO fluxes are more consistent with an HCHO emission rate of 350 ng/g/h (or an unknown VOC oxidation source). Clearly this warrants further study.

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.

This may have come off too strong. We have reworded as follows:

“Our results suggest that accurate partitioning of ozone fluxes between deposition and chemistry is challenging and may depend on our understanding of BVOC emissions and photochemistry in forested regions.”

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 (O3). Although the bulk lifetime of ozone is long – emission and subsequent fast chemistry perturbs the atmospheric fluctuations and concentration profile near the surface.

The question of what constitutes “fast” versus “slow” chemistry is admittedly worthy of debate, especially in the context of a system that is also subject to vertical mixing. In this case, we are

defining these terms according to the bulk lifetime. Thus, the chemistry under discussion is “fast” for VRVOC ($\tau < 2$ min) but “slow” for ozone ($\tau > 30$ min). To our knowledge, there are several examples in the literature where comparison of a bulk chemical lifetime with the canopy mixing timescale seems to have been used as evidence against the importance of chemistry for fluxes (Gao et al., 1993; Turnipseed et al., 2006; Darmais et al., 2000). This is sometimes presented as the “Damköhler number,” $Da = \tau_{\text{mix}}/\tau_{\text{chem}}$. Our goal is to highlight that this metric is not appropriate in all cases.

At any rate, “essentially proves” is likely too strong of phrase. We have changed this sentence as follows:

“This work also illustrates that chemistry can perturb fluxes of reactive species even when the timescale for that chemistry is slow relative to canopy mixing, implying that a comparison of these timescales (e.g. the Damköhler number) may not be an appropriate metric for the role of chemistry in forest-atmosphere exchange.”

We have also added some text on page 18 (Sec. 3.2) to clarify our point.

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.

Thank you. We have modified this section as follows:

“Controlled experiments in both the laboratory and field should be able to provide insight on this process. Such studies would include direct ozone uptake measurements on both actual and simulated plant surfaces (e.g. Cape et al. (2009)) and should take special care to minimize the confounding influence of ozone-VOC reactions.”

Cited Literature

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