Author Response to C. Stroud (Referee)

We thank Dr. Stroud for taking the time to carefully review our manuscript and provide important feedback and insights. Our responses to questions and suggestions are outlined below.

REFEREE: 1) One issue to address is how general are the conclusions derived from the CAFE model compared to other forest-boundary layer environments given the model is highly optimized to measurements from the BEARPEX-2007 study?

RESPONSE: This question is important but quite difficult to answer. The meteorology and chemical concentrations of CAFE are optimized to match observations from BEARPEX 2007, and it is inevitable that many aspects of chemistry and composition will vary between forests due to differences in emission profiles, proximity to anthropogenic influences, vegetation types and density, etc. Quantitatively, the gradients of VOCs, ROx and NOy compounds are specific to BFRS; qualitatively, however, similar gradients should be expected for similar forests, e.g. young ponderosa pine forests in Mediterranean climates. The sensitivity tests are likely also more of a general nature; indeed, these tests start to give us an idea of how the conclusions developed from studies at the BEARPEX location might change in a different (e.g. denser) forest.

We have added some text clarify our opinions on this matter in our conclusions.

2) Do the three sensitivity tests reflect the largest uncertainties in the model?

Yes and no. We include an analysis of model sensitivity to in-canopy diffusion, laminar sublayer resistance and radiation extinction because the parameterizations for these are inherently highly tunable and are not particularly well constrained by the observations available from the BEARPEX study, i.e. we have no measurements of radiation or friction velocity in the lower canopy. Moreover, our choices for these parameters have the potential to impact all model results, whereas other uncertainties (e.g. those stemming from chemical rate constants or non-stomatal resistances) would likely have a smaller and more specific impact on a particular chemical constituent. Also, the latter uncertainties are more difficult to quantify succinctly. Our goals for the sensitivity studies included here (we have done others) are to demonstrate the effects of our choices on model output and to provide a more thorough, but still general, picture of the mechanics that underlie and drive forest-atmosphere exchange of reactive species.

We have added a statement to this effect in the beginning of section 4.

3) Given the recent Science Express publication on the importance of oVOC deposition to vegetation surfaces, do the authors believe their canopy exchange rates and vertical profiles of oVOCs will improve compared to observed fluxes and profiles during BEARPEX-2007?

Unfortunately, we have no observations of speciated oVOC fluxes from BEARPEX 2007, and the few observations of oVOC vertical profiles are limited to PTR-MS data. It is likely that implementing deposition for MVK and MACR following the recommendation of (Karl et al.,

2010) would yield a more positive in-canopy gradient in these compounds. As is evident in Fig. 2 of the companion paper, however, PTR-MS data suggests no resolvable gradient in these species at BFRS. We have added some notes about this point in Sec. 5.1.

4) It is difficult to assess the model optimization in the manuscript as the authors do not present the vertical trace gas profile data or surface trace gas measurements. The authors refer to tree surveys or observed canopy top flux measurements from other papers, but no data is shown in this manuscript itself.

Our goal with this particular paper was to present a succinct but complete discussion of the model architecture and sensitivity to key assumptions that we make (and that are also made for a number of similar models), which have a broad impact on the model predictions and functioning. We felt it important to separate from this discussion our evaluation and optimization of the model with observations that are inherently specific to a particular location or chemical constituent. We agree with the reviewer that both (model architecture and optimization) are important to describe in close proximity, but we found it difficult to adequately describe both while also discussing specific scientific conclusions resulting from model-measurement comparison all in one paper. Moreover, the measurement data ultimately requires some additional description and discussion, and thus including it in this paper would introduce redundancy between this and the companion paper. Thus we have chosen to omit any discussion of the specific measurements in this manuscript.

5) How might soil moisture affect the emission factors chosen? Maybe a statement characterizing the state of the soil moisture during the time of the BEARPEX observations would be useful.

The soil is fairly dry at BFRS during late summer (8 – 9 % water by volume at a depth of 10 cm). According to (Gray et al., 2003), MBO emissions from P. pine are not perturbed by drought stress, though we may not be able to extrapolate this result to other emissions (e.g. monoterpenes and sesquiterpenes).

We have added a statement to this effect in Sec. 3.4.

Specific Comments
3.1 Canopy Structure
Given that the tree survey conducted in October 2007 yielded a the tree height of 7.9 m, why was the model canopy height set at 10 m.

The mean tree height is 7.9m, while 10m represents the 80th percentile for ~125 surveyed trees in the fetch. We have added a statement to clarify this in Sec. 3.1.

How do the chosen overstory leaf area index (3.2 m2/m2) and chosen leaf dry mass (219 g/m2) compare to other pine forests published in the literature? Similar question for the chosen understory leaf area index and dry mass densities.? How do the values compare to estimates in BEIS and MEGAN?

Unambiguous (to us) reports on canopy statistics are surprisingly difficult to locate in the literature. In particular, it is often unclear whether the reported LAI is 1-sided or all-sided. Moreover, comparison to large inventories like BEIS or MEGAN would be rough at best, as these are, to our knowledge, not regularly updated to account for forest growth.

We feel that it is sufficient to state that our estimates for these values are based on tree surveys performed at the site and to describe the values as unambiguously as we can for the benefit of future comparisons.

3.2 Meteorology
How does the radiation extinction coefficient compare to other pine forests?

We state in Sec. 4.3 that "typical values of k_{rad} range from 0.4 – 0.65 for conifers and understory shrubs (Law and Waring, 1994; Runyon et al., 1994)." We have not found any other references for this value in the literature, though our search has not been exhaustive.

Why does modeling the isoprene advection as an emission source a better representation than using the advection operator, section 3.8?

We thank the reviewer for bring up this issue. As noted in the companion paper:

"The current construction of CAFE is unable to simultaneously reproduce the concentrations of isoprene and its main oxidation products, methyl vinyl ketone (MVK) and methacrolein (MACR), solely through our advection scheme. Thus, in addition to advecting isoprene at a rate of 1 ppbv hr^{-1}, we invoke a substantial emission rate of isoprene (~40% of the MBO emissions). While local (e.g. < 500 m upwind) isoprene emissions are likely smaller than modeled in CAFE, our isoprene emission rate is nearly identical to that used in the 4 km x 4 km grid cell of a three-dimensional model that contains BFRS (Steiner et al., 2007)."

In short, if advection is treated as the sole isoprene source, the model predicts 1.5 ppbv of ISOP throughout the boundary layer, as opposed to the decaying profile characteristic of an emission. As a result, MVK and MACR are overestimated when only advection is used. We stress that we are not attempting to make any conclusions about the importance of local emission sources relative to advection sources for isoprene. We have no observational constraints on the isoprene vertical profile and our advection scheme is too simplified to have confidence that the boundary layer profile that results from advection as the only isoprene source is at all accurate. In the end, this issue is relevant to reproducing the absolute values of isoprene and its oxidation products and not the near-canopy gradients or exchange velocities. We have altered the statement about this point in Sec. 3.4 to be more specific.

3.6 Deposition
The aerodynamic resistance may be smaller for conifers than deciduous and the result is that conifers may be just as sensitive, if not more, to mesophyll resistance. In Table 5, APNs, PNs, HCHO, CH3CHO, C2H5CHO, HO2NO2 all may deposit faster as suggested by Karl et al., 2010. I would suggest a sensitivity run by setting fo=1 for these species to see impact on OH and canopy top fluxes, especially for APNs given

the attention in the manuscript to the reactive nitrogen budget. On page 34, line 2, it is stated that "intra-canopy losses are underestimated" for APN. Maybe enhanced mesophyll deposition referred by Karl et al. would be a possibility to explain the underestimate?

For our conditions and for most molecules, the mesophyll resistance is typically 10 to 100 times smaller than the stomatal resistance (Fig. 5), thus decreasing its value would have little effect on modeled deposition. Changing f0 could, however, have an impact on the modeled cuticular deposition; thus, we have carried out a sensitivity test as suggested. Increasing f0 to 1 for the above listed species has no impact on ROx partitioning, as HCHO concentrations only decrease by ~2%. APN exchange velocities become 30% more negative, which does improve agreement with measurements. We have added a statement about the results of this test in the companion paper.

In the manuscript, ANs are tuned to match above canopy measurement-derived deposition velocities by increasing H in the model. Karl et al. (2010) suggests it is the fo value that should be raised to unity to increase deposition velocities. Maybe the authors could suggest this alternative interpretation in the paper. The isoprene and terpene oxidation products are set at a deposition velocity of HNO3 which should be representative.

To match the AN exchange velocity of -2.7 cm/s from (Farmer and Cohen, 2008), we require that the denominator in the equation

$$R_{cut} = R_{cut}(O_3) \Big/ \left(10^{-5} H + f_0\right)$$

Be equal to ~1000. We accomplish this by setting H=1e8 and f0=0.1. From a physical standpoint, it does seem more correct to tune the "reactivity" parameter, f0, rather than the effective Henry's Law coefficient; however, f0 is traditionally only allowed to range from 0 to 1, which is insufficient to reproduce the observations. This may be due to a poor choice of $R_{cut}(O_3)$, though the latter is based on literature estimates.

We have added a statement regarding this point in Sec. 3.6.

4.3 Radiation
Since MBO is very sensitive to radiation extinction in canopy, it would be helpful to show MBO observations in-canopy or at ground level to assess the choice of k=0.4.

MBO concentration profiles could be helpful in assessing the choice of k_{rad}; however, the PTR-MS gradients represent the sum of MBO and isoprene, and the available GC-MS data was only recorded at 6.4m. Moreover, the modeled MBO profile will also be sensitive to vertical diffusion in the canopy, which is also somewhat uncertain. We do provide a comparison to the measured gradient of the sum of MBO and isoprene in the companion paper.

Technical corrections
Page 4, line 11: correct "0. 1m"

Fixed. Thank you.

Cited Literature

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