<u>Author Response to Anonymous Referee #3</u>

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

The authors use the recently described and evaluated CAFE model for their air chemistry analysis. Since there are only few changes from the published version, a repetition of the model description is certainly not needed. Nevertheless, some more detailed basic descriptions of the site (tree species, stand height) and the model are necessary to better understand the modelling exercise. Particularly, I suggest to briefly mention the principles of the canopy model (leaf are distribution, voc emission calculation, stomata conductance and transpiration, heat balance calculation, time step(s), drivers) and how ground emissions are estimated (i.e. NOx is 'prescribed' but where direct measurements available for the whole period or does this include some model assumptions?). For example the VRVOC emission is assumed to origin from specific storages (Eq. 6) – are other VOC treated similarly, or is a light driven emission of isoprene and other terpenoids considered?

We have modified Section 2 to include more details as suggested by the Referee. We have added the following text:

"BVOC emissions, including isoprene, 2-methyl-3-buten-2-ol (MBO), methyl chavicol and a suite of monoterpenes and sesquiterpenes, are parameterized as a function of vegetation type, leaf area density, temperature and light following standard algorithms (Guenther et al., 1995) and observed leaf-level emissions for this site (Bouvier-Brown et al., 2009). Soil NO emissions are assumed as 3 ngN m^{-2} s^{-1}, which is consistent with previous NO flux measurements in this region (Bytnerowicz and Fenn, 1996) and with soil NO fluxes observed at this forest in 2009 (E. Browne, personal communication, 2010). Deposition follows the standard resistance parameterization (Wesely, 1989; Wesely and Hicks, 2000) and includes stomatal, non-stomatal and ground deposition for 35 species. Parameters for stomatal uptake have been adjusted to optimize agreement with observationally-derived stomatal conductances (Wolfe and Thornton, 2011). Advection is treated as a simple first-order process of mixing with "background air" (Dillon et al., 2002) and is used to help constrain chemical concentrations to observations. Meteorological profiles (i.e. temperature, friction velocity, radiation, etc.) are held constant throughout a model run according to measured and/or parameterized values; CAFE does not include an explicit online calculation of these variables. The model is initialized with chemical concentrations and run to steady state using operator splitting for the diffusive and chemical terms (emission, deposition and advection are also included in the chemical operator). Diffusion is solved with a Crank-Nicolson scheme and chemistry with a forward Euler scheme, both with a time step of 0.05s."

"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 x 10^3 and 2.9 x 10^4 cm^2 s^{-1}, respectively. Above z/h = 1.25, K(z) is based on the values used by Gao et al. (1993)."

"The canopy consists of an overstory dominated by Ponderosa pine (height = 10 m, LAI = 3.2 m^2 m^{-2}) and an overstory of Ceanothus and Manzanita shrubs (height = 2 m, LAI = 1.9 m^2 m^{-2}), both of which are vertically resolved in CAFE."

P2, L23ff: Although the high-time of ozone damage studies might have passed, there are more recent papers around that those mentioned (e.g. Bytnerowicz et al. 2008, Goumenaki et al. 2010, Matyssek et al. 2010, Zapletal et al. 2011). The flux-based index is also vigorously demanded by Matyssek and Innes 1999).

We thank the Referee for these references, which we have added to the text.

P8, L7ff: I am not sure here but Archibald et al. 2010 also suggested an increased OH recycling mechanism. Is this the same here? Is it somewhat related? Or is it something totally different?

A number of "OH recycling" mechanisms have recently been proposed, due to the inability of models to reproduce OH mixing ratios observed in high-VOC environments (Hofzumahaus et al., 2009; Lelieveld et al., 2008; Paulot et al., 2009; Peeters and Muller, 2010; Peeters et al., 2009; Thornton et al., 2002). The study of Archibald et al. (2010) mentioned by the Referee represents an attempt to integrate some of these mechanisms into a global chemical transport model. As outlined in the CAFE evaluation study (Wolfe et al., 2011), we attempted to implement each of these mechanisms but found that none were able to bring out model into agreement with measured OH during BEARPEX-2007. The mechanism implemented in CAFE is designed to maintain OH at observed levels while also controlling RO2, which otherwise grows to unrealistic concentrations. As these details are discussed in the CAFE evaluation paper, we do not feel it necessary to repeat them here; however, we have modified this paragraph as follows:

"This mechanism is a hypothesized fix to the base model OH source, which is otherwise a factor of six too small compared to observations, though we caution that it may not reflect the actual chemistry underlying the observed HO_x abundance and partitioning (Wolfe et al., 2011)."

P12, L5ff: This chapter describes the scenarios applied. However, it would be much more convenient to derive those from a table indicating the basic differences and similarities of the runs.

We have added a new table (Table 2) to summarize the model runs (see end of this document).

P15, L10ff: If the noon-time relative carbon loss at a hot day is 1.4-2.1% it is certainly not 'well in agreement' with annually losses of 4%. This would mean that the relative loss is higher in spring and autumn to match this number. On the other hand, it is a rate well in accordance to estimates (e.g. Sharkey and Ye 2001, Tingey et al. 1980).

In the final sentence of this paragraph, we did not mean to refer specifically to the carbon flux estimate, but also to some of the other values in Table 3 (e.g. the VRVOC emission flux); we have modified the sentence to indicate this, and have added some wording to clarify the carbon flux estimate:

"For comparison, the carbon flux associated with known BVOC (primarily 2-methyl-3-buten-2-ol, methyl chavicol, MT and SQT) is estimated to be 1.8 – 12% of the annual net ecosystem exchange at this forest (Bouvier-Brown et al., 2011). Our model results for highly-reactive BVOC emission fluxes agree well with previous canopy-integrated estimates of 13 – 66 μmol m^{-2} h^{-1} derived from observations at this forest (Table 3)."

P26, L8ff: To investigate the potential effects of deposition on VROX is certainly valuable. However, I wonder why this is none with only a single assumed velocity rate. It would be more convincing if the sensitivity would have been tested over range of velocities. The results could be used to underline the argumentation later on used in this paragraph. Also, I would like to encourage the authors to provide a figure about this.

We have added a new figure to illustrate the effects of changing deposition for VROX levels (see end of this document), and we have modified the text of Sec. 3.6.1 to accommodate this figure as follows:

"Figure 6 illustrates the impact of deposition on modeled VROX concentrations. The slight curvature of this plot reflects the limiting influence of turbulent transport to the surface at higher deposition velocities. At the aerodynamic limit (equal to the deposition velocity of nitric acid, -3.5 cm s^{-1}), canopy-averaged VROX concentrations are lowered by ~40% relative to the case with no deposition."

P6, L12: The abbreviations used in Eq. 1 should be indicated in parenthesis close to the respective descriptions.

Fixed.

P7, L3: sometimes? I don't understand the need for this sentence.

Sentence deleted.

P21, L15: replace 'decreases' by 'changes'

Done.

P27, L11: insert 'or all' after 'fraction'

Our estimate of SOA mass from VROX has been altered to a more conservative value of 0.5 – 0.7 μg m^{-3}, thus we have not made this correction.

P27, L21: reference for this 'likeliness'?

We have added a reference to (Holzinger et al., 2005), which reported PTR-MS observations of unidentified BVOC oxidation products within this forest.

Fig. 5: The description here should be improved. How are the RO2 concentrations derived? Is this necessary for steady state calculations?

Speciated RO2 concentrations are not prescribed but are calculated online in the model using MCM-based chemistry, with modifications as described in this manuscript and the CAFE description/evaluation papers. We have added the following text at the top of Sec.3.5:

"The RO_2 mixing ratio, which represent the steady-state sum of 155 organic peroxy radicals, is not constrained by observations but has been shown to be consistent with previous steady-state estimates for this forest (LaFranchi et al., 2009)."

Cited Literature

Bouvier-Brown, N. C., Holzinger, R., Palitzsch, K., and Goldstein, A. H.: Large emissions of sesquiterpenes and methyl chavicol quantified from branch enclosure measurements, Atmos. Environ., 43, 389-401, 2009.

Bouvier-Brown, N. C., Schade, G. W., Misson, L., Lee, A., McKay, M., and Goldstein, A. H.: Contributions of biogenic volatile organic compounds to net ecosystem carbon flux, Journal of Geophysical Research, [Biogeosciences], in review, 2011.

Bytnerowicz, A., and Fenn, M. E.: Nitrogen deposition in California forests: a review, Environ. Pollut., 92, 127-146, 1996.

Dillon, M. B., Lamanna, M. S., Schade, G. W., Goldstein, A., and Cohen, R. C.: Chemical evolution of the Sacramento urban plume: Transport and oxidation, J. Geophys. Res., 107, 4045, 10.1029/2001JD000969, 2002.

Gao, W., Wesely, M. L., and Doskey, P. V.: Numerical modeling of the turbulent diffusion and chemistry of NO_x, O_3, isoprene, and other reactive trace gases in and above a forest canopy, J. Geophys. Res., 98, 18339-18353, 1993.

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M. T., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A global model of natural volatile organic compound emissions, J. Geophys. Res., 100, 8873-8892, 1995.

Hofzumahaus, A., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C.-C., Fuchs, H., Holland, F., Kita, K., Kondo, Y., Li, X., Lou, S., Shao, M., Zeng, L., Wahner, A., and Zhang, Y.: Amplified Trace Gas Removal in the Troposphere, Science, 324, 1702-1704, 10.1126/science.1164566, 2009.

Holzinger, R., Lee, A., Paw U, K. T., and Goldstein, A. H.: Observations of oxidation products above a forest imply biogenic emissions of very reactive compounds, Atmos. Chem. Phys., 5, 67-75, 2005.

LaFranchi, B. W., Wolfe, G. M., Thornton, J. A., Harrold, S. A., Browne, E. C., Min, K. E., Wooldridge, P. J., Bilman, J. B., Kuster, W. C., Goldan, P. D., de Gouw, J. A., McKay, M., Goldstein, A. H., Ren, X., Mao, J., and Cohen, R. C.: Closing the peroxy acetyl

nitrate budget: observations of acyl peroxy nitrates (PAN, PPN, and MPAN) during BEARPEX 2007, Atmos. Chem. Phys., 9, 7623-7641, 2009.

Lelieveld, J., Butler, T. M., Crowley, J. N., Dillon, T. J., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M. G., Martinez, M., Taraborrelli, D., and Williams, J.: Atmospheric oxidation capacity sustained by a tropical forest, Nature, 452, 737-740, 10.1038/nature06870, 2008.

Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kurten, A., St Clair, J. M., Seinfeld, J. H., and Wennberg, P. O.: Unexpected Epoxide Formation in the Gas-Phase Photooxidation of Isoprene, Science, 325, 730-733, 2009.

Peeters, J., Nguyen, T. L., and Vereecken, L.: HOx radical regeneration in the oxidation of isoprene, Physical Chemistry Chemical Physics, 11, 5935-5939, 2009.

Peeters, J., and Muller, J. F.: HOx radical regeneration in isoprene oxidation via peroxy radical isomerisations. II: experimental evidence and global impact, Physical Chemistry Chemical Physics, 12, 14227-14235, 2010.

Raupach, M. R.: A practical Lagrangian method for relating scalar concentrations to source distributions in vegetation canopies, Q. J. R. Meteorol. Soc., 115, 609-632, 1989.

Thornton, J. A., Wooldridge, P. J., Cohen, R. C., Martinez, M., Harder, H., Brune, W. H., Williams, E. J., Roberts, J. M., Fehsenfeld, F. C., Hall, S. R., Shetter, R. E., Wert, B. P., and Fried, A.: Ozone production rates as a function of NOx abundances and HOx production rates in the Nashville urban plume, J. Geophys. Res., 107, 4146 - 4163, 10.1029/2001JD000932, 2002.

Wesely, M. L.: Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models, Atmos. Environ., 23, 1293-1304, 1989.

Wesely, M. L., and Hicks, B. B.: A review of the current status of knowledge on dry deposition, Atmos. Environ., 34, 2261-2282, 2000.

Wolfe, G. M., and Thornton, J. A.: The Chemistry of Atmosphere-Forest Exchange (CAFE) Model - Part 1: Model Description and Characterization, Atmos. Chem. Phys., 11, 77-101, 2011.

Wolfe, G. M., Thornton, J. A., Bouvier-Brown, N. C., Goldstein, A. H., Park, J.-H., McKay, M., Matross, D. M., Mao, J., Brune, W. H., LaFranchi, B. W., Browne, E. C., Min, K.-E., Wooldridge, P. J., Cohen, R. C., Crounse, J. D., Faloona, I. C., Gilman, J. B., Kuster, W. C., de Gouw, J. A., Huisman, A., and Keutsch, F. N.: The Chemistry of Atmosphere-Forest Exchange (CAFE) Model - Part 2: Application to BEARPEX-2007 observations, Atmos. Chem. Phys., 11, 1269-1294, 2011.

Yi, C.: Momentum Transfer within Canopies, Journal of Applied Meteorology and Climatology, 47, 262-275, 10.1175/2007JAMC1667.1, 2008.

Table 2. Summary of sensitivity simulations. Specific details for individual model runs can be found in the appropriate sections of the text.

Scenario	Parameter(s) adjusted	Values	Section Discussed
Base	-	-	3.1
NS deposition	Non-stomatal (cuticular + ground) O_3 deposition velocity	-0.15 cm s^{-1}	3.3
High reactivity	VRVOC emission flux	30 µmol m^{-2} h^{-1}	3.2
Diffusion sensitivity[a]	Canopy mixing time (τ)[b]	2[c], 4, 6, 8, 10 min	3.4
Temperature sensitivity[a]	Average in-canopy air temperature	10, 15, 20, 25, 30[c] °C	3.4
Ozonolysis OH source[a]	OH yield (y) from VRVOC + O_3	0[c], 0.2, 0.75[d]	3.5
VROX deposition[a]	VROX deposition velocity	0[c], -0.7, -1.4, -2.1, -2.8, -3.5 cm s^{-1}	3.6.1
VROX ozonolysis[a]	VROX + O_3 rate constant	0[c], 1.2, 3.6, 6.0 x 10^{-13} cm^3 molec^{-1} s^{-1}	3.6.3

[a]Also includes high VRVOC reactivity.
[b]Adjusted by uniformly decreasing in-canopy diffusion coefficient, K(z).
[c]Starting value for base and high reactivity scenarios.
[d]For this model run, enhanced OH recycling was not implemented.
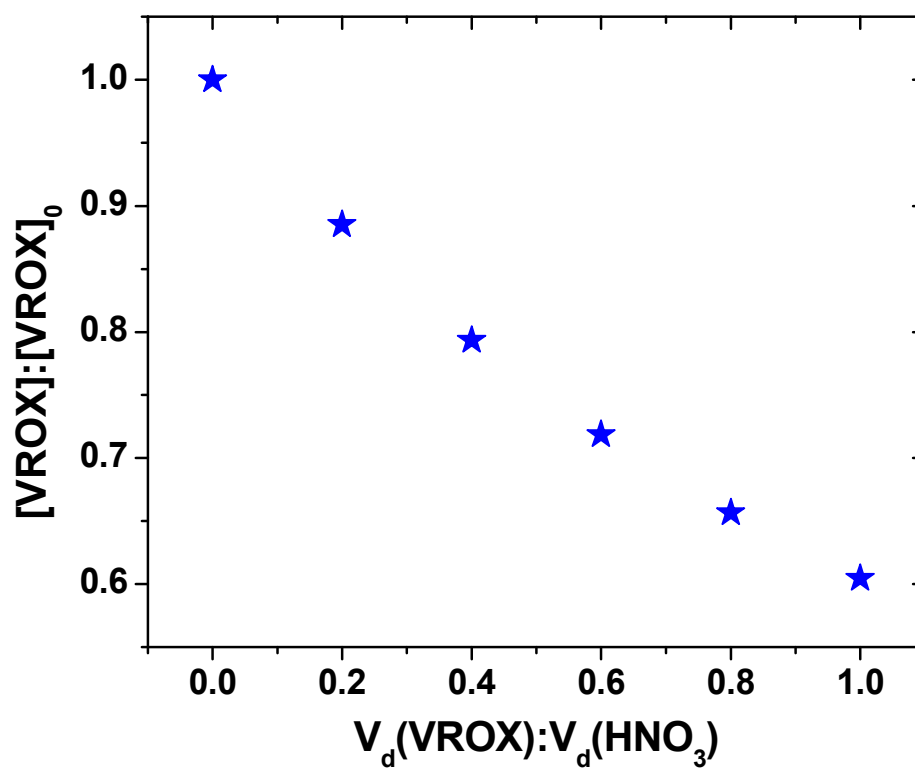
Figure 6. Influence of deposition on modeled VROX concentrations. The VROX deposition velocity (V_d) is given as a ratio to that of nitric acid, which represents the "aerodynamic limit" for deposition. VROX concentrations represent an average over the canopy and are normalized to the concentration for the case with no deposition (3.3 ppbv).