

Author Response to Referee L. Ganzeveld

We thank Dr. Ganzeveld for providing a critical and insightful review of our manuscript. Our responses to questions and suggestions are outlined below.

REFEREE: Pp 21794, line 14-15; **Since you are also in this introduction referring to the relevance of in-canopy interactions for the effective exchange of reactive compounds in regional and global scale modeling (and mentioning feedback mechanisms, see below), you could include some reference to studies that aimed to assess the significance of in-canopy processes on these scales in coupled chemistry-climate studies, e.g., modifying the sentence “gradients in radiation, O₃ and turbulent transport on fluxes of NO_x (Gao et al., 1991; Ganzeveld et al., 2002a and b, Dorsey et al., 2004; Duyzer et al., 2004)”.**

Ganzeveld, L., J. Lelieveld, F. J. Dentener, M. C. Krol, and G.-J. Roelofs, Atmosphere-biosphere trace gas exchanges simulated with a single-column model, J. Geophys. Res., 107, 2002.

Ganzeveld, L., J. Lelieveld, F. J. Dentener, M. C. Krol, A. F. Bouwman, and G.-J. Roelofs, The influence of soil-biogenic NO_x emissions on the global distribution of reactive trace gases: the role of canopy processes, J. Geophys. Res., 107, 2002.

RESPONSE: We thank the referee for providing these references. We will include them in our revised introduction.

Line 23; “biosphere-atmosphere feedbacks”; could you provide an example of such feedbacks? e.g., how ozone stomatal uptake can effect photosynthesis which in turn effects the energy balance and turbulent transport of ozone to the surface and into the canopy.

As CAFE is not currently sophisticated enough to investigate such feedbacks explicitly, we have removed this sentence altogether.

Pp 21795; line 2-3 “CAFE is the first model of its kind to incorporate the extensive master chemical mechanism (MCM)”. This is an interesting claim recognizing the observation that most likely the main limitations in understanding the role of canopy interactions in atmosphere-biosphere exchange are related to our understanding and quantification of biogenic emissions, deposition and, especially, turbulent exchange, and not so much a very detailed representation of chemical transformations.

Following the comments of another referee for the companion manuscript, we have since discovered that CAFE is not the first canopy model to incorporate MCM chemistry, and we have modified this sentence accordingly.

We agree that a lack of observational constraints on physical processes will limit the utility of any resolved-canopy model. As such, we feel that accurate representation of the chemistry is a critical prerequisite for using such models to identify deficiencies in our understanding of

emissions, deposition and transport. Moreover, previous studies at BFRS have suggested that significant gaps remain in our understanding of chemistry in the forest, and that this chemistry can alter fluxes of key reactive species in unexpected ways (e.g. Farmer and Cohen (2008), Kurpius and Goldstein (2003)). By incorporating the MCM, we hoped to address such issues in the greatest detail possible. The MCM is also a pragmatic choice, as it is readily available in a format that does not require us to manually code in many reactions.

Pp 21796, line 15; “36 layers within the forest canopy”; what is the main motivation to use such a large amount of canopy layers recognizing the fact that characterization of the vertical distribution of biomass and sources and sinks is probably mostly limited to characterization of first-order differences between under- and upper storey. Is this main motivated by numerical issues or by the representation of particular processes, e.g., turbulent transport or extinction of radiation?

We set up the model to provide a high degree of resolution within the canopy because this is where the vertical gradients in all processes – emission, deposition, diffusion and chemistry – are largest. By shrinking the grid size and integration interval, we also aim to limit any artifacts caused by the operator-splitting of chemistry and diffusion. We will add some text stating these considerations.

Pp 21798, line 16, here and before there is a reference to the over- and understorey inside the canopy suggesting a distinction between these two parts of the canopy. It is then indicated that the upper- and understorey deposition resistances are scaled to the 36 layers of the canopy scaling with the LAD profile. But would it be not more essential to scale with the radiation extinction profiles jointly with the LAD profiles? In other words, I am asking a short description of the disaggregation method to scale the coarsely calculated source and sink distributions to the 36 layers of the numerical system.

The overstorey and understorey are essentially treated as two different classes of vegetation, each with their own LADF, BVOC emission profiles and deposition resistances. The source and sink distributions are calculated in each model layer using the prescribed temperature and radiation in that layer. For example, during model initialization the radiation profile is prescribed as having an exponential decay in the canopy that is a function of the cumulative LAI. This profile is then used to calculate the stomatal resistance in each layer. Thus, we are calculating emissions and deposition in each layer with appropriate consideration of canopy microclimate, rather than just calculating them at the top and distributing them throughout the canopy. Ultimately these must still be scaled by the amount of leaf area or mass in each layer to give a rate or rate constant.

We will add some additional details to the text to clarify the overall modeling strategy.

Pp21800, line 4-5; Rather than applying a advection rate constant, did you ever consider to “nudge” the model simulated surface or boundary layer concentrations of the “long-lived” species such as ozone, CO (and NOx) to the observed concentrations (e.g. Ganzeveld et al., 2006) ? In this way you implicitly add the advection tendency to the vertical transport tendencies and secure the model to simulate realistic surface and

boundary layer concentrations. This would have also been an optimal approach to consider the role of advection of isoprene and its oxidation products as indicated at pp21802.

We did indeed consider this; and while we were unable to locate a detailed description of how nudging has been implemented numerically, we feel the advection parameterization is qualitatively similar. Our “background” concentrations are analogous to observational constraints used in nudging, and our advection constant of 0.3/hour is analogous to a relaxation constant. If so, model results should be similar regardless of whether this mechanism is imbedded in the chemistry or diffusion operators.

Line 10; it is stated that the diffusion parameters are initialized based on input meteorological parameters. It makes me wonder to what extent the model also simulates online the development of meteorological properties, e.g., temperature and moisture profiles, radiation etc. I am also asking that this would be essential to know in order to study potential feedbacks in the system which cannot be studied in an offline model system with imposed meteorology. Possibly that some more detail on this is given in the accompanying paper but it would be useful to include some short statement about this feature of the model set-up in this paper.

The current version of CAFE is driven with imposed meteorology only and is not designed as a prognostic tool. We will include these details more explicitly in the model description.

Line 16; what is the reason to consider the soil NO emission into the diffusion operator whereas the other source/sinks are considered in the chemical operator?

During model development, we did include NO emission as a 0th-order source in the lowest model box; however, this was found to lead to NO and NO₂ gradients at the ground that were somewhat discontinuous (i.e. much larger concentrations in the lowest box than what would be expected from the rest of the gradient profile). Thus, the choice was primarily for numerical reasons. A similar choice was made for ground deposition.

Pp 21803, line 10-12; what would be the uncertainty in VOC emissions associated with issues on the representation of the extinction of radiation of the coniferous forest? What is the main issue with the representation of this feature relevant to VOC emissions (and deposition)?

According to Schade et al. (2000, AE), the potential issues with using a top-down modeling of radiation attenuation in a coniferous forest are 1) younger needles grow on the periphery of the tree, meaning that older needles (which have a lower emission potential) are not exposed to the same amount of light, and 2) LAI-dependent attenuation does not account for clumping of needles, meaning that light attenuation might be over-estimated (P. pine needles grow in fascicles of 3). Schade et al. (2000) dealt with the first issue by modeling radiation attenuation with several vertical layers instead of horizontal layers. Blodgett forest has grown considerably since that study, and inter-tree shading is no longer negligible; thus, we deemed the standard horizontal treatment more appropriate. We still include a correction for needle age in the MBO

basal emission parameterization. It is not known, at least to us, how needle age affects deposition rates. The second issue is more difficult to address but should be roughly accounted for by an appropriate choice of the radiation extinction coefficient, k_{rad} , as outlined in the companion paper.

We will add some text to summarize these points.

Pp2104, line 25; it is not completely clear from the site information but I could imagine that the soil is relatively well covered resulting in a presence of an inversion inside the canopy with cooler soil temperatures compared to the canopy temperature, which could partly explain a misrepresentation of the deep-canopy profiles. Is there any experimental information available to confirm the presence and relevance of such an in-canopy stratification?

Unfortunately, soil-surface temperatures are not available for BEARPEX-2007, thus we lack information on the temperature profile below 3 m. For this study, we have assumed that temperature continues to increase below 3 m, which is consistent with unpublished data recorded in previous years at BFRS and with temperatures recorded at 1.5 m during BEARPEX-2009. If this “weakly coupled” layer is present, we do not think it is due to a temperature inversion but rather a lack of wind penetration into the deep canopy. Following the suggestions of Referee #1, we have carried out a sensitivity test to examine this hypothesis. We find that decreasing K in the lower canopy does lead to an increase in MT and NO₂ and a decrease in PAN, as we suspected.

We will add some text about this sensitivity test and try to clarify our thoughts on the underlying mechanism of the weakly-coupled ground layer.

Pp21805; line 8; when you use the term “negative-in canopy gradient” you should indicate if a negative gradient reflects a decrease in concentration with height or vice versa. Would it be more useful to apply the terms “deposition gradient” and “emission gradients”?

We will add some text clarifying that a negative gradient implies a decrease in concentration with height. While we agree that deposition and emission gradient terminology could be used for clarification we would prefer to avoid that usage for this particular manuscript where we are providing an estimate of the extent to which chemistry affects gradients as well.

Line 14; why do you not consider the canopy-/ground deposition of MVK and MACR although references are listed that have reported these numbers??

The parameters listed by Zhang et al. (2002) are not based on observations. Moreover, the observed gradient of MVK + MACR (Fig. 2b) suggest that the molecules do not deposit very strongly at BFRS.

This also brings me to a comment that I want to make with respect to the Zhang et al. 2003 reference on “improved” dry deposition parameterizations. I want to express my concern that it appears that this model has been somehow established as a benchmark

model system (also being referenced in the recent Karl et al. 2010 paper on VOC deposition) to treat dry deposition in CAFÉ and regional air quality models system. Possibly that this review is not the most optimal medium to express this concern about other scientific activities but since your model relies largely on this work, I want to stress that according to me the Zhang et al. parameterizations, especially those on nonstomatal uptake, are based on non-existing correlations. The evaluations were only based on reporting the fact that model provided reasonable numbers (the minimum that you would expect from a model) generally being seen for O₃ and SO₂ dry deposition velocities but not based on a direct comparison of simulated and observed V_d's.

We agree with the referee. It was not our intention to imply that this particular reference was somehow an accepted benchmark – only that it is one of only a few papers where such evaluations have been done, even if only to first order. One of the themes in our manuscript is that current resistance parameterizations are likely not as accurate as typically assumed. In particular, the non-stomatal resistances are rarely constrained by laboratory measurements, which is what is needed to accurately identify the underlying mechanisms. Indeed, part of our motivation for creating CAFE was to identify cases where a chemically-driven flux might be misidentified as due to purely physical processes (i.e. thermochemical PAN fluxes). We rely on the available parameterizations, such as those of Zhang et al. (2002, 2003), to remain consistent with other models; however, we do try to point out when modeled fluxes are subject to a (potentially incorrect) non-stomatal deposition parameterization, as in the case of ozone fluxes. Clearly, much work remains to sort out the underlying processes controlling forest-atmosphere exchange.

Pp 21806; the role of HCHO in explaining the discrepancy between the observed and simulated OH reactivity for the cold period is interesting also reading that measurements show noontime maximum mixing ratios up to 12 ppbv. What would be the lifetime of HCHO for the specific conditions in terms of temperature and radiation. Would it be long enough to point at a distant anthropogenic source or biogenic source from high-emitting isoprene landscape. How did the diurnal cycle in HCHO look like? Does it point at an important role of nocturnal processes and downward mixing of HCHO associated with elevated concentrations higher up in the BL?

It is noteworthy that the high observed HCHO mixing ratios improve agreement with observed OH reactivity; however, as we note in the manuscript, forcing the model to 12 ppbv of HCHO leads to a sizable over-prediction of HO₂, which is more difficult to reconcile. As detailed in Choi et al. (2010, ACP), the lifetime of HCHO is estimated to be 3 – 5 hours at BFRS during midday, meaning that biogenic sources from the upwind isoprene emitters may play a large role in its concentration. Oxidation of anthropogenic VOC is thought to be a small source compared to the biogenic component. For other details (e.g. the diurnal profile and the factors controlling HCHO concentrations), we would refer the Referee and interested readers to Choi et al. (2010).

Pp21807, line 12; here you actually make the point that I raised before by explaining what the positive gradient reflects.

We will try to replicate this wording elsewhere as well.

Pp21815, line 1-3, the discussion about the underprediction of O₃ deposition is interesting and especially raises the issue on the model representation of the non-stomatal sinks based on the already mentioned Zhang et al. dry deposition model. This model is supposed to do a better job on non-stomatal uptake compared to the classic Wesely approach but this is apparently not the case for the BFRS site. What is the value of the selected soil uptake resistance? What are the soil properties at this site, is it a site with a relatively high organic content (which would likely enhance soil deposition). It would be useful to see how sensitive the simulated O₃ deposition is to assumptions on the ground versus the cuticular resistances.

Arguably, the Zhang et al. (2003) deposition parameterization does an adequate job of reproducing the observed ozone fluxes (to within 20%). Our concern is whether we are getting “the right answer for the wrong reasons” if cuticular and soil deposition is much slower than what we have modeled.

As detailed in the companion paper, the ground resistance for ozone is 2 s cm^{-1} and the resistance for aerodynamic transfer to the ground is 20 s cm^{-1} . Since these two resistances add in series, ground deposition is mostly controlled by aerodynamic transfer in our model. According to Goldstein et al. (2000), the top 30 cm of the soil contained 6.9% organic matter by weight in 1998; however, we are not aware of a way to work this information into our parameterization of soil uptake.

In regards to the relative importance of different deposition pathways, we attempted to demonstrate this by breaking out the various deposition velocity components in Table 7. Currently, ground deposition contributes $\sim 0.05 \text{ cm/s}$, while cuticular deposition is modeled as 0.12 cm/s . We will state and discuss these values more explicitly in the text.

Pp21816; especially with the NO_y you would expect a very significant contribution by advection due to relative long lifetimes of the various contributing compounds; how much is the relative contribution by advection compared to the local production and downward mixing? This also brings me to a point that I should have raised earlier; how did you initialize the vertical concentration profiles all the way to the top of the vertical domain and how do you treat the concentrations higher up? Did you fix the concentrations at 800m height?

Advection is certainly important in determining absolute concentrations; for example, modeled NO_x would be much lower than measurements if we did not include an advection term for NO₂ of $\sim 200 \text{ pptv/h}$. For vertical fluxes near the surface, however, advection generally plays a minor role compared to chemistry, deposition and emission. The source/sink profile is large and variable for these species in the canopy, and also the timescale for advection is relatively long.

Concentrations are initialized with constant profiles throughout the vertical. We do not fix the concentrations in the top model layer, as this was found to lead to irregular gradients at the top. Instead, we let the concentrations in the top layer “float” and set the boundary condition for

diffusion through the top box to force a constant concentration gradient. We will add some of these details to the model description section.

Pp21818; line 11-12; you state that “if above canopy NO₂ fluxes are a good indicator of the soil NO flux suggesting that the soil NO flux is overestimated by about 50%. This is initially confusing since from the initial introduction of the model soil NO emission flux I inferred that this was scaled to reproduce the observed soil NO flux but this is apparently not the case. It would be useful to already mention this fact with the introduction of the treatment of the soil NO emission flux. Why would the NO₂ flux be a good indicator of the soil NO emission flux? assuming that all NO would be transformed into NO₂ and that a substantial fraction of this would be deposited inside the canopy, you would expect a NO_x/NO₂ canopy top upward flux (apparently, the contribution by advection in NO_x is small compared to the soil NO source) that would be substantially less than the soil NO emission flux. In other words, what is the canopy reduction factor (CRF) for this site?

Soil NO fluxes were not measured during BEARPEX-2007, thus we originally estimated a “reasonable” emission flux of 3 ngN/m²/s by comparison with the available literature. Soil chamber studies were carried out during BEARPEX-2009, and we note in the companion paper that our value is consistent with the (still preliminary) results from those experiments. We will try to clarify these details in the model description.

Comparing the soil NO emission flux with the modeled total NO_x flux at $z/h = 2$, we find a CRF of ~11% for the conditions of our study. Thus, most of the soil-emitted NO_x escapes the canopy (the modeled above-canopy NO₂ deposition velocity is actually ~0.2 cm/s, not 0.4 cm/s as stated in the text). Because the CRF is relatively small and because the modeled NO_x flux is almost entirely comprised of NO₂, we are hypothesizing that canopy-top NO₂ fluxes might provide an indirect check on our soil NO emission flux. Unfortunately these observations were not available during BEARPEX-2007, so we instead try to draw a comparison to the 2005 observations of Farmer and Cohen (2008). This comparison is rough at best, as we note. We will add a brief discussion of the CRF and try to clarify our analysis in the discussion.

Pp21822; in the discussion on the chemical versus the exchange velocities of some of the APN compounds it would be useful to indicate the chemical timescale of the production of the various APN compounds relative to the turbulent timescale as a function of height inside- and above the canopy. According to the discussion the chemical timescales should be really short to effect the exchange velocities but to put this in perspective it would be useful to see how the models turbulent timescales compares to values reported for other sites.

The canopy residence time, according to our current parameterization for eddy diffusivities, is approximately 2 minutes (details on this calculation can be found in Sect. 4.1 of the companion paper). By comparison, the timescales for APN production and loss in the canopy are long. Considering PAN and C4PAN5:

- At the ground, where thermal decomposition dominates, net loss timescales after properly accounting for the equilibrium are 36 and 90 minutes, respectively.

- At the top of the canopy, where these species are net produced, the production timescales are 190 and 36 minutes, respectively.

These results suggest that comparison of the canopy mixing timescale with chemical lifetimes may not be the appropriate metric by which to gauge the potential contribution of chemistry to forest-atmosphere exchange. This is a key point, and we will add a discussion of it in this section.

Pp 21825; in the discussion about AN and HNO₃ deposition, with inferred V_d's large as 2.7 (AN) and 3-4 cm s⁻¹ (HNO₃), which should be close to the turbulent limit, you would expect a negligible role of surface uptake resistance including the stomatal resistance. How do you explain then that you still see a role of the difference in stomatal resistance between the cold and warm period?

It is fortunate that the Referee brought up this point, as it has led us to discover a potential error in the resistance parameterization employed in our model. As currently implemented, the calculation of total deposition resistance in each canopy layer takes the form

$$\frac{1}{R_{dep}(z)} = \frac{1}{R_b(z) + R_s(z) + R_m} + \frac{1}{R_b(z) + R_{cut}}$$

This equation was taken from the work of Gao et al. (1993). On close inspection, however, we now believe that it is not appropriate to include the laminar sublayer resistance, R_b , in the denominators. Considering a case where R_s , R_m and R_{cut} were very small, for example, we would find the total deposition resistance to be $R_b/2$, which is physically inconsistent with the assumptions of the parameterization. We have thus modified the equation to take the form

$$R_{dep}(z) = R_b(z) + \left(\frac{1}{R_s(z) + R_m} + \frac{1}{R_{cut}} \right)^{-1}$$

This results in a decrease of 2 – 3 % in modeled fluxes. The seasonal dependence in HNO₃ and AN fluxes remains. On closer inspection of model parameters, it turns out that this is not due to changes in stomatal uptake as is the case for ozone. Instead, we find that a slightly higher value of the friction velocity during the cool period (by ~8%) propagates into a 3% lower laminar sublayer resistance, which is the primary reason for the 7% seasonal variation in the fast-depositing species.

We will alter the text here and in the companion paper accordingly.

Cited Literature

Choi, W., Faloon, I. C., Bouvier-Brown, N. C., McKay, M., Goldstein, A. H., Mao, J., Brune, W. H., LaFranchi, B. W., Cohen, R. C., Wolfe, G. M., Thornton, J. A., Sonnenfroh, D. M., and Millet, D. B.: Observations of elevated formaldehyde over a forest canopy suggest

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