Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-485-AC1, 2016

Atmospheric Chemistry and Physics
Discussions
Open Access

Interactive comment on “Differences in BVOC oxidation and SOA formation above and below the forest canopy” *by* Benjamin C. Schulze et al.

Benjamin C. Schulze et al.

rob.griffin@rice.edu

Received and published: 30 September 2016

We thank both reviewers for their insightful comments regarding the manuscript. Many of the issues addressed had a substantial impact on the modeling framework and subsequently the results. These are described in detail below.

REVIEWER #1

1. Referee:

The validity of 2 0D box models. Surely the authors are aware that there is efficient mixing of below canopy air with above canopy air, and vice versa. This fact is apparently not mentioned (or at least not thoroughly discussed), and without some additional discussion and figures of actual data, the modeling results are very difficult to interpret.

Printer-friendly version

Discussion paper

The canopy layer makes up <10% of the full boundary layer, so are findings of production rates, etc. normalized or corrected for this small contribution to the mean boundary layer concentrations? Presumably the observations used to constrain the model are vertically resolved, but no vertical profiles of the observations are shown to evaluate how representative the two boxes used for modeling actually are. Oxidation products formed below the canopy, or above, would cycle many times between the two regions over the course of a day, scrambling the signatures and likely diluting the effect of chemistry occurring within the canopy itself.

Author Response:

While our original aim was to consider specifically the changes (relative to above canopy) in gas- and particle-phase chemistry caused by canopy shading, we acknowledge that mixing within forest canopies substantially influences overall forest chemistry (Wolfe et al., 2011; Bryan et al., 2012). Thus, we have added a parameterization of transport between the above- and below-canopy boxes as well as upward from the above-canopy box, as described subsequently. This inclusion of transport also addresses the comment posted by B. Bohn (including citation of Bohn, 2006).

Measured and modeled in-canopy residence times vary substantially depending on the forest environment studied. For instance, Fuentes et al. (2006) report average residence times of ∼8 minutes for a parcel emitted near the ground in a forest with a 26-m high canopy, while Farmer and Cohen (2008) calculate residence times of 1-7 minutes for a forest with a canopy height of only 5.7m. Maximum residence times of up to 50 minutes have been reported in tall forests (Strong et al., 2004). Transport back into the canopy is an even more complicated process, as coherent structures (i.e., sweeps of air downward), rather than simple turbulence, often produce the majority of scalar fluxes (Steiner et al., 2011).

Rather than simply selecting a reasonable characteristic residence time, we have run a sensitivity study to optimize it based on model output. A cost function has been applied to compare modeled and measured diurnal concentrations of methacrolein and methyl vinyl ketone (MACR+MVK) above and below the canopy, in order to determine ideal transport residence time values. In addition, we have included a diurnal vertical dilution rate based on the average of methanol and acetaldehyde above-canopy vertical loss calculated by the FORCAsT 1-D model for summertime conditions (Ashworth et al., 2016).

Resulting changes in manuscript:

The revised manuscript will show a subsection within the Methods that describes this transport parameterization in detail, and the revised Supplemental Information will display a figure to portray the cost function output. In addition, a new sentence will emphasize that because the above-canopy model was based on conditions observed only a few meters above the canopy, the modeled concentrations of oxidation products and SOA cannot be assumed to exist throughout the entire mixed boundary layer. This is appropriate for the emphasis of the paper on how daytime in-forest NO3 chemistry impacts SOA.

2. Referee:

While the MCM is becoming more useful, it is still rather a dangerous model to use for SOA studies because the mechanisms are not complete at the 5% level of carbon mass, but that 5% might be 90% of carbon capable of forming SOA. For example, the MCM does not include auto-oxidation of monoterpenes (Ehn et al Nature 2014 and others) - thereby missing a likely significant fraction of SOA mass, as well as highly oxygenated nitrates (Lee et al PNAS 2016). How might this affect the conclusions?

Author Response:

Despite the detail included in and the recent advances that have been made to the MCM, we agree that only modeling the partitioning of MCM oxidation products may result in an under prediction of SOA (depsite the MCM being among the most complete mechanisms available). Rather than simply explaining the likely under-prediction, we have altered the model to include two mechanisms of aerosol formation other than simple partitioning of the MCM oxidation products: production of extremely low-volatility organic compounds (ELVOCs) formed from the autooxidation of α-pinene and isoprene (Ehn et al., 2014; Jokinen et al., 2015; Mentel et al., 2015) and reactive uptake of isoprene epoxydiol, glyoxal, and methylglyoxal onto aerosol surfaces (Paulot et al., 2009; Ervens and Volkamer, 2010; Lin et al., 2012; Li et al., 2015). ELVOCs are thought to constitute a substantial fraction of total SOA in environments with low overall OA mass loadings (Ehn et al., 2014), and the reactive uptake of isoprene products has been shown to constitute over half of total SOA in isoprene-dominated forests (Li et al., 2015). In this way, we address both the under-prediction of total SOA addressed here and the high fraction of organic nitrate products contained within the simulated SOA in our original manuscript (see referee #1, point 5 below).

In terms of ELVOC production, α-pinene and isoprene are each assumed to produce one ELVOC product from oxidation by both O3 and OH, following published yields for each of the four relevant reactions (Jokinen et al., 2015). The ELVOC products observed in chamber studies are often either C10 monomers or C19-20 dimers from α-pinene oxidation and C5 monomers from isoprene oxidation (Jokinen et al., 2015); however, as monomers are generally observed with a mass spectral signal an order of magnitude higher than those of dimers, and in order to ensure that uncertainty in the modeling parameters results in under-prediction rather than over-prediction of ELVOC mass concentrations, both products are assumed to be monomers. These ELVOCs are highly oxidized species with multiple hydroperoxide moieties (Mentel et al., 2015) and have chemical formulas of C10H16O9 and C5H8O8 from α-pinene and isoprene oxidation, respectively. These specific products were selected based on their intensity in observed ELVOC mass spectra and the fact that their O:C ratios are generally representative of the average ELVOC product distributions observed (Ehn et al., 2014; Jokinen et al., 2015).

In order to model the reactive of uptake of isoprene epoxydiols, glyoxal, and methylglyoxal, we adopted the method of Li et al. (2015). The formula for the rate of uptake is dependent on the mass concentration, the thermal velocity of the species, the ambient aerosol surface area, and a reactive uptake coefficient (Li et al., 2015). Ambient aerosol surface area data during CABINEX were obtained from VanReken et al. (2015). In accordance with Li et al. (2015), glyoxal and methylgloxal were both assigned a dimensionless reactive uptake coefficient of 2.9 x 10-3, following the findings of Lin et al. (2012), while the reactive uptake of epoxydiols was assumed to be 0.5 x 10-3, representative of conditions modeled in Michigan.

Resulting changes in manuscript:

The revised manuscript will include a section in the Methods describing these changes in detail, and the results will be updated accordingly.

3. Referee:

Lack of deposition. Deposition of oxidation products appears not to be included. This seems rather problematic for interpreting the SOA formation potential. Deposition in the canopy will be much more significant than above the canopy, at least during nighttime, and during daytime deposition from both would significantly impact the available vapors for SOA formation, especially given the equilibrium partitioning assumption used for modeling SOA. With any horizontal wind through the canopy, there will presumably be a significant depositional sink given the proximity to canopy elements. What is the lifetime of a product formed in the canopy against deposition compared to mixing out of the canopy layer or to SOA formation? How was the vertical distribution of the condensation sink constrained?

Author Response:

Please see the earlier author response about ignorance of transport. Dry deposition of both gases and aerosol is now included in the modeling framework.

Printer-friendly version

Discussion paper

In the above-canopy model, deposition is assumed to occur onto the top of the canopy, and the resistance to deposition is determined using Meyers and Baldocchi (1988). Deposition velocities for each chemical species are calculated based on resistances from the quasi-laminar boundary layer and the leaf mesophyll, cuticular surfaces, and stomata. A thorough description of the particular equations used in this method can be found in Bryan et al. (2012). The above-canopy box height was assumed to vary diurnally based on the boundary layer values utilized in Giacopelli et al. (2005) for a previous box model of the PROPHET location. As our model does not calculate aerosol sizes, size distribution data obtained from VanReken et al. (2015) were used to calculate a volume-weighted average settling velocity of aerosol particles.

In the below-canopy model, deposition was assumed to occur to the ground and was modeled following the method of Gao et al. (1993). The box height was set to 6m (the assumed bottom of the canopy layer or top of the trunk space) for the entire diurnal period. In a sub-canopy environment, turbulence may result in upward transport and deposition onto foliage in the bottom of the canopy layer; however, as modeled concentrations of certain oxidation products (MACR+MVK and HCHO) are lower than those measured assuming deposition only occurs to the ground, no loss to foliage in the trunk space was considered.

Resulting changes in manuscript:

The revised manuscript will include a section within the Methods that describes the parameterization of deposition, and the results will be updated accordingly. The revised supplemental information will include a table that contains a description of the specific parameters used in the calculation of these resistances. For the majority of VOC oxidation products, these parameters, Henry's Law constants and diffusion coefficients, for example, were obtained from Nguyen et al. (2015). Data obtained elsewhere in the literature are specified as such in the supplemental information.

4. Referee:

Given 2 and 3 above, the discussion on SOA seems rather limited in its usefulness to actual SOA formation potential. In addition, more interesting would be to incorporate the lapse rate and vertical mixing impacts on SOA formation given the cycling of oxidation products across a 10K temperature gradient.

Response:

Having addressed issues 2 and 3, we believe model results with respect to SOA formation potential are now valid. In addition, we wish to stress that the aim is to evaluate impacts of shading on chemistry.

Resulting changes in manuscript:

None.

5. Referee:

If I understand correctly, RONO2 form âĹij45% of the SOA mass in the model. In the SE U.S., it was more like 3-10% (Xu et al PNAS 2015, Lee at al PNAS 2016). The authors cite Fry et al, and note consistency with that study, but, are the distributions of BVOC emissions at all similar between Manitou and UMBS? Presumably the high fraction of particulate RONO2 at Manitou was the dominance of monoterpenes, is that the case at UMBS?

Author Response:

We thank the reviewer for highlighting this discrepancy. We believe that the high fraction of RONO2 within the SOA was largely the result of a both a lack of SOA production (by mechanisms not captured by simple reversible partitioning of MCM oxidation products) and a lack of nitrate hydrolysis within the SOA. The first of these issues was addressed above (reviewer #1, point #2). However, in order to improve the accuracy of the model, we have also added a mechanism for nitrate hydrolysis within the aerosol. The heterogeneous hydrolysis of organic nitrates has recently received significant attention. Multiple chamber experiments on the hydrolysis of both α-pinene and isoprene nitrates have been performed, and while many questions remain regarding the specific mechanisms of hydrolysis, these studies have defined lifetimes or loss rates of nitrates within organic aerosol, necessary parameters for modeling simple first order loss (Cole-Filipiak et al., 2010; Darer et al., 2011; Hu et al., 2011; Bean and Hildebrandt Ruiz, 2016; Rindelaub et al., 2015).

In order to characterize more accurately the nitrate content of the SOA, both isoprene and α-pinene nitrate products are assumed to undergo first-order loss within the aerosol. Isoprene nitrate loss is parameterized using the average lifetimes found by Hu et al. (2011). As primary and secondary nitrates are found to only slowly hydrolyze even under the most acidic conditions observed in aerosol (τ = 500 hr at pH = 0), which are not likely to occur at PROPHET, those products have an effective hydrolysis loss rate of zero within the model (Hu et al., 2011). However, tertiary nitrates, which are efficiently hydrolyzed even at neutral pH, have an effective lifetime of 0.67 hours, corresponding to a first-order loss rate of 1.73 x 10-5 s-1 (Hu et al., 2011).

Two sets chamber experiments have been performed regarding hydrolysis of α-pinene organic nitrates within organic aerosol (Rindelaub et al., 2015; Bean and Hildebrandt Ruiz, 2016). Of these, only the study by Bean and Hildebrandt Ruiz (2016) quantified rates of nitrate hydrolysis within the aerosol. The hydrolysis rate was found to be highly dependent on RH; experiments with RH 20-60% produced a hydrolysis rate of 2 day-1, while those with RH above 70% had rates as high as 7 day-1 (Bean and Hildebrandt Ruiz, 2016). As RH values measured during CABINEX are generally above 60%, we utilized the rate of 7 day-1, corresponding to an organic nitrate lifetime of 3.4 hr.

Resulting changes in manuscript:

The updated manuscript will include a short section within the Methods describing this change and will update the results accordingly.

6. Referee:

Printer-friendly version

Discussion paper

Odd model set up choices. The "urban" case, which apparently mixes data from Detroit and Houston is a bit odd. Why not make it purely hypothetical? I don't see why the authors fix the NO/NO2 ratio - that would seem to be a good metric to test the chemistry in the model as it is sensitive to total RO2, not just HO2 and O3. Moreover, as NOx increases the NO/NO2 ratio isn't going to be fixed, there are important feedbacks between O3, HO2, RO2, and NO concentrations that are important and why one would want to use a model in the first place. Fixing the NO/NO2 ratio makes nitrate formation rates a linear extrapolation with increasing NOx when the non-linear couplings of HOx and NOx might lead to a different result than found here.

Response:

We agree that the overall method of testing the sensitivity of the results could be better designed. In order to more reasonably test the sensitivity of forest environments to different concentrations of anthropogenic pollutants, we have removed the second and third model cases and replaced them with a more structured sensitivity analysis. This method independently modifies the O3 and NOx concentrations by scaling the diurnal profiles of O3, NO, and NO2 under different NO/NO2 ratios. As a result, we are able to evaluate the results under high pollutant concentrations when NO3 formation is favored (high NOx, high NO2/NO ratio) and when NO3 formation is suppressed (low NOx, low NO2/NO ratio).

Resulting changes in manuscript:

The revised manuscript will include an updated section on input data in the Methods and will include updated results accordingly.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-485, 2016.