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Interactive comment on "Biogenic SOA formation through gas-phase oxidation and gas-to-particle partitioning – comparison between process models of varying complexity" *by* E. Hermansson et al.

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Thank you for the comments on the manuscript.

Each comment will be listed with the following answer.

1.) "A recent study by Ehn et al. (2014) found large yields of highly oxygenated products in the first step(s) of the oxidation of _-pinene under atmospherically relevant conditions in chamber experiments. These highly oxygenated products with both monomer

or dimer patterns were irreversibly taken up by the seed particles, even at very low particle loadings. This immediately points to limitations of the concept of equilibrium gas-to-particle partitioning in general, and of the VBS scheme (log10 of C*=0 is not defined) specifically. However, the implementation of gas-phase reactions shown in the extended materials of the Ehn et al. (2014) study (Extended Data, Figure 7) into the Master Chemical Mechanism appears to be straight forward, and should be included in the current model comparison."

Answer:

This is indeed an interesting subject and we are currently working on implementing ELVOC-chemistry based on the study by Ehn et al. (2014) into our models in another ongoing study. Since the Ehn-study was published quite recently and after the submission of this manuscript, and furthermore that the implementations of these gas-phase reactions are not that straight forward, we feel it is better suited in a separate study, where also particle chemistry is included. To emphasize that this is an important area for further studies we will add the following paragraph to the manuscript on page 11012 after line 17:

"Moreover; a recent study by Ehn et al. (2014) indicates that the ozonolysis of alpha-pinene might lead to products of extremely low volatility that condense irreversibly to form SOA and thus have the potential to increase the SOA yield significantly. These products are currently not included in the model simulations in this study but we are planning to implement them in future studies."

We did however one simulation where the alpha-pinene + ozone reaction lead to a 7 % molar yield of ELVOC (based on results from Ehn et al. (2014)) which lead to about a factor of 3 increase in mass concentration. We do not want to publish this result since we want to wait until we have implemented the complete ELVOC-chemistry.

2.) "A discussion of the assumptions behind the use of an air mass trajectory that happens to pass (close-by) all the three sites (at respective ground level) needs to be provided. Important details about the procedure to derive this speciïňĄc trajectory with the HYSPLIT model are missing. In the boundary layer, the concept of a single trajectory being representative for the path of an air parcel does not hold since the air mass parcel will quickly loose its identity by turbulent mixing (Stohl et al., 1998). The accuracy of trajectory calculations will also be affected by the orography between the station locations. Terrain-following trajectories usually neglect vertical motions of synoptic origin, which could quickly modulate the air mass in the boundary layer"

Answer:

It is true that an air parcel loses its identity quickly in the boundary layer by mixing with other air parcels (Stohl, 1998). A single trajectory does not represent the entire source area when talking about point sources, but new particle formation and growth of particles by biogenic vapors in northern Scandinavia are large scale phenomena (Hussein et al., 2009; Tunved et al., 2006; Väänänen et al., 2013). Therefore the air parcel mixes with similar air around it, which means that the uncertainty created by choosing a single trajectory is not large.

One should also keep in mind that this is not a closure study. Therefore the measured values should not be compared directly to the modeled ones. They are there to give the initial particle size distribution at Abisko, and to provide realistic values for comparison.

On page 11007, after line 22, we will add this new paragraph describing the details about deriving the trajectory:

"The three stations are located on a west-to-east line roughly 200 km apart from each other. Description of the stations and the instrumentation can be found in Väänänen et al. (2013). Even though the Pallas station is located on a hill top, all three stations are considered as ground level sites in this study. Since the boundary layer is assumed to be well-mixed, the air arriving to the stations represents the boundary layer in a larger scale. The specific trajectory was chosen by analyzing hourly HYSPLIT trajectories (Draxler and Rolph, 2013) from years 2005-2007 arriving at Värriö at the altitude of

the station. The analysis was limited to trajectories arriving from the Atlantic Ocean and passing over Scandinavia between latitude parallels 67°6′ N and 69° N within 1000 m above ground level in order to ensure similar source areas and clear transport route between the stations. Furthermore, the trajectories had to pass over Abisko and Pallas within 25 km from the respective station during its path. This is in line with the general 10-30% uncertainty of trajectories (Stohl, 1998). The aerosol particle number size distributions at the three stations were analyzed at the times when the trajectories passed them. A trajectory that had a low particle number concentration in Abisko which increased between the stations was chosen. Additionally, this trajectory had to remain in the boundary layer between the stations with no precipitation along its path."

3.) "The description of fragmentation in 2DVBS does not state whether fragmentation takes place only for the first oxidation step or also for the subsequent oxidation steps. Did the authors took any precautions to avoid excessive fragmentation of smaller molecules, forming upon first functionalization (that will have high O:C due to short chain length), in the subsequent oxidation steps?"

Answer:

In the first oxidation step (alpha-pinene + O3) in the 2DVBS it is assumed that fragmentation does not take place, see page 11009 Lines 22-25. All subsequent oxidation steps include fragmentation as described in Appendix A. The fragmentation scheme is based on Jimenez et al. (2009), with the exception that fragmented molecules are assumed to have the same O:C-ratio as the parent molecule. Since we wanted to keep the scheme similar to that of Jimenez et al. (2009) we did not add any restrain to fragmentation of small molecules; all bins have the same fragmentation ratio relationship (O:Cˆ1/6). The description of functionalization and fragmentation can be made clearer in the manuscript. In section 2.3.2 on page 11009, after the sentence that ends on line 25 we will add:

"This means that the oxidation of α-pinene by ozone is assumed to include no fragmentation."

In Appendix A we will change the first sentence to:

"Each oxidation step, after the oxidation of α-pinene, in the 2DVBS includes functionalization where between 1 and 3 oxygen atoms are assed, causing a reduction in saturation vapor concentration (C*) and the O : C-ratio to increase."

4.) "A general problem of using the volatility (C*) axis is that since C* depends strongly on temperature (Clausius Clapeyron equation, Eq. (A-2)), a temperature change by 10 degrees or more will cause a change of the bin assignment. This is less critical when relatively low values of Hvap is used, as in the 1DVBS approach (with Hvap = 30 KJ/mol). It is however critical for the Hvap dependence on C*298 (which refers to Donahue et al., 2006) used in the 2DVBS model that results in higher values (65-129 KJ/mol). Diurnal variation of ambient air temperature by 10 degrees is quite common in summer. At a temperature of 281 K the bin assignment in the 2DVBS (with reference temperature of 298 K) will change more or less by one decade (depending on the volatility bin). Did the authors consider the bin shifting within (and beyond) the VBS scale for changing temperature?"

Answer:

The volatility axis in the VBS-scheme in the chemistry module is log10C*298 (saturation concentration at the reference temperature 298 K). This means that the products are distributed in this fixed grid during first generation chemistry and subsequent functionalization/fragmentation. After the products have been distributed in the VBS grid in the chemistry module, their saturation vapor pressures (which are used in the condensation/evaporation algorithm) in each VBS bin are calculated with the Clausius Clapeyron equation. The saturation vapor pressures of the products are not constrained to the VBS-grid. The calculated saturation vapor pressure for each product is saved every simulated 10 minutes along the trajectory and plotted in Fig. 5 and 6. Since the saturation vapor pressure can fall between the VBS-bins, they are splitted back to the grid

again. The products that fall outside the grid are placed in the bins with highest and lowest saturation concentration respectively. To clarify this, we will add the following sentences to section 2.3.1 after the sentence that end on line 24 (page 11008):

"After the products in the VBS simulations have been distributed in their respective VBS-space due the gas-phase reactions, their temperature dependent saturation vapor pressures are calculated. These pressures, no longer bound to the VBS-grid, are used in the condensation/evaporation module."

5.) "It is clear from the title of the paper and section 2.4 (Processes not investigated in this study), that condensed phase reactions (accretion reactions, oxidative reactions, and aqueous phase reactions) were not topic of this paper. However, there is some evidence that SOA is not fully describable through equilibrium partitioning theory on short timescales (as in chamber experiments) likely as result of condensed phase reactions (Kroll et al., 2007), which could explain that the volatility of model SOA tends to be substantially higher than that of ambient organic aerosols (Cappa and Jimenez, 2011). The authors should add a discussion of the uncertainties of the modeled SOA in this respect."

Answer:

We will add the following paragraph on page 11020, line 22:

"Other uncertainties, beyond the scope of this study, include particle-phase chemistry and aerosol phase state. Studies have shown that these processes have the potential to affect SOA formation (e.g. Chan et al., 2007; Kroll and Seinfeld, 2008; Perraud et al., 2012; Roldin et al., 2014). The diurnal trend, caused by temperature variation, of the particle mass concentration in the base case scenarios in this study might in part be a result of excluding particle chemistry and assuming equilibrium partitioning. If the condensing gas-phase species are allowed to undergo chemical reactions in the particle phase to form low volatile products, evaporation and re-condensation of these species will be inhibited."

Technical corrections

“Abstract p 11002, line11: Replace “allows us to, under atmospheric relevant conditions compare” by “allows us to compare, under atmospheric relevant conditions,”.”

Answer:

We will change this.

“P.11012, lines 4-8; Figure 2: Since an aerosol dynamics model was used (with only condensation) it would be more informative, especially with respect to CCN growth, to show how the modeled number size distribution changes as function of time (instead of volume concentration which merely is mass concentration divided by density). In Figure 2 initial distribution (at Abisko) together with size distributions at Pallas and Värriö should be plotted for ADCHEM, MALTE-BOX, and ADCHEM DensMalte.”

Answer:

We will replace Figure 2 with a new figure (see attached Fig. 1. In this figure we have chosen to show the initial size distribution together with distributions at times with local maxima and minimum in volume concentration since the difference between the models are highest at the local maxima. We will replace the text at page 11011-11012, lines 22-8, with the following text:

“Condensation was the only aerosol dynamics process included in both box models for the comparison and the result is shown in Fig. 2. The upper panel shows the volume concentration of SOA along the trajectory, where the dotted blue line is the result from the MCM-ADCHEM coupling and the pink, dashed line the result from the MCMv3.2 being coupled to the MALTE-BOX model. The discrepancy between the modeled mass concentrations is largely due to the overall lower densities of condensable organics in MALTE-BOX compared to those in ADCHEM. These densities are used when the change of particle mass during condensation (or evaporation) are translated to the corresponding change in particle volume. The solid blue line in the upper panel in

Fig. 2 is the result of using the same method as in MALTE-BOX to parameterize the densities of the condensing organic oxidation products in ADCHEM (see Sect. 2.1.2 for more details about the parameterizations). The lower panel in Fig. 2 shows the number size distribution at different times along the trajectory (represented by different colors). The smaller particles seem to grow faster in MALTE-BOX compared to those in ADCHEM, especially during nighttime when the temperature is low. Considering the complexities of both models, they agree fairly well, with a maximum difference in volume concentration of 14 % at t = 129 hours along the trajectory (3rd of August 03 UTC), corresponding to a maximum difference in the modeled geometric mean diameter of about 10 %.”

The following figure text to the attached Fig 1 will be added:

“Fig. 2. Evolution of particle volume concentration (upper panel) and particle number size distribution (lower panel) modeled with the aerosol dynamics box model MALTE-BOX or ADCHEM (modeled with a constant SOA density of 1400 kg m-3 or SOA densities from MALTE-BOX). The color of each size distribution plot represents the size distribution at a specific time along the trajectory, indicated by the corresponding color of the vertical line in the upper panel.”

“P.11020, line 20-21: This is an important conclusion that needs to be added to the Abstract.”

Answer:

We will add the following sentence to the abstract (page 11002, line 21):

“Based on the result from this study, fragmentation should be included to get a realistic SOA formation.”

“P.11021, Equation (A-2): Equation (A-2) contains a typo. It has to be “ΔHvap/R” and not “ΔHvap/T ”.”

Answer:

This will be changed.

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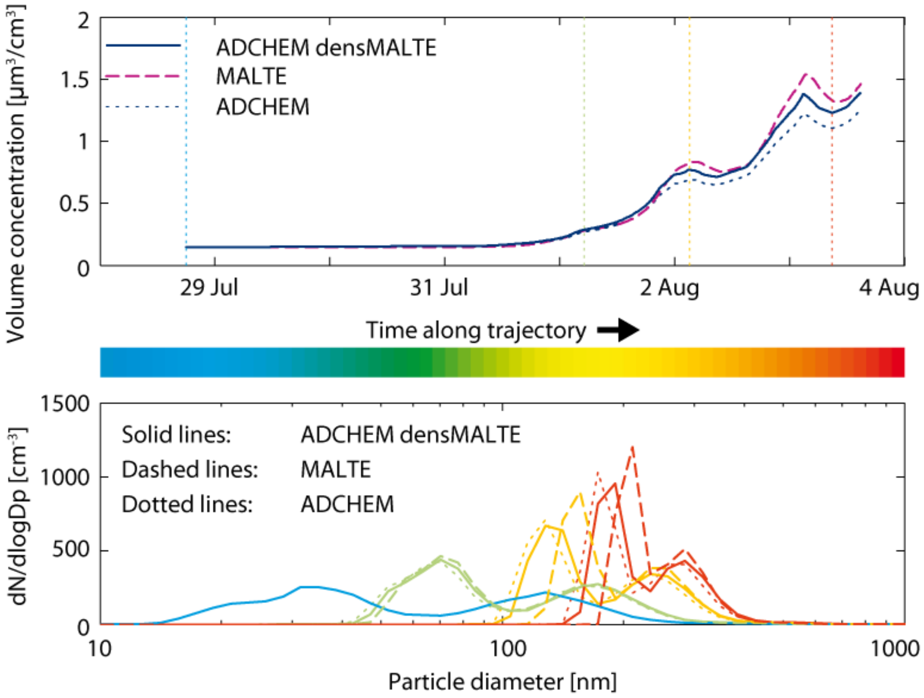

Fig. 1. Fig. 2. Evolution of particle volume concentration (upper panel) and particle number size distribution (lower panel) modeled with the aerosol dynamics box model MALTE-BOX or ADCHEM (modeled with a con