Answers to M. Karl:

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 specific 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 67º6´ N and 69º 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 ($O:C^{1/6}$). 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 $\log_{10}C^*_{298}$ (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.

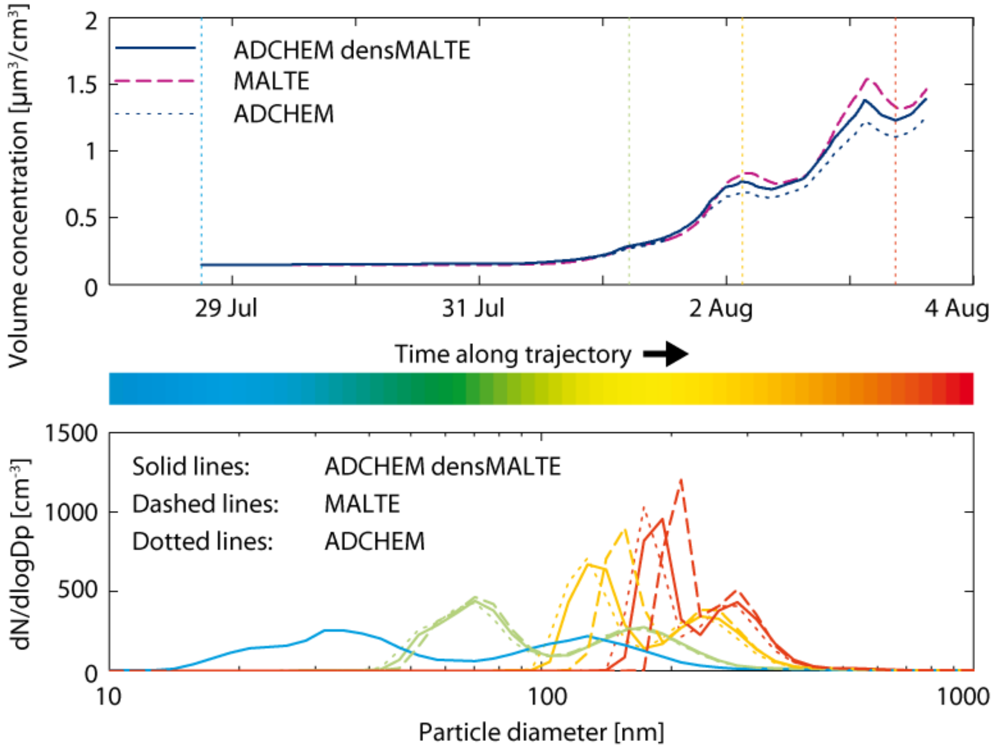
"P.11012, lines 4-8; Figure 2: Since an aerosol dynamics model was used (with only condensation) it would be more informative, especially with respect to CCN growth, to show how the modeled number size distribution changes as function of time (instead of volume concentration which merely is mass concentration 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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Answers to Anonymous Referee 2:

1.) “Although this is a very useful study, it’s not clear why the authors choose unrealistic parameters for the 1D VBS: e.g. very low OH reaction rate, and a small T dependence of enthalpy of vaporization(delH). They could have had delH varying with T as in the 2DVBS.Finally Shrivastava et al. [2011] demonstrated that using 7.5% increase of oxygen per aging step leads to large underpredictions of O:C ratio compared to field measurements during MILAGRO 2006. Why not use 15% oxygen added in the 1D VBS? I would think this would result in a more consistent comparison.”

Answer:

As stated on page 11005 lines 14-17 we wanted to compare the near-explicit modeling of SOA formation with VBS approaches that have been applied in previous model studies. The 1DVBS simulation is based on the EMEP chemical transport model (as stated on page 11008 Line 25, page 11009 Lines 1), which is a model that has been important during development of air quality policies in Europe. The aim of our study was to investigate the implementation of different gas-phase oxidation scheme used to model SOA formation since this includes many uncertain parameters. We did however choose to present results from sensitivity tests on the 2DVBS simulation instead of the 1DVBS.

Regarding the specific parameterizations mentioned:

-Aging: EMEP is not the only model that uses a 1-dimensional VBS and a common feature of these models is an overprediction of SOA when aging of biogenic SOA is included:

> - The chemical transport model, PMCAMx (Lane et al., 2008) does not even include aging of biogenic SOA in their base case scenario due to large overpredictions when they do include it in a sensitivity test.
>
> - In Shrivastava et al. (2011) they also chose to exclude aging of biogenic SOA (sorted under the acronym V-SOA – SOA formation from biogenic and traditional anthropogenic VOCs), also due to overprediction of SOA in other studies where it is included (Dzepina et al., 2011) and with the argument that biogenic SOA molecules are smaller (less carbon atoms) than POA (that uses an order of magnitude higher reaction rate).

This overprediction of biogenic SOA in 1-dimensional VBS when the aging is included with a realistic aging rate is probably due to the fact that they often do not include fragmentation (see page 11018 lines 2-6). A 15 % mass increase per oxidation step will lead to an even bigger overprediction if a realistic aging rate is used. If the slower aging rate is used, the mass increase per oxidation step will not affect the result in any significant way since almost no aging takes place.

-Enthalpy of vaporization: other studies have also used a fixed value of 30 kJ/mol to represent the various temperature effects during SOA formation (Lane et al., 2008; Pathak et al., 2007).

2.) “Page 11015 Lines 13:15: The authors mention that 2DVBS simulations show a strong diurnal trend in O:C ratio compared to 1D VBS. But there is no figure supporting this observation. Am I missing something?”

Answer:

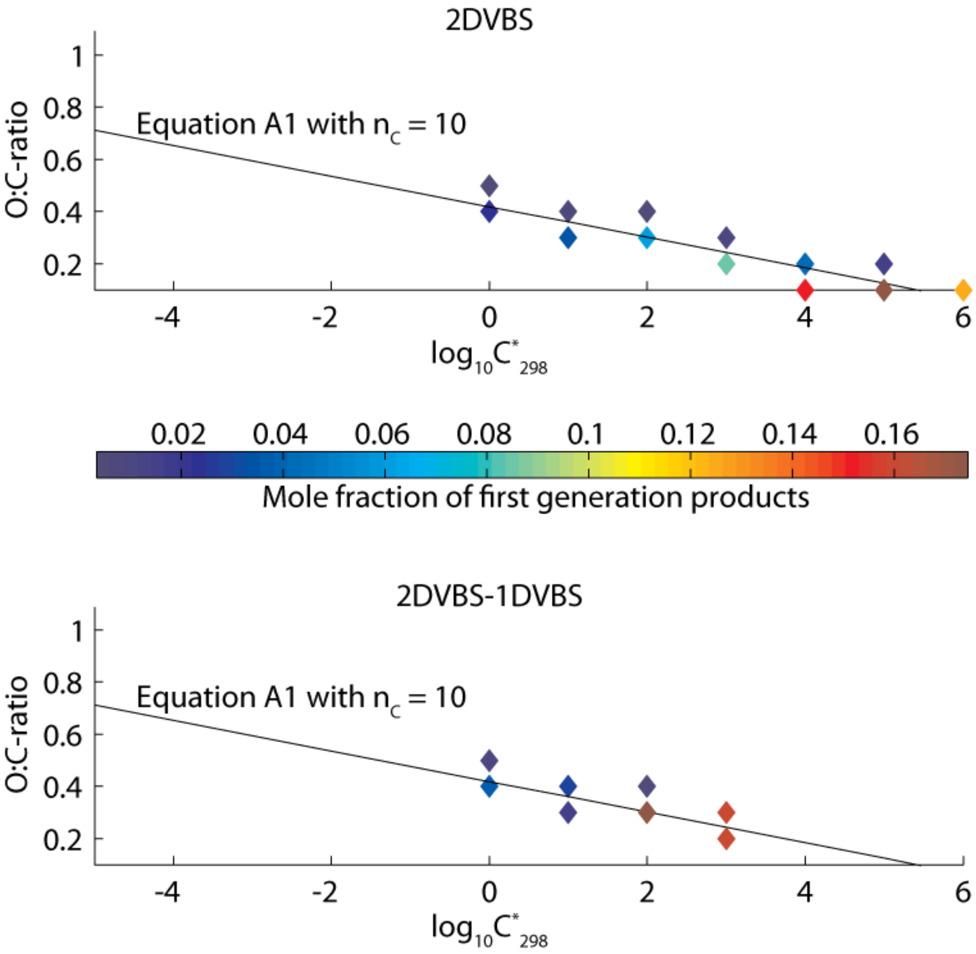
It is not explicitly stated in figure 6, but the trend in O:C-ratio of the three simulations can be seen in figure 6 by looking at the time evolution of the particle properties. Since this figure already is quite busy, we chose to have the time along the trajectory indicated by marking the particle properties at the stations (filled circles in different colors) with arrows in-between, instead of explicitly have the dates in the figure. The variation of O:C-ratio in the MCM and 2DVBS simulations is due to the diurnal trend in temperature; the O:C-ratio in the 1DVBS simulation show a much smaller variation.

3.) “Page 11016 Lines 5-10: The authors assume that most first generation oxidation products do not include fragmentation. But Figure A1 shows that even for O:C ratio=0.2, 70% of the products in the 2D VBS are fragmenting. This seems contrary to their description. Note that first generation oxidation products of a-pinene have O:C between 0.2-0.4. They also need to better explain why O:C ratio of first gen products in the 2D-1D VBS will be larger than the 2DVBS. It would be helpful to demonstrate with a figure how the O:C of the first generation oxidation products is a function of Equation A1 for the 2D-1DVBS vs the 2DVBS.”

Answer:

Page 11016 Lines 5-10 states that most first oxidation steps do not include fragmentation. By that we mean that the a-pinene + ozone reaction does not include fragmentation. The oxidation of the products that are generated in this step do however include fragmentation. The range of O:C-ratio of these products are illustrated in figure A1. We agree that the explanation to the difference in O:C-ratio of the first generation products in the 2DVBS-1DVBS vs the 2DVBS could be made clearer. To clarify we will add a figure (see attached Fig. 1) and change Page 11016 Lines 5-10 to:

"However; due to the relationship between carbon number and volatility in the 2DVBS simulation (Eq. A1) and the assumption that the oxidation of α-pinene by ozone do not include fragmentation (i.e.: most first generation products will have carbon number 9 or 10), the O: C-ratio of the first generation products will be higher in 2DVBS-1DVBS than in the base case 2DVBS. This is illustrated in Fig and explained as follows: Since the carbon number of the products are known, the O : C distribution of the products can be calculated based on the known volatility distribution of the first generation products. Figure illustrates how the O : C-ratio is a function of the volatility when the carbon number is 10 (black line). The first generation products in the 2DVBS-1DVBS (lower panel, Fig) are distributed towards lower volatilities than the 2DVBS (upper panel, Fig) which explain their higher O : C-ratios."



The figure text to the attached Fig. 1:

“First generation product distribution in the 2-dimensional VBS space modeled with the 2DVBS simulation (upper panel) and the 2DVBS-1DVBS simulation (lower panel). The black line shows the linear dependence between the O : C-ratio and volatility when a carbon number of 10 is assumed.”

4.) “Page 11017: Line 5-13: The authors mention that the 2DVBS-MCM particle growth is much lower than the 2DVBS. Their Figure 7a shows that the 2DVBSMCM is closer to observations than 2DVBS. Can the authors comment on whether the aging approximation in the 2DVBS about fragmentation equal to OtoC raised to power of 1 by six is reasonable based on this exercise?”

Answer:

Based on this exercise we can see that the aging mechanism in the 2DVBS shows similar features to the near-explicit MCMv3.2. The aging mechanism does however include many variables which makes it hard to draw any detailed conclusion about the fragmentation parameterization. What we can say, based on the result of the study, is that fragmentation needs to be included in the 2DVBS scheme in order to get reasonable SOA growth (figure 7b). The study also shows that the first generation products generated with MCMv3.2 on average have higher volatilies and higher O:C-ratios than those generated by the 2DVBS base case, due to fragmentation during the first oxidation step in MCMv3.2. The distribution of these high volatility products has an impact on the SOA growth if allowed to age.

5.) “Table 4 and page 11018 line 5: The authors note that neglecting fragmentation causes models to use unrealistically low aging or neglect aging. Yet in their Table 4 they say fragmentation is potentially important. I would recommend classifying fragmentation as “Important””

Answer:

We will make changes in table 4, as suggested, to:

“Fragmentation during aging process Important

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