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Atmospheric Chemistry and Physics Discussions

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.

The comments will be listed with the following answers.

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 ïňĄrst 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 ïňĄrst 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 ïňĄrst gen products in the 2D-1D VBS will be larger than the 2DVBS. It would be helpful to demonstrate with a ïňĄgure how the O:C of the ïňĄrst 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 approxi-

mation 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

References

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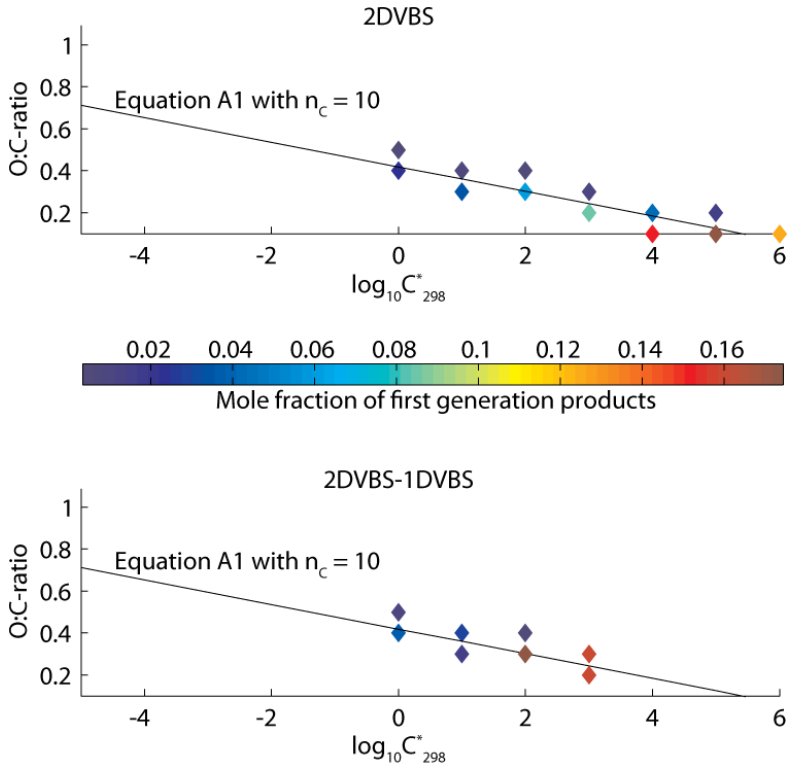

Fig. 1. First generation product distribution in the 2-dimensional VBS space modeled with the 2DVBS simulation (upper panel) and the 2DVBS-1DVBS simulation (lower panel). The black line shows the linear depen