

## General Comment

This paper details the development and implementation of an updated SOA parameterization into CMAQ. The update consists of fitting an Odum-2P parameterization to predictions based on recent VBS parameterizations for several traditional SOA precursors. The benefits of this update are two-fold: (1) no computational expense is added because the update still uses only two products per parent hydrocarbon, and (2) the accuracy of the VBS at lower OA loadings is captured. The paper is well written and the results represent a much needed update for CMAQ's SOA module. That being said, the paper has some serious shortcomings that must be addressed prior to a final decision on publication.

## Detailed Comments

### Measurement comparison

My main problem with the paper in its current form is that it spends a considerable amount of time discussing why the updated parameters are the best available, and virtually no time discussing the impact of these updates. This imbalance results in very few conclusions being drawn. The authors basically state that changing the SOA parameters will change the spatial and temporal distributions of SOA predictions, which may affect the accuracy of the predictions. I think a more balanced approach should be taken and a comparison to surface measurements is absolutely necessary. For instance, given CMAQ's documented history of underpredicting SOA concentrations nationwide, I was very surprised to read that CMAQ predictions in areas that are dominated by anthropogenic SOA decreased by 20% as a result of these updates (first paragraph of section 3.3). More surprising is that this finding was given only two sentences of discussion and no figures. I do not agree with the authors statement in the Conclusions section, "Recognizing the importance of processes not currently treated in the CMAQ SOA model (e.g., gas-phase aging beyond that typically captured in chamber studies and partitioning of POA), CTM predictions were not compared with ambient measurements." Any update significant enough to merit publication is significant enough to merit comparison with available measurements, even if the update worsens an existing discrepancy. For instance, how many regional CTM modeling papers have hypothesized that using an Odum-2P model as opposed to a VBS is a possible explanation

for SOA measurement/model discrepancies? The results mentioned in section 3.3 suggest strongly that this is not the case, at least for anthropogenic SOA. Therefore, I encourage the authors to include surface measurements as well as additional discussion regarding how their recent updates to both biogenic and anthropogenic SOA compare to those measurements and to previous studies. Once this is done, the conclusions section should be considerably stronger.

## Chamber data vs Odum-2P vs VBS

The authors mention that the VBS parameters may be better able to represent SOA formation at low  $M_o$ , even when limited data exist. It should be mentioned that this is because the VBS is designed to weight each VBS  $C^*$  equally, regardless of the number of data points available at, or near a given loading. For instance, if a hypothetical data-set contained 100 yields measurements all taken near  $M_o = 100 \mu\text{g m}^{-3}$  and 1 data point taken near  $M_o = 1 \mu\text{g m}^{-3}$ , the VBS parameters ( $C^* = 1,100 \mu\text{g m}^{-3}$  in this hypothetical) would capture the yield behavior at both loadings, and since the Odum-2P  $C^*$  parameters are not fixed, they would be biased towards  $100 \mu\text{g m}^{-3}$ . With the authors' approach, the VBS is used to generate 99 additional synthetic data points near  $1 \mu\text{g m}^{-3}$ , thereby giving yields at  $C^* = 1$  and  $C^* = 100$  equal weighting when fitting the Odum-2P parameters. However, the yield predictions from either the VBS or the 2P-VBS will still only be as accurate as the single measured data point at  $M_o = 1 \mu\text{g m}^{-3}$ . This is important because yield measurements at atmospherically relevant conditions (e.g.  $\leq 10 \mu\text{g m}^{-3}$ ) are more susceptible to things like high signal-to-noise ratios, gas-phase and particle-phase wall loss, etc. Therefore, any apparent improvements in agreement between predictions and observations may be somewhat fortuitous and/or incorrect. This is true for the VBS and the 2P-VBS. At least some additional discussion regarding this point should be added to the manuscript.

I am also not convinced that chamber data at atmospherically irrelevant conditions should even be used at all in the development of these parameterizations. For instance, instead of fitting a VBS to all chamber data, and then fitting the Odum-2P parameters to the VBS, I wonder why the authors do not just refit the Odum-2P parameters using only chamber data at atmospherically relevant  $M_o$  (say  $\leq 40 \mu\text{g m}^{-3}$ ). I understand the chamber yields at high loadings would not be constrained, but I wouldn't be surprised if the SOA yields from the traditional parent HCs could be represented with a 1-product

model if only atmospherically relevant range of  $M_o$  were considered. This would further reduce the computational burden of CMAQ.

## Instantaneous Reversible Equilibrium

In light of the growing body of evidence [*Shrivastava et al.*(2013), *Saukko et al.*(2012), *Perraud et al.*(2012), *Kuwata and Martin*(2012), *Abramson et al.*(2013), *Zelenyuk et al.*(2012), *Cappa and Wilson*(2011), *Vaden et al.*(2011), *Vaden et al.*(2010), *Virtanen et al.*(2010)] suggesting that the SOA in most of the chamber experiments used in this study may have been a highly viscous liquid or semi-solid, the authors need to defend the assumption of reversible equilibrium in CMAQ. The fact that experimental yields can be fit to the G/P partitioning framework of [*Pankow*(1994a), *Pankow*(1994b)] does not prove that instantaneous reversibility is an appropriate assumption. For instance, [*Cappa and Wilson*(2011)] showed that experimental SOA yield curves from  $\alpha$ -pinene ozonolysis can be reproduced by the sequential partitioning model which does not assume reversible equilibrium. [*Shrivastava et al.*(2013)] implemented this methodology into WRF-Chem and used observations during the MILAGRO campaign to show that SOA predictions are higher throughout their entire domain. CMAQ predictions would be significantly different than what is shown in Figure 7-9 if this methodology, which is also consistent with chamber data and which would be very straightforward to implement into CMAQ, were to be adopted.

## Minor Comments

- Introduction: “ $\alpha$ -pinene ozonolysis experiments by Yu et al. (1999) essentially all of the SOA mass formed was attributed to identified oxidation products that are relatively volatile”. In Table 1 of Yu et al. (1999), the  $M_o$  ranges from 11.2 to 65.1  $\mu\text{g m}^{-3}$ . The majority of the mass associated with oxidation products with  $K_p$  values on the order of  $10^{-6}$  to  $10^{-1}$   $\text{m}^3 \mu\text{g}^{-1}$  will not be in the particle phase under these conditions.
- Introduction: “only  $\sim 50\%$  would be expected in the condensed phase.” I think the authors meant 33%. At equilibrium,  $G = A \times C^*/M_o \rightarrow G/A = C^*/M_o = 10/5 \rightarrow G = 2 \times A$ . Therefore, 2/3 of the material is in the gas phase and one third is in the particle phase.

- Section 2.1: “...retaining source attribution in CTMs is computationally cost prohibitive for many applications.” One of the primary motivations of this work is to exploit the advantages of the VBS while maintaining the computational efficiency of the Odum-2P framework. It would be helpful if the authors added a couple sentences discussing the computational burdens associated with CMAQ modeling. For instance, how many tracers are in the unmodified version of CMAQv4.7.1 using SAPRC07, and how many tracers would be added if the authors were to use a standard VBS for each traditional SOA precursor as opposed to a 2P-VBS?
- Section 3.1.1: “In contrast, the low-NO<sub>x</sub> VBS parameterization was extrapolated from the high-NO<sub>x</sub> VBS parameterization as follows:”. I do not understand why the low-NO<sub>x</sub> VBS parameterization was extrapolated from the high-NO<sub>x</sub> parameterization. In Table 1 of the Lane et al. 2008a paper, separate isoprene VBS parameterizations are given for high-NO<sub>x</sub> and low-NO<sub>x</sub> conditions.
- Last paragraph of section 3.2.3: “Pye and Pouliot (2012) recently reported on the explicit treatment of C6-C19 alkanes and PAHs, represented by naphthalene, in CMAQv.5.0. They concluded that C6-C19 alkanes and PAHs could represent 20-30% of SOA formation”. Please mention that although Pye and Pouliot (2012) estimated alkanes and PAHs would contribute 20-30% of the predicted SOA, they predicted average SOA concentrations from alkanes and PAHs would be very small ( $\leq 30 \text{ ng m}^{-3}$ ).

## References

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