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Interactive comment on "Modeling of secondary organic aerosol yields from laboratory chamber data" *by* M. N. Chan et al.

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We would like to acknowledge the reviewer's insightful comments and suggestions. Please see our responses below.

In this manuscript Chan et al. present an updated product-specific model for SOA formation and compare their model to experimental a-pinene ozonolysis data. Five semi-volatile products, identified as important components of a-pinene SOA in previous publications, are chosen as representative compounds. The equilibrium partitioning constants of these species are then estimated from an updated group contribution method and equilibrium partitioning theory is used to predict SOA yield, chemical composition, and temperature dependence. The paper is well-written and some interesting conclusions are drawn. The paper is appropriate for ACP and could be published with *relatively minor modifications.*

General comments

My major comments have to do with the estimated K_p values and their implications. It seems clear from the paper that most if not all measurable experimental quantities are better fit using $K_p = 100$, relative to $K_p = 1$. Can the authors comment on the errors in the vapor pressure estimation? Is vapor pressure the most uncertain quantity in the K_p calculation? It seems unlikely that the errors in the group contribution method are two orders of magnitude for all the products.

We agree that the group contribution method gives reasonable vapor pressure estimates of a number of compounds (e.g., pinic acid). However, because of the scarcity of experimental data, the accuracy of the vapor pressure estimation of organic compounds using the group contribution method remains uncertain. This may cause the vapor pressure to be the largest uncertain factor in the K_p calculation. We do not address the accuracy of the vapor pressure estimation in the paper. In addition, particle-phase reactions can significantly enhance the K_p of the products. In order to evaluate the effect of the uncertainty in the K_p values (e.g., vapor pressure, activity coefficient, particle-phase reactions), the estimated value of K_p is multiplied by a factor of 100 for all the products.

Can the authors comment further on the relatively poor performance of the $K_p = 1$ case? For example, do any simple oligomerization reactions of the model products produce the 100x reduction in K_p? If not, what functional groups are necessary to produce a 100 x reduction in K_p?

For the $K_p \times 1$ case, the predicted SOA yields are lower than those measured at low organic mass loading. Also, the mass yields of the selected products are unrealistically high. The uncertainty in the estimation of the K_p of the products is likely a factor. The estimated vapor pressures of the products using the group contribution method are too high, and the products are estimated to be too volatile. In order to match experimental

SOA yields, large mass yields of the products are predicted from the data fitting so that a significant amount of the products can be partitioned into the particle-phase. This results in unrealistically high mass yields of the products in the $K_p \times 1$ case.

Most recently, ester formation has been observed in this system (Müller et al. 2008). The K_p of an ester, which is formed between pinic acid and hydroxy pinonic acid, can be estimated. At 293K, the estimated K_p of the ester is 4.957×10^5, which is much larger than that of both hydroxy pinonic acid ($K_p = 0.2802$) and pinic acid ($K_p = 0.2822$). This result suggests that ester formation (or oligomerization reaction) of the products may significantly enhance the K_p of the products. We have added the following sentences in the revised ms.

"For the $K_p \times 1$ case, the predicted SOA yields are lower than the measured ones at low organic mass loading. The data fitting produces the unrealistic result that the mass yield of the pinonaldehyde is unity. The sum of fitted molar yields exceeds 1. One likely explanation is the uncertainty in the estimation of the K_p of major products (vapor pressure and activity coefficient). The estimated vapor pressure of the products using the group contribution method is too high, and the products are estimated to be too volatile. In order to match experimental SOA yields, large mass yields of the products are predicted so that a significant amount of the products is partitioned into the particle phase. This results in unrealistically high mass yields of the products. Another likely explanation is that other products (gas-phase and/or particle-phase) of higher K_p (and lower volatilities) are present. Particle-phase reaction products (e.g., oligomers and esters), which are likely present, tend to have higher molecular weights and lower volatilities (Gao et al., 2004; Iinuma et al., 2004; Müller et al., 2008), effectively enhancing the K_p values (Kroll et al., 2005). For example, an ester, which is formed between pinic acid and hydroxy pinonic acid, has been detected (Müller et al. 2008). At 293 K, the estimated K_p of the ester is 4.96×10^5, which is much larger than that of hydroxy pinonic acid (K_p = 0.2802) and of pinic acid (K_p = 0.2822)."

If the K_p values have to be empirically increased by a factor of 100 for the model to *reproduce the data, is there any advantage to the Odum-type fitting over the basis-set method, which appears to fit the low-loading data more accurately?*

We have added the following to the revised ms.

"The performance of the product-specific model is most likely hindered by lack of explicit inclusion of particle-phase accretion compounds that are almost certainly present but have yet to be identified in this system. Prospects for identification of the majority of SOA products for major VOC classes remain promising. However, for the near future, empirical product Odum-type or volatility basis set models remain the approaches of choice."

The authors should further comment on the large alpha values necessary for fitting the data (beyond just stating they are aware of the large values). The sum of the yields is close to or greater than one, which isn't physically realistic under the experimental loadings studied. What does this mean for the model? Does it imply that the K_p values of the products in the experimental studies are even lower than in the $K_p \times 100$ case?

We address this point above. The large mass yield of the products in the $K_p \times 1$ case is likely a compensation for the underestimation of the K_p of major products. Large mass yields of the products are needed in order to reproduce the experimental SOA yields.

How unique are the solutions to the fitting equations? Can the data be fit equally well if the solver is seeded with other values of alpha?

In the optimal fitting, different sets of α_i values produce essentially the same goodness of fit to the overall mass yield. However, not all of these sets give a good prediction of the SOA composition compared to that measured. We present the α_i values which give the best fit to experimental SOA yields and SOA composition. In addition to measured SOA yields, available SOA composition data give important additional constraints on the optimal fitting. We have added the following sentences in the revised ms.

"In each case, the α_i values are determined by optimal fitting to the data. Different sets

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of α_i values produce essentially the same goodness of fit to the overall mass yield. The sets can be discriminated according to how well they fit the SOA composition as compared to that measured. The α_i values are chosen to give the best fit to experimental SOA yields and SOA composition."

Specific Comments:

P 9471, lines 10-12. The authors state that their O/C ratios are somewhat lower than those of Shilling et al. (Shilling et al., 2009). Did the authors assume atmospheric concentrations of CO_2*? Pure air generators generally deplete* CO_2 *well below atmospheric values (Shilling et al., 2009). The default Aiken et al. code corrects the total* CO_2 *signal (gas + particle) for atmospheric* CO_2 *concentrations (Aiken et al., 2008). In the case of pure air, the code may overestimate gas-phase signal, thereby underestimating particle-phase* CO_2 *and consequently O/C. Because so many other ion signals are estimated based on the particle-phase* CO_2 *signal, it is extremely important to accurately quantify particle-phase* CO_2*.*

The O/C ratios reported here are quite close to those measured in Shilling et al. (e.g., 0.30 at 60 $\mu g/m^3$ compared to approximately 0.33 in Shilling et al.(2009)). The difference is well within the error of this technique, but the reviewer is correct in emphasizing the importance of verifying the contribution of CO_2^+ to particle and air signals. In our study, chamber air did not originate from a pure air generator but came from ambient air that had been cleaned through a series of chemical denuders and filters. Recent Fourier transform infrared spectroscopy measurements have shown the concentration of CO_2 in our chamber air is nominally the same as in the atmosphere. In addition, due to the relatively large SOA loadings generated in this study, the sensitivity of the O/C calculation to the CO_2 concentration input is small. We add the following information in Appendix B in the revised ms.

"It is noted that chamber air is cleaned through a series of chemical denuders and filters. Fourier transform infrared spectroscopy measurements show that the concentration of CO_2 in the chamber air is nominally the same as that in the atmosphere. Due to the relatively large SOA loadings generated in this study, the sensitivity of the O/C calculation to the CO_2 concentration input is relatively small."

P9466, lines 26 – 28. Qualitative descriptions such as "weak" and "slight" are not very useful, especially when a quantitative measure is available. A quantitative comparison between the measured T dependence with the modeled T dependence would be much more informative.

We calculate the mean absolute fractional error between the measured and predicted SOA yields at different temperatures as

$$err = \frac{1}{n} \sum \left(\left| Y_{meas,i} - Y_{pred,i} \right| / Y_{meas,i} \right) \tag{1}$$

where n is the number of experimental data points, Y_{meas} is the experimental SOA yield, Y_{pred} is the predicted SOA yield. We have revised the sentences in the revised ms as follows:

"As shown in Fig. 2, the predicted SOA yield increases as the temperature decreases, as lower temperature favors the partitioning of gas-phase reaction products into the particle phase. The model predicts a stronger temperature dependence of SOA yield than that observed by Pathak et al. (2007). The predicted SOA yields agree well with those measured at 293 and 303 K. The mean absolute fractional error between the measured and predicted SOA yields, err is 0.1666 and 0.0895 at 293 and 303 K, respectively. On the other hand, the predicted SOA yields are higher than those measured at 288 K (err = 0.6728) and 273 K (err = 0.6266) but slightly lower than those measured at 313 K (err = 0.1968)."

P9462, lines 3 – 11. The authors interrupt the flow of the discussion by switching between basis-set and Odum-type fitting routines. I suggest separating the basis set discussion into its own paragraph.

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The volatility basis set discussion now appears in a separate section in the revised ms.

P9470 lines 20-25. Please change the wording of this sentence. If a HR-AMS is available, a-priori knowledge of the composition is not needed. The composition is measured during the course of the experiment. In fact, the authors rely on a-priori knowledge of the chemical composition for their own particle resolved model, so the authors' statement is misleading.

The HR-AMS measurement gives the overall element-to-carbon ratios of SOA particles during the course of the experiment. However, the element-to-carbon ratio of volatility bins cannot be determined by using the HR-AMS measurement alone. To obtain the element-to-carbon ratios of volatility bins, a thermodenuder coupled with the HR-AMS may be needed. Since the information about the chemical composition of volatility bins is not required, aerosol O/C and H/C ratios cannot be directly determined from the quantity of aerosol in the bins. To obtain the element-to-carbon ratios of volatility bins from optimal fitting, a-priori knowledge of the SOA composition is needed to determine the reasonable value/range of the element-to-carbon ratios of volatility bins.

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