

## ***Interactive comment on “Evaluation of new secondary organic aerosol models for a case study in Mexico City” by K. Dzepina et al.***

### **Anonymous Referee #2**

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This paper applies recently proposed SOA models to an SOA formation episode measured in Mexico City. This is the episode that was analyzed by Volkamer et al. (GRL 2006), in which SOA models substantially underpredicted the estimated SOA production. The paper illustrates that the new SOA models can largely close the SOA mass balance, but there are many important issues with these models that need to be addressed. The paper raises these issues by considering concentrations of SVOC vapors and comparing measured and predicted oxygen-to-carbon ratios and aerosol volatility. These sorts of comparisons provide interesting perspectives on the SOA issue and important tests of models.

Overall I think that this is an important paper. It addresses an important issue and makes many interesting points. There are a few that the authors should address before

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publication.

I have a number of concerns about interpretation of thermodenuder data.

1. Fig 10 which compares thermodenuder (TD) data to equilibrium calculations. The figure and associated discussion implies large discrepancies between the model output and TD data. While this may be true there is significant uncertainty associated with the TD data. For example, Fig 10 assumes the aerosol inside the TD reaches equilibrium. However, Fig SI-12 indicates that even with an evaporation coefficient of 1 the system does not reach in the TD. Therefore the best estimate for the model would be the kinetic/dynamic calculation and not the equilibrium calculation. Therefore, the kinetic/dynamic calculation should be shown in Fig 10 not the equilibrium. The dynamic model output is closer to measurements (though admittedly the agreement is still not great). The question then becomes what evaporation coefficient should be used in the dynamic model. A reasonable value might be 1 (as discussed in the text), but as discussed below recent data suggest a value much less than 1 may be more appropriate.

2. A key uncertainty for the interpreting the TD data is what is the evaporation/accommodation coefficient. The text at the bottom of page 4445 cites a number of older papers that report evaporation coefficients near 1 and claims that the difference in responses between measurement and model are likely real and not due to differences in evaporation kinetics. I do not think that the evidence is clear cut for a value of 1 and that this statement is much too strong. Recent work suggests that 1 may be right for simple mixtures or single components but for realistic/complicated aerosols (chamber SOA or actual emissions) that values are much less than 1. See for example,

Stanier, C. O.; Pathak, R. K.; Pandis, S. N., Measurements of volatility of aerosols from alpha-pinene ozonolysis. *Environmental Science & Technology* 2007, 41, 2756-2763.

Bilde, M.; Pandis, S. N., Evaporation rates and vapor pressures of individual aerosol species formed in the atmospheric oxidation of alpha- and beta-pinene. *Environmental Science & Technology* 2001, 35(16), 3344-3349.

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Recent work by Grieshop et al. (GRL 2007 cited in manuscript and an ASAP EST manuscript) suggest evaporation coefficients for complex aerosols are smaller than 1.

At least for the POA the TD and model are in pretty good agreement if an accommodation coefficient of 0.1 is used. In light of the recent papers that report particle evaporation coefficients less than one (cited above), a value of 0.1 seems completely reasonable (or at least as defensible as 1 for complex mixtures).

As for the NT-SOA, it seems clear that the 1 bin shift is too simple, stacking too much material in the C\* bin that corresponds to COA to reproduce the broad distribution of evaporation observed in the field. This point is discussed in the text. Therefore, even accounting for the uncertainty in the evaporation/accommodation coefficient, the volatility distribution of the NT-SOA does not appear to be correct (in contrast I am not convinced you can say this about the POA).

3. A final issue for interpreting the TD data is the delta\_Hvap. The NT and T/UT models use very different values. This seems to be a key uncertainty/difference and as discussed in the paper if they same values are used in both models the predictions are not that different. The values for T and UT-SOA models (36 kJ/kmole) does not seem physically realistic. What is the origin of that value? Fitting of experimental partitioning data?

The bottom line on the TD data is that there obviously there is a lot more work that needs to be done to sort out and properly interpret it. Given this uncertainty we need to be careful drawing specific conclusions from comparisons with TD data.

Another important issue that needs clarification is the representativeness of this episode. There has been some debate on this issue at meetings. Therefore, I was glad to see the authors addressing it and providing Figure 2. However, I think that the authors need to boost up the discussion of that figure and the various datasets and analysis techniques. Right now the discussion is buried in a paragraph on page 4423. I would recommend the authors making this it a stand alone short, separate section.

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Minor suggestions:

Page 4419 "Measured" SOA – You are not measuring SOA, you are inferring it from AMS data. This point is made clear on page 4421, but you should probably modify the wording in the introduction.

Page 4419 - Model measurement discrepancy. Might be worth mentioning that chamber studies with dilute exhaust also indicate large discrepancy between SOA models and production, very similar to what is observed in field studies (Robinson et al. 2007, Grieshop et al. ACP 2009). This seems like important corroborating evidence given the uncertainty of estimating SOA from field data.

Page 4425 discussion of partitioning. May want to add a pointer to section 3.2 which discusses how the partitioning calculations are made. The manuscript implies, but never states, that the modeling assumes that the aerosol is in thermodynamic equilibrium.

The modern carbon section should be shortened or cut. I agree with the authors that modern carbon is a potentially important constraint; however, without data they are largely speculating. It is worth pointing out in the discussion that using things like O/C and volatility provide important tests of SOA model.

The acronym PVOC seems awkward. I kept think it was primary VOC.

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 4417, 2009.

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