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

K. Dzepina et al.

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We would like to thank Anonymous Referee #2 for his/her review of the manuscript and for many useful comments, most of which we have adopted and which helped us improve the manuscript. The referee agrees that this is an important paper on implementing recently published SOA mechanisms to SOA models, and that it should be published after taking into account suggested changes.

In this reply all the original comments were copied, and *italicized*. Our reply is given after each comment in non-italic font. All the references cited in both this reply and the manuscript are given with the same format as in the manuscript and are included in the reply. The references cited by Anonymous Referee #2 and the authors of the manuscript that are NOT included in the ACPD manuscript are cited at the end of this reply.

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 publication.

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

R2.1. 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.

The reviewer seems to have missed that Fig 10 shows results from both the equilibrium

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(Fig. 10a on the left) and kinetic (Fig 10b on the right) calculations for comparison purposes. We agree with the reviewer that the main comparison with the thermal denuder results should be made with the kinetic calculations. The main points of showing the equilibrium calculations are (a) because this is the best estimate of the evaporation of the SOA under real atmospheric conditions where longer time scales apply and equilibrium is expected to be reached and (b) to serve as a comparison point for the kinetic calculations, to allow the reader to evaluate how far the TD is from equilibrium and what the evaporation would potentially be on a TD of long residence time and low particle losses. Probably these points were not explained clearly in the manuscript. Thus, we changed the manuscript text to clearly state that the kinetic calculation gives the best estimate of model OA volatility. We changed the text on page 4444, lines 15-17 to read: “**This calculation is simpler but it likely overestimates the evaporation of the model SOA as it ignores kinetic limitations to the evaporation (An et al., 2007; Faulhaber et al., 2009). However, it is useful to show the equilibrium calculation due to at least two reasons: (a) because this is the best estimate of the evaporation of the SOA under real atmospheric conditions where longer time scales apply and equilibrium is expected to be reached and (b) to serve as a comparison point for the kinetic calculations, to allow the reader to evaluate how far the TD is from equilibrium and what the evaporation would potentially be on a TD of long residence time and low particle losses.**“

We also changed the order of Figures 9 and 10. Namely, ACPD-Figure 10 (ACP-Fig. 9) summarizes the volatility behavior of the model OA for the equilibrium and kinetic calculations, and compares it to the ambient measurements. Therefore, it seems more appropriate that ACPD-Figure 10 (ACP-Fig. 9) comes first. ACPD-Figure 9 (ACP-Fig. 10) describes in more detail the volatility of only UT- and NT-SOA under the equilibrium assumption which is more appropriate to long atmospheric residence times. We will discuss the evaporation coefficient values in response to comment R2.2 below.

R2.2. A key uncertainty for the interpreting the TD data is what is the evapo-

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tion/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.

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 reasonably (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).

We thank the referee for this detailed comment. Some recent work cited above suggests lower evaporation coefficients for complex aerosol mixtures, although the evidence from those studies is also far from conclusive given the large experimental un-

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certainties, and/or may be influenced by processes such as oligomer decomposition in α -pinene SOA which may or may not apply to ambient urban SOA. We do agree that further research to constrain the evaporation coefficients of real aerosols should be a high priority of the OA community. We changed the sentence starting on page 4445, line 27 and ending on page 4446, line 2, and the new text now reads: “**The evaporation coefficients of various organic species in single-component aerosols and simple mixtures reported in the literature are near 1 (Pound, 1972; Cammenga, 1980; Davis et al., 1980). However, recent work suggests that the evaporation coefficients may be lower than one for more complex organic aerosol mixtures, such as those produced in chamber studies of SOA formation, although the evidence is far from conclusive (Stanier et al., 2007; Grieshop et al., 2007; Grieshop et al., 2009c).**“

We also added the following text on page 4446, line 7: “**For example, an evaporation coefficient of 0.1 makes the agreement between the volatility of model NT-POA and HOA measured during MILAGRO somewhat better (Fig. SI-12a). Likewise, lowering the evaporation coefficient reduces the disagreement between the modeled and measured evaporation (Fig. SI-12b), although low evaporation coefficients result in calculated curves for the UT-SOA model which diverge greatly from TD measurements of SOA formed in chamber experiments (e.g. Fig. 4e in Huffman et al., 2009b), casting doubt on the likelihood of evaporation coefficients much below unity. Further research to constrain the evaporation coefficients of real POA and SOA in the laboratory and the field should be a high priority of the OA community.**“

We also added the statement of the importance of future research on evaporation coefficients to the conclusions of the manuscript.

R2.3. A final issue for interpreting the TD data is the ΔH_{vap} . 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

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not that different. The values for T and UT-SOA models (36 kJ/mole) 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.

As mentioned in the manuscript, we used the value of $\Delta H_{vap} = 36 \text{ kJ mol}^{-1}$ which was adopted by Volkamer et al. (2006) from previously published work (Offenberg et al., 2006; Takekawa et al., 2003). This value is indeed very low compared to values for individual compounds. However this effect is understood following the work of Donahue et al. (2006), who showed that it was due to the lumping of species with a wide range of vapor pressures into 1 or 2 lumped products. The work of Robinson et al. (2007) chose to use many more lumped products divided according to the volatility basis set, and these authors argue that for this model representation the values of ΔH_{vap} should be on the range of those for realistic compounds for each volatility bin. We have merely implemented in our base case the values proposed by Robinson et al. (2007), but included Figure SI-13 to call attention to the large effect of this parameter and the need for more research on this topic.

We agree with the reviewer that there are significant uncertainties on the quantitative interpretation of TD data and that our ACPD manuscript was perhaps stating too strong conclusions. We have toned down our statements throughout the paper to better reflect current understanding and uncertainties in TD interpretation and parameters, including in the conclusions.

R2.4. 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

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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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We thank the referee for this suggestion, and have added the following new text to the page 4423, line 22, after “during MILAGRO 2006.“: **“We calculated the photochemical age for our case study and for de Gouw et al. (2009) by defining the start of photochemistry (age = 0 days) to be the time when OH starts rising in the morning, and the end of the photochemically-active period after sunset. We define the photochemical age as the integral OH-exposure until a given point in time, divided by the average OH exposure during MCMA-2003 based on the measurements of Shirley et al. (2006), updated with the revision of their calibrations described above. A detailed description of the of the photochemical age calculation for Kleinman et al. (2008) is given in their manuscript. Briefly, Kleinman et al. (2008) define the photochemical age as $-\text{Log}_{10} (\text{NO}_x/\text{NO}_y)$, with a value of 0 for fresh emissions (as $\text{NO}_y=\text{NO}_x$) and a value of 1 when 90% of NO_x is converted into oxidation products.“** We also note that the large underestimation of SOA with traditional models observed in our case study has been reported recently by two publications which use the regional models CHIMERE and PMCAMx as described in the revised text in the introduction: **“... Hodzic et al. (2009) and Tsimpidi et al. (2009) who report model-measurement discrepancies of the same order when using traditional SOA models inside two different regional models over Mexico City.“**

Minor suggestions:

R2.5. 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.

We agree with the referee that in several of the studies cited SOA was inferred from factor analysis of AMS data. However some of the studies cited used other non-AMS means of estimating SOA such as water-soluble organic carbon analysis or just total

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OC in the absence of significant EC. To be more precise we have changed the wording to “Recent field studies have found large discrepancies between the SOA mass concentrations estimated from measurements and those calculated from traditional SOA models in both urban and regional polluted atmospheres (Heald et al., 2005; de Gouw et al., 2005; Johnson et al., 2006; Volkamer et al., 2006; Kleinman et al., 2008; Matsui et al., 2009).“

We have also added the following text to section 2.1 to further clarify this point: “We note that several recent studies have shown that the estimate of SOA based on total OOA from the AMS is consistent with estimates from other methods such as the EC-tracer method (Zhang et al., ACP 2005), WSOC (Kondo et al., 2007), the CO-tracer method (Takegawa et al., 2006), the chemical mass balance of organic molecular markers (Aiken et al., 2009), and with all four of those methods at one location (Docherty et al., 2008).“ Through the use of other sources of information, such as the high degree of oxygenation of the mass spectra, clear increase in time of OA/ Δ CO much above that of POA, correlation with secondary tracers etc. these papers and our case study have established that the OOA extracted from the AMS data is typically dominated by SOA with a high degree of certainty (and certainly much higher certainty than in many papers based on e.g. the EC-tracer method which used the term “SOA” quite freely to refer to the difference between the total OC and the estimated primary OC).

R2.6. 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.

We thank the referee for this suggestion, and have added the following text on page 4419, line 22, after “MILAGRO 2006 campaign.“: “Chamber studies of SOA formation from diluted diesel exhaust and wood smoke also indicate very large dis-

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crepancies between measured and model SOA, very similar to what is observed in field studies (Robinson et al. 2007, Grieshop et al., 2009a).“

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R2.7. 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.

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We agree with the referee on this point, and have added the following text on page 4424, line 17 after “(Pankow 1994ab).”: **“Partitioning calculations in this manuscript assume that the aerosol and semivolatile species in the gas phase are in thermodynamic equilibrium, which is reasonable based on the time scales of gas-particle equilibrium for submicron particles (Seinfeld and Pandis, 1998).”**

R2.8. 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.

In response to the comments of all three referees that Section 4.5.3 on modern carbon should be shortened or removed, we have removed the section and kept a much shorter discussion on the contribution of biogenic SOA to UT-model at the end of page 4438, as explained in more detail in response R1.11 to Referee #1.

We also added the following text in the conclusions on page 4458, line 24: **“Characterization of model SOA volatility and atomic O/C ratio and its comparison to measurements provide important tests for SOA models.”**

R2.9. The acronym PVOC seems awkward. I kept think it was primary VOC.

We agree with the referee that this can be confusing since capital “P” is also used to describe “Primary” in the abbreviations in the manuscript. Thus, we have changed the abbreviation “PVOC” to “pVOC” everywhere in the manuscript to make this distinction

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more clear visually.

Additional References to the Response to Anonymous Referee #2:

Takekawa, H., Minoura, H., and Yamazaki, S.: Temperature dependence of secondary organic aerosol formation by photo-oxidation of hydrocarbons, *Atmos. Environ.*, 37, 3413-3424, 2003.

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

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