**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Sensitivities of the absorptive partitioning model of secondary organic aerosol formation to the inclusion of water" *by* M. Barley et al.

Anonymous Referee #2

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1. Overview

The **Abstract** (page 20312 lines 3-5) summarizes the authors' two main conclusions for the paper:

". . . .the prediction of the distribution of semi-volatile organic component between the gaseous and condensed phases is shown to be highly sensitive to the ambient relative humidity and the formulation of the partitioning model used."

Regarding the assertion that organic PM levels in the atmosphere (or in chamber situations) can be sensitive to RH, this has been established in the literature by theoretical

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partitioning model calculations in several papers from the last 8 years. Thus, the authors may wish to tone down the implication in the abstract that the paper is considering this for the first time. Second, the statement in the abstract that model predictions will depend on the formulation of the [equilibrium] partitioning model used needs expansion. Namely, the authors have used some hypothetical cases to show how, as indicated by absorptive partitioning theory, varying number average molecular weight in the organic PM phase can greatly affect partition coefficients. So, the abstract needs to be more specific about which formulations of absorptive partitioning theory allow this variation to be considered, and which do not. That is the role of the abstract, to give the most important conclusions of a paper. Overall, with significant corrections and clarifications, this paper could be published in *Atmospheric Chemistry and Physics*.

2. Corrections

2.1. Prior Work on RH Effects

The authors discussion on page 20314 lines 7-10 omits consideration of two recent papers that investigate the effects of varying RH on organic PM levels, namely Chang and Pankow (2008) and Pankow and Chang (2008).

2.2. Number Average Molecular Weight

The authors' partitioning model considerations begin with Eq.(4). Most of the parameters in the equation are defined on page 20316 (lines 1 to 5). The authors then turn to a discussion of the definition of molecular weight term in Eq.(4), which they give the symbol M_{om}. The authors state (page 20316, lines 9-10):

"*....Pankow et al. (2001) is vague in the definition of molecular weight ("number averaged molecular weight of the absorbing om phase") it is interpreted here as ....*"

Incorrect. First: 1) Pankow et al. (2001) cites Pankow (1994) as the origin of the number average molecular weight (MW) as a term of importance for absorptive partitioning; and 2) the definition of this form of the MW is clear in Pankow (1994) because

it is the mole fraction X_I that is viewed as governing gas/liquid partitioning, and a particular type of average MW, namely the number average MW, is needed to calculate X_I. Second, if there had been any uncertainty concerning the definition, a web search on "number average molecular weight" (with quotes) would have provided an enormous number of versions of the answer. For example, while not an error-free repository of scientific knowledge, Wikipedia (`http://en.wikipedia.org/wiki/Number_average_molecular_weight`) does give a nice explanation of the different types of average MW, including the number average and the weight average. In any case, with the meaning of the "number average molecular weight" not properly resolved, the authors proceed to "interpret" that the needed quantity is given by Eq.(5). However, with C_i having been defined as the total mass concentration of species i in units of μ**g m**$^{-3}$, Eq.(5) unfortunately equates M_{om} with the **weight average MW**.

Much of the balance of the paper is concerned with organic PM calculations carried out using various partitioning model forms. The model form using Eq.(4) with Eq.(5) is referred to as "Mass_4" modeling. Given that Eq.(4) requires use of the number average MW and not the weight average, the validity of those calculations would necessarily seem in question. **However**, on page 20318, lines 18-19, the authors **re-define** their C_i and C_i^* to have units of μ**mol m**$^{-3}$. With these units, Eq.(6) will now give the number average MW. It would seem that they believe the reader will automatically use this redefinition in the execution of Eq.(5). Indeed, this redefinition must be the reason why all the authors' results for the "Mass_4" method are the same as for the "Mol" method. Clearly, cleaning up the entire discussion of number average MW is essential.

Also, since the "Mol" method is the same as the "Mass_4" method, there is no reason to suggest either that they are different, or to present all the results twice when comparing to the "Mass_3" method (which uses the C_i^* of Donahue et al. (2006) and does not correct for variations in the number average MW of the organic PM).

2.3. Neglecting Activity Corrections

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The paper does not take any activity corrections into account. Obviously, given the range of chemicals that are condensing, this is an exceedingly gross simplification. In many regards, then, assumption of ideality reduces the calculations to mathematical exercises that allow illustration of the importance of considering molecular weight effects, but have little basis in reality. It would seem that some additional cautionary statements to the reader in this regard are advised.

2.4. Equivalence of $K_{p,i}$ by Eq.(4) and C_i^* by Eq.(3)

Page 20316, lines 15-16: "*It can be seen that the equilibrium coefficient $(K_{p,i})$ is the reciprocal of the mass concentration of the saturated vapour (C_i^*) so long as...*"

Comment: There is no "so long as" to this equivalence. In the nomenclature of this paper, $K_{p,i} = (C_i^{\text{cond}}/C_i^{\text{vap}})/C_{\text{OA}}$, and $C_i^* = C_i^{\text{vap}}C_{\text{OA}}/C_i^{\text{cond}}$. Thus, $C_i^* \equiv \quad K_{p,i}$.

2.5. Model "Reformulation"

Page 20318, lines 6-8: "*The provision of the identity of a large number of potential species contributing to the SOA mass allows reformulation of the partitioning model in terms of the molar abundance of components.*"

Comment: The absorptive partitioning model can be formulated equally easily in terms of molar concentration or mass concentration, regardless of what is known about the system. Perhaps what the authors really mean to say is that knowledge of the identities of the condensing species allows consideration of the effects of varying number average molecular weight as required in an exact application of absorptive partitioning theory, but not allowed in the generic $C_i^*(\mu\text{g m}^{-3})$ approach of Donahue et al. (2006).

3. Clarifications Needed

3.1. "Calculation Simpler"

Page 20320, lines 6-8: "*Removing the molar mass term makes the calculation simpler while providing identical results to those from the model using mass-based partitioning*"

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and averaged molar mass (see below)."

Comment: Since the final quantity of interest is the mass concentration of organic PM, it is not in fact any simpler to perform calculations using molar concentrations than when using mass concentrations.

3.2. "Volatility Range"

Page 20320, lines 23 et seq.: "... dimethyl ether,

Comment: The range of compounds considered is biased to include compounds that would not condense to any significant degree at ambient concentrations. This may be due to a desire to include very volatile compounds per current interest in acknowledging the presence of volatile compounds as precursors to condensable compounds. However, it might have made sense for the paper to also include compounds less volatile than succinic acid since we know they are present in the ambient atmosphere and contribute to ambient organic PM. In any case, assuming that the authors would not redo their calculations, there needs to be some short discussion of this matter.

4. Minor Comments

4.1. OVOCs

Page 20313, line 21. "producing a range of oxidized VOCs (OVOCs) of widely varying volatilities..."

Comment. Consider a "scratched red car". Both adjectives apply. The car is scratched, but also still red. However, the authors' usage violates this: the compounds are oxidized, but may no longer be volatile. Not clear writing in the opinion of this reviewer.

4.2. Water Soluble and Water Insoluble Compounds

Page 20313, lines 23-24. "*The organic aerosol fraction contains a mixture of water soluble and water insoluble compounds...*"

Comment. There is no "bright line" between "water soluble" and "water insoluble".

4.3. No Requirement for a Single Phase in Absorptive Partitioning Theory

Page 20314, lines 1-4. *"However, instead of dissolution of components in a single dominant solvent, the absorptive partitioning model for organic material considers absorption of semi-volatile organic components into an organic medium sufficiently similar in nature for the system to act as a single phase organic solution."*

Comment. Incorrect. Absorptive partitioning theory does not require a single phase.

4.4. Nomenclature for Average Molecular Weight

Page 20317, line 6.

Comment. The authors hereby introduce a second symbol for number average MW. Also, the origin of Eq.(6) is not Seinfeld and Pankow (2003), but Seinfeld et al. (2001).

References

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 20311, 2008.