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Interactive comment on "Particle partitioning potential of organic compounds is highest in the Eastern US and driven by anthropogenic water" *by* A. G. Carlton and B. J. Turpin

A. G. Carlton and B. J. Turpin

carlton@envsci.rutgers.edu

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Comment: It would be appropriate to note or summarize those modeling efforts that have focused on aqueous partitioning and to indicate their findings (i.e., the Pun et al. model, any modeling efforts that simply used Henry's law). The Pun model allows for the type of aqueous partitioning process described by the authors, but it may underestimate the aqueous process by not considering enough of the gas-phase oxidation products (what the authors call WSOM). In general, it should be better emphasized that the water-soluble organic gases that can form aqueous SOA and the semi-volatile organic gases that partition into OM are not necessarily two different sets of compounds.

Although the WSOM species are too volatile to partition into the OM according to their vapor pressures, there are likely reactive pathways that lead to these species being present in the OM. Correspondingly, it is highly probable that some of the species included in the semi-volatile class are at least partially water-soluble. This type of analysis would be best served by a model that allows species to partition into whichever phase is preferred or to split their mass. I recognize that this is a large model development effort that is likely beyond the 'proof of concept' idea of this manuscript. Still, I believe it should be better emphasized as a limitation in the manuscript.

We added to the manuscript and modified the text to address this concern. In the introduction we now specifically mention the Pun et al. and Zuend and Seinfeld (2012) manuscripts. Important differences between Pun/Zuend and this work to point out are that previous SOA modeling work describes partitioning of semi-volatile material to the particle liquid phase "only", while our work describes the partitioning of organic gases followed by condensed phase oxidation reactions. We make this more clear in several places of the manuscript:

In the Introduction: "Despite studies of the effects of liquid water on the gas-particle partitioning of these semi-volatile products (Pun et al., 2002; Zuend and Seinfeld, 2012) . . ."

"This could be, at least in part, because derived empirical formulations do not include the potential for polar organic gases to partition to polar solvents such as water, and react in that medium to form low volatility products."

". . .abundant presence of small, water-soluble organic compounds (e.g., formic and acetic acids, glyoxal, methylglyoxal, acetone) (Spaulding et al., 2003). These compounds are too small to form SOA through traditional semi-volatile partitioning theory in atmospheric models (e.g., SOAgas)."

In the Methods section: "It should be noted that in reality some fraction of species included in the semi-volatile class would likely also partition to liquid water (Chang, et

al., 2010).”

In the conclusion: “Future investigations regarding the controllable fraction of organic aerosol should include simultaneous explicit phase partitioning of water soluble and semi volatile gases to condensed organic matter and liquid water.”

Comment: Page 12751. I understand why the aqueous SOA forming potential is set to unity. However, would it be possible to use a range of values based on their Henry’s law constant? Or based on some other parameter that is available in the model (including those mentioned by the authors and the free acidity).

We now conduct a sensitivity as suggested by the Reviewer. We have calculated the partitioning potential using phi =0.1 (in addition to phi =1 used initially). Figure 3 is now a 4 panel figure with Φ=1 and 0.1. The original ACPD submission had the surface and vertical totals with Φ=1 only.

In response to this sensitivity and the new results presented in Figure 3 we have made the following changes to the text.

In the Methods, “...a value of 1 is assigned to all species...” has been changed to: “To explore sensitivity of the partitioning potential to φ we perform two calculations with constant phi values, the first with φ set to a value of 1 and another with φ set to 0.1 for all species.”

We point out that the results of this sensitivity do not change the conclusions. The potential for SOAAQ continues to be highest in the Eastern U.S. and is driven by particle phase liquid water that is absent in the Western U.S.

Comment: With regard to the free acidity, I understand that quantity is linked fairly strongly to particle water and such, but it was not until I read the supplement that I truly made this connection and saw how it fit into the authors’ arguments. There is adequate room in the manuscript for the supplement to be incorporated into the body of the text, obviating the need for the supplement altogether.

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Figure S1 from the supplemental information has been moved to the main text of the manuscript and is now Figure 6.

Comment: Following on the previous comment, why not just do a first-order simulation in which individual WSOM material is allowed to partition to the particle water via its Henry's law constant? The WSOM would then distribute itself based on changes in said water with meteorology, changes in aerosol predicted by ISORROPIA etc. One could then look at the change in OA compared to a base case. This would then truly address the issue without necessarily having to rely on showing the absolute concentrations of all of the species and making a qualitative comparison (which are good frameworks and introduction for the full model run). I recognize that there would be uncertainty in this type of model calculation (i.e., the phi values discussed above are not unity), but I believe this would be an appropriate addition to paper if possible.

Initially we were reluctant to calculate concentration based on Henry's Law because several investigators have shown that organic species are present in the condensed phase at concentrations higher than predicted by Henry's Law, in particular for species studied here (e.g., glyoxal). We now compute and report those values here in the supplemental information. We note that these calculations reinforce our findings because particle phase liquid is only present in the Eastern U.S. and Henry's Law calculations indicate aqueous partitioning only in the Eastern US as a consequence. We reference the Supplemental Information in the results section of the manuscript. We now include Figures S1 and a paragraph of text describing the concentrations that arise when a Henry's Law approach is used.

Minor comments Comment: Line 9, page 12744 needs a semicolon The comma has been changed to a semicolon.

Comment: Line 24, page 12744 Yet should start a clause, not a sentence Line 3, page 12745 add 'as a result' at the end of the sentence "Yet" has been changed to "however".

Comment: Line 16, page 12746 although likely minor, I assume that the aqueous

phase also becomes a positive feedback on the formation of aqueous SOA from anthropogenic precursors (since they might not have been emitted from the same source as the SO2). This could be included.

Yes, SOA from anthropogenic precursors is also likely to be impacted by the availability of anthropogenic liquid water, since gas-phase photooxidation of anthropogenic emissions also produces water-soluble compounds (e.g. glyoxal from aromatics and alkenes).

We note in the Introduction: "Gas phase photochemistry oxidizes and fragments biogenic and anthropogenic VOCs resulting in the ubiquitous and abundant presence of small, water-soluble organic compounds (e.g., formic and acetic acids, glyoxal, methylglyoxal, acetone) (Spaulding et al., 2003)" and now expand with this new text in the introduction: "Further, anthropogenic influences on H2Optcl would also increase SOA derived from anthropogenic VOCs, which also oxidize to form gas phase WSOMg.

Comment: Line 5, page 12748, is it Aiken or Aitken? Aiken has been changed to Aitken.

Comment: Line 8, page 12748, the nomenclature for the inorganic ions should be explained. We had added the following explanatory text: "CMAQ output species: SO4 = ASO4I + ASO4J; NO3 = ANO3I + ANO3J; Cl = ACLJ; Na = ANAJ; NH4 = ANH4I + ANH4J. A in the species name denotes aerosol, I denotes Aitken mode and J denotes Accumulation mode."

Comment: Line 25, page 12753 And should start a clause, not a sentence "And" has been removed.

Comment: In Table 1, it appears that acetic acid and peroxy acetic acid are mixed up, values should be corrected (i.e., acetic acid does not have a MW that is greater than that of peroxy acetic acid) We have switched the species names and thank the Reviewer for catching this typo.

Comment: For clarification, in Figure 2, it specifically says that all species in Table 1 are included. It does not say this in Figure 1. Are we comparing apples to oranges then? Should primary VOCs be included?

Unfortunately we were not clear. Initially we evaluated WSOMg in Figures 1 and 7 and compared semi-volatile absorptive partitioning to water-soluble partitioning. We compared only species for which formation of SOA (SOAAQ or SOAGAS) has been demonstrated in experiments.

In contrast, when calculating of MGLYequiv (Figure 2) we investigated all organic gases in CMAQ. We have made this more clear in the figure captions (Fig 1, 2, 7) and in the manuscript with the following changes in the Methods section of the text where MGLYequiv is introduced:

"In order to account for the combined effects of compound-specific water solubility and concentration, a solubility index for describing organic gas concentrations of all organic gases was adopted (e.g., not only water soluble species for which laboratory experiments have been conducted, but all CMAQ-modeled species)."

Figure 1 caption: "Sum of gas phase CMAQ water-soluble organic gases shown in lab experiments to make SOAaq: ..."

Figure 2 caption: "Note that all species included in Table 1 are used in the calculation of MGLYequiv"

Figure 7 caption: "Includes species for which laboratory experiments have been conducted, as in Figure 1."

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 12743, 2013.