

Interactive comment on “Using the chemical equilibrium partitioning space to explore factors influencing the phase distribution of compounds involved in secondary organic aerosol formation” by F. Wania et al.

Anonymous Referee #2

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Reviewer comments on: Using the chemical equilibrium partitioning space to explore factors influencing the phase distribution of compounds involved in secondary organic aerosol formation F. Wania, Y. D. Lei, C. Wang, J. P. D. Abbatt, and K.-U. Goss

The authors present here a novel representation with which to understand the partitioning of typical atmospheric organic compounds into gas, aqueous and organic phases. They calculate volatility and solubility using a variety of methods and comprehensively address uncertainty and gaps in knowledge. Gas-particle partitioning is still a highly

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uncertain facet of atmospheric chemistry, and this work presents an important advance in thinking by quantitatively and qualitatively considering the role of water in this process. The framework described in this work is sure to be highly cited and widely used. This reviewer recommends publishing this work with only relatively minor changes.

Major comments

(1) On Page 26558, the author admirably and thoroughly discusses the assumptions about phase miscibility and separation, but there is one possibility not discussed. The author raises the possibility of a “single condensed aqueous phase at high relative humidity ... if the organic material is highly oxidized”. However, if there is sufficient organic matter, but most or all of it is highly oxidized, is it not possible to have a phase that cannot be properly considered aqueous or organic, but is instead a mixture of both? That is, approximately equal parts LWC and OM, but not phase separated, as might be expected in a highly oxidized, high relative humidity region of high emissions. How would such a scenario be properly considered in the context of this work? Is it still reasonable to consider it as the 3-phase representation presented, or should it be considered as a single phase (and should that phase be thought of as organic or aqueous), or something else entirely?

(2) Some data is available to compare the results in this manuscript with observations, but this has not really been attempted. Doing so would greatly improve this manuscript by demonstrating that the described theoretical framework can be applied to real data. For example, on page 26559 line 17-19, All of the aromatic products are solidly in the gas-phase region of Fig. 2, which the author explains by pointing out that “oxidation products of the mono-aromatic hydrocarbons ... are too volatile to notably contribute to organic aerosol formation.” However, mono-aromatics have been found to have surprisingly high SOA yields (5-20% under atmospherically relevant loadings: Ng et al., 2007, Wyche et al., 2009). Do the authors have any ideas or insights into this discrepancy? Perhaps unknown products or oligomers are less volatile than currently known products, or there are additional effects not being considered in the authors’

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graphical representation? Some discussion reconciling known observations with this theoretical representation would be warranted. Similarly, from the Jordan et al. 2008, an SOA yield can be calculated for n-alkanes, which could be qualitatively compared with the n-alkanes shown (or the predicted SOA yields for n-alkanes and aromatics at atmospherically relevant loading can just be found in Gentner et al., PNAS, 2012)

(3) At various points throughout the manuscript, I find the discussion of water effects on partitioning muddled by a conflation between "high LWC," which I interpret as high RH aerosols, and levels of water more typical for clouds, which to me goes beyond simply "high LWC" and more toward "cloud droplets." The main place I find this confusing is page 26565-66, line 19 and on: The phrase "analysis of phase partitioning that ignores liquid water in the atmosphere can lead to erroneous conclusions" should be clarified as referring primarily to conditions in clouds, as the authors go on to point out that few compounds shown in Fig. 6 are in the aqueous phase during LWC levels of 10 $\mu\text{g}/\text{m}^3$, as is more typical of ambient aerosols near the ground.

(4) At the end of the manuscript (and Figs. 10 and 11), normal alkanes are used here to gain insight into aliphatic reactions, but functionalization reactions of unsaturated aliphatics are not explored, though these are amongst the more common reactions in the atmosphere. Using α -pinene, mostly only dimerization is explored, but this passes up the opportunity to explore terpene functionalization more fully to characterize its movement in the partitioning space. It is not clear that α -pinene functionalization will occur with the same slope as alkane functionalization, especially given that Hodzic et al., 2014 see a slope in volatility-solubility dependence of α -pinene products closer to 1:1, as opposed to the 1:2 slope observed for alkane products.

Minor comments:

(5) Page 26548 line 1: I find it odd to repeat the exact same first sentence in the Introduction and the Abstract. Perhaps it can be reworded slightly to be less repetitive.

(6) Page 26548 line 20-21: Include a reference for the sentence "lower temperatures

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shift the gas/aqueous phase equilibrium of volatile substances, such as α -pinene and n-alkanes, to the gas phase", as this is counterintuitive

(7) Page 26549 line 21-22: While Donahue et al. 2011, 2012 are referenced later, they should also be included in this citation as they describe one of the recent quintessential uses of graphical tools to understand partition. For a more complete list I also recommend, though by no means think it is absolutely necessary, to include the carbon number by polarity grid of Pankow and Barsanti, Atmos. Env., 2009, possible the carbon number by oxygen number model of Cappa and Wilson, ACP, 2012, and the various work of Isaacman et al. using GCxGC and GCxMS to categorize SOA constituents through graphical analysis

(8) Page 26549 line 28-29: Saturation concentration is more accurately "defined as", not "shown to be" "the reciprocal of a gas-particle partitioning coefficient" and can/should be briefly described here, as many people find it confusing that our community so often discusses vapor pressure in mass concentration units.

(9) Page 26550 line 20 and throughout: should be "partitioning coefficient" in place of "partition coefficient"

(10) Page 26550 line 25: missing the word "is" after KX/Y.

(11) Page 26553 line 26-29: a bit more discussion of the central region is warranted. While the white triangle is clearly described, there is presumably a region in which a compound is majority in one phase, but the non-majority fraction is split between the other two phases. These are, as I understand it, the regions within the dashed lines of Fig. 1A, which should be made clearer or discussed in the text.

(12) Page 26555 line 22: A reference or online availability should be given for SPARC

(13) Page 26556 line 1: which n-alkanes?

(14) Page 26561, Fig. 4: It is interesting and worth noting (and frustrating to those of use that study partitioning), that nearly all the products of terpenes and aromatics fall

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in the SV-OOC and the SV-WSOC region, so exist most likely in all three states in the atmosphere.

(15) Page 26564, line 14-23, and Fig. S3: Use of the terms “high” and “low” are confusing. I interpret “low” as a decreased in KX/Y , thus, “prediction of KW/G appear to be generally biased low relative to SPARC predictions and the KW/G appear to be biased high” should be an arrow to the lower left, not upper right, so that the tip of the arrow has a higher value in KW/G and a lower value in KW/G , unless I am somehow mistake. This continues to be confusing in line 19-21. It appears from Fig. S3 that for the compounds with a long uncertainty line, the $pLFER$ value is up and to the left of the SPARC value, so it is more toward the gas-phase, not “unduly favouring the aqueous phase.” In general, I find this paragraph confusing, and several times, compounds are referenced but not labeled on any figures

(16) Page 26565 line 16: It is somewhat speculative to suggest that it is implausible that activity coefficients vary by several orders of magnitude. What few measurements of partitioning do exist (i.e. Williams et al., 2010), shows effective activity coefficients several orders of magnitude from ideality. These may be inaccurate as they ignore partitioning into an aqueous phase, but they were also measured in a relatively dry environment, so phase separation is not necessarily likely. I agree that it is suspect that SPARC differs from the other two, but observations do support that gas-particle organic partitioning is still poorly understood.

(17) Page 26567 line 22: typo, “be” should be “ by”

(18) Page 26567 line 27: “functionalization roughly increases the KW/G by two log units for every log unit increase in $\log KW/G$ ”. Interestingly, and perhaps unsurprisingly, this is in agreement with the relationship between Henry’s law and vapor pressure observed for alkanes by Hodzic et al., 2014

(19) Fig. 1: At first glance, units and thresholds are confusing. Based on the definition of KX/Y as m^3 of phase Y per phase X, the 50% line in Fig. 1 seems like it should be

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at $\log K = 0$. The reason as I understand it that this is not the case is due to volume ratios, made clear in equations 5 through 9 and discussion on page 26553, but these are introduced after Fig. 1 (which is first mentioned on line 8 of page 26551), so the first look at Fig. 1 is very confusing. Perhaps consider referencing the equations in the caption of Fig. 1. Or adding axes that showing fraction in each phase φ_X/φ_Y in each phase.

(20) Fig. 2: The families of products are very clear in n-alkane oxidation. Presumably the horizontal spacing is carbon number, and the vertical diagonal spacing are degrees of oxygenation. It would be helpful to label families or carbon number in some way to remove the guess work from interpreting the blue dots.

(21) Fig. 6: Describe the red outlined regions in the caption

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