Response to Anonymous Referee #1

The manuscript by Wania et al. presents a graphical approach to evaluating phase partitioning of organic compounds in complex (multi-phase) systems relevant to formation of secondary organic aerosol (SOA). The potential benefits of such an approach, described by Wania et al., are the ability to simultaneously consider multiple factors influencing phase partitioning and their relative importance. The factors that can be considered include atmospheric variables (e.g., temperature and liquid water content) and chemical properties of the condensing compounds and absorbing phase (e.g., molecular size and functionalization). One of the most attractive features of this graphical approach, as it is presented, is its use for prioritizing data gaps. The authors suggest that the graphical approach can be used to identify parameters/conditions for which some uncertainty can be tolerated and others for which better constraints are needed. Another attractive feature is the use of models that predict partitioning explicitly, eliminating the need for separate (and highly uncertain) estimations of saturation vapor pressures and activity coefficients. This appears to be the subject of a companion manuscript also under review in ACPD. One potential limitation of this approach is the ability of one modeled system to represent partitioning behavior under diverse ambient conditions (discussed further below).

There is much interest in improving model representations of SOA formation, including simultaneous consideration of multiple phases. Efforts are greatly needed to reduce uncertainty in existing approaches. The manuscript is thus highly relevant within the scope of ACP. However, it is not clear that the graphic approach presented truly represents a significant contribution to the field, and that it is substantially different from existing approaches and analyses. It is recommended that the manuscript be reconsidered for publication in ACP following attention to the comments on scientific and presentation quality provided below.

We appreciate the generally encouraging assessment and refer to the detailed response to the critical elements of the review given below.

Technical Comments Scientific quality: One of the biggest concerns with the graphical approach as written, is the consideration of partitioning between an aqueous (mostly water?) and a water insoluble organic phase. It is known that organic particulate matter can be up to 80% water-soluble (e.g., Sullivan et al., GRL, 2004). It is not clear exactly how this substantial component of the absorbing phase is conceptualized within the presented approach. Is the aqueous phase an aqueous+organic phase (as seems to be supported by the discussion of the disappearance of the WIOM phase in section 2.4)? If this is the case, at what point is that phase considered an organic phase and how are the properties along this continuum (mostly aqueous to mostly organic) to be treated in the presented approach? Or is the water insoluble phase a water insoluble and/or water-soluble phase? This latter description seems more likely given the choices of surrogate structures for "WIOM" in SPARC, as well as use of organic aerosol load (Eq 8) to determine the size of the "insoluble" absorbing phase. If this is the case, why isn't the organic phase referred to more generally as an organic phase (that spans a continuum between insoluble and soluble organics represented by some end members)? It is not clear from the manuscript, as written, that the likely compositions of phase(s) are well understood and well represented by the current application.

Phase separation in aerosol, involving a mostly aqueous and a mostly organic phase, has been observed and is also rationalized by thermodynamic calculation (see 26558, line 15: "Support for separation into predominantly organic and aqueous phases in aerosol stems from laboratory (e.g. Song et al., 2012), field (You et al., 2012) and theoretical investigations (e.g. Bertram et al., 2011; Zuend and Seinfeld, 2012)."). The two condensed phases (referred to as aqueous, W, and water-insoluble organic matter, WIOM) in the partitioning space approach simply refer to these two phases (see page 26557, line 22: "The second [assumption] is that the condensed phase separates into a largely aqueous phase and a phase largely made up of water-insoluble organic matter"). Phase separation is not absolute, the organic phase will contain some water (especially on a molar basis) and the aqueous phase will contain some organic molecules. Under some circumstances, no phase separation occurs and there is just one condensed phase.

Typically, the term water solubility refers to the maximum aqueous concentration a chemical achieves at saturation, i.e., is determined by the partition between the pure substance and the aqueous phase. For the phase distribution of an organic chemical in a phase-separated aerosol, it is not this water solubility that is relevant (there is no pure substance present in the aerosol), but the compound's relative solubility in the mostly aqueous and in the mostly organic phase. This relative preference is expressed with the water-WIOM equilibrium partition coefficient $K_{\mathrm{W/WIOM}}$.

The use of the terms "water solubility", water soluble", and "water insoluble" in the current context can therefore be misleading, because it is not a compound's water solubility that determines in which aerosol condensed phase it will be found. For example propanal's water solubility of 310,000 g/m^3 (or 5338 mol/m^3) is many orders of magnitude higher than fluorene's water solubility of 1.9 g/m^3 (or 0.011 mol/m^3), yet they have almost identical $K_{W/G}$ (all property data from Mackay et al. 2006). In other words, even if 80 % of organic particulate matter was found to be water-soluble, this does not mean that it will partition into the mostly aqueous phase. By the same token, a chemical predicted to fall into the part of the partitioning space taken up by WIOM, is not necessarily "water-insoluble", but merely has a higher preference for the mostly organic than for the mostly aqueous phase.

In light of this, we acknowledge that the term "water-insoluble organic matter" could be misunderstood and we considered changing this term. However, the same terminology was used in Arp et al. (2008), Arp and Goss (2009), and Wania et al. (2014) and for the sake of consistency with those earlier papers, we prefer to retain the WIOM label. We will however add a sentence at the end of section 2.1 stating: "We should mention that the use of term WIOM does not imply that the compounds making up this phase necessarily have low water solubility. Even relatively water-soluble compounds can have a higher preference for solvation in an organic phase than in a mostly aqueous phase."

p. 26556, line 10-15: How do the measured $K_{WIOM/G}$ values vary by sampling location (urban to coastal)? Why are these values averaged? It seems valuable information on composition dependent partitioning is being lost. Do the model comparisons improve/worsen if individual values are used instead of an average?

This is an issue addressed in more detail in Wania et al. (2014), where the predictions from the four individual ppLFERs are presented and compared with each other and with their average. The issue of information on composition dependent partitioning is addressed in the response to reviewer comments on Wania et al. (2014):
http://www.atmos-chem-phys-discuss.net/14/C8817/2014/acpd-14-C8817-2014-supplement.pdf
Briefly, the information available on the composition of these four aerosols is very limited and insufficient to establish relationships between partitioning and composition. Additional studies could indeed attempt to explore – by using more detailed aerosol characterization – if there is a difference in $K_{WIOM/G}$ values between aerosol from different locations. In the current manuscript, we are interested in representing the typical/average phase distribution behavior within the partitioning space, so the use of an averaged prediction of $K_{WIOM/G}$ is justified.

p. 26556, line 21: If the goal is to better understand atmospheric SOA formation, why are different solvents considered for different partitioning compounds? Are distinct regimes expected under atmospheric conditions? If so, this needs further explanation/ clarification in the manuscript.

It is not that different solvents were considered for the oxidation products of different precursors, but that in the case of the α-pinene oxidation products, different solvents were considered as potential surrogates. It is conceivable that under different atmospheric conditions, organic aerosol with different solvation properties develop. Whether it will be possible to find a single surrogate with solvation properties that are representative of most atmospheric conditions or whether the solvation properties of aerosol can be so distinct that not one solvent will suffice, remains to be confirmed. As a discussion of this topic is found on page 13202 in Wania et al. (2014), it shall not be repeated here.

p. 26562, section 3.3: There seems to be two types of uncertainty represented between the three models that are not clearly differentiated in this discussion. One is the unknown properties of the solvent, as represented empirically (in ppLFEr) or by surrogate(s) (in SPARC/COSMOtherm). The other is uncertainties associated with calculating phase partitioning using a semi-empirical approach (SPARC) vs. a quantum chemical approach (COSMOtherm).

The observation that two sources of uncertainty contribute to the uncertainty of the predicted Ks and therefore of the chemical placement in the partitioning space is correct. This issue was addressed in Wania et al. (2014). For example, we compared the partitioning coefficients

$K_{\mathrm{WIOM/G}}$ for the same surrogate solvents (octanol and WIOM B) predicted with two different methods to specifically quantify the second type of uncertainty. In the current manuscript we are ultimately interested in the overall uncertainty of the K prediction, which is a composite of the uncertainty of the conceptual approach and the uncertainty of the prediction method. We will add the following sentence: "The uncertainty of $K_{\mathrm{WIOM/G}}$ had previously been explored in Wania et al. (2014) and had been found to be a composite of the uncertainty of the prediction method and the uncertainty of the conceptual approach (How well do a surrogate's solvation properties match those of the organic aerosol phase? How representative are the solvation properties of the four real aerosol types characterized by Arp et al. (2008) of those of aerosol in general?). The uncertainty of the $K_{\mathrm{W/G}}$ is solely due to the uncertainty of the prediction method."

p. 26548, line 22: How do lower temperatures shift the partitioning of more volatile organics to the gas phase?

This occurs if a substance's water solubility is predicted to decrease faster with decreasing temperature than its vapor pressure. While a very slight decrease in the $K_{\mathrm{W/G}}$ of α-pinene with decreasing temperature is predicted by SPARC (Fig. 6A), this is not confirmed by measurements (Zhang et al., 2003). We therefore will delete the sentence "For example, lower temperatures shift the gas/aqueous phase equilibrium of volatile substances, such as α-pinene and n-alkanes, to the gas phase, but have the opposite effect for less volatile substances, such as the oxidation products formed from those volatile substances".

Discussion: Given the relatively large number of "visualization" spaces that have been proposed and presented for representing SOA, could a similar analysis be presented in the context of existing representations (rather than introducing a new one)?

This is an odd question to respond to. If we had felt that a similar analysis was possible in the context of previously proposed visualization spaces, there would have been no motivation for introducing the chemical partitioning space approach in the first place. So, clearly, we do not believe that a similar analysis is possible with existing graphical approaches, because none of them appears to account for the possibility of simultaneous partitioning into a mostly aqueous and a mostly organic phase.

Editorial Comments Presentation quality: The introduction is somewhat poorly written and could be revised to build confidence in the approach presented by the authors. Clarity in the first paragraph could be improved by first discussing environmental/atmospheric variables together and then chemical properties and their interactions (for example as grouped in the abstract).

As currently written the first paragraph first mentions chemical properties (*molecular size*, *functional groups*) and then environmental/atmospheric variables (*temperature*, *concentration and the polarity of the organic particulate matter present in the atmosphere*, *relative humidity and the resultant liquid water content*, *presence of electrolytes*). In other words, they are already grouped as in the abstract ("atmospheric parameters (such as temperature, salinity, WIOM phase polarity, organic aerosol load, and liquid water content), and chemical properties (such as oxidation state, molecular size, functionalization, and dimerisation)". The only difference is that we first mention chemical properties and then environmental variables.

Also, it is suggested that consistent terminology be used to describe the phases and partitioning compounds (condensed vs. aqueous vs. particle). For example, it is not clear why, on page 26548 line 20, the authors are discussing gas/aqueous phase equilibrium. Typically higher molecular weight organics would be expected to partition to a mostly organic phase.

As mentioned above, we propose to delete the sentence on page 26548, line 20. This means that the Introduction then refers to the condensed aerosol phases only twice: in the very first sentence on line 4, page 26548 ("Many atmospheric and chemical variables influence the partitioning equilibrium between gas phase and condensed phases of compounds implicated in the formation of secondary organic aerosol (SOA)") and again on line 2, page 26550 ("no attempt has been made so far to similarly display graphically the distribution behaviour of SOA compounds between the gas phase, the atmospheric liquid water phase, and the organic aerosol phase at the same time”).

26548 line 8: Size and polarity influence the extent to which compounds prefer the gas or particle phase, but it isn’t an either/or for the semi-volatile compounds as written. It also isn’t clear (as written) that the gas and condensed phase(s) together make up the aerosol, and the compounds of interest are continuously shifting (to some degree) between these phases.

This sentence reads: “For example, the molecular size of the compounds and the functional groups they contain have a strong influence on their preference for either gas phase or the condensed phase(s) making up an aerosol.” We don’t understand why it would not be either/or. Even semi-volatile compounds either **have a preference** for the gas phase or the condensed phase(s) under a given set of circumstances. This doesn’t imply that they have to be exclusively in either gas or condensed phase(s).

We had worked with the assumption that the term aerosol refers only to the condensed phase(s) and that the gas phase is not part of the aerosol. We will now specifically state “the condensed phase(s) making up the aerosol particles”.

We agree that the phase distribution is shifting in response to a wide range of atmospheric/environmental variables, which is the subject of the three sentences that follow.

It is suggested that the assumptions of the chemical partitioning space (2.4) be presented before the discussion of partitioning coefficients (2.3).

We will change the sequence of sections 2.3 and 2.4, as suggested by the reviewer.

p 26558, line 10: replace “acknowledged” with “accepted”

This sentence reads: “this view is not yet universally acknowledged”. The meaning of the word “acknowledge” is to “1. accept or admit the existence or truth of. 2. (of a body of opinion) recognize the fact or importance or quality of” (Google). As such, we think the term is expressing precisely what we had in mind.

p 26565, line 17: The statement that SPARC predictions for highly polar solvents should be considered suspect seems like an overgeneralization and not necessarily well supported by the results.

We disagree. Please note that the sentence states “for the highly polar solvents” and not “for highly polar solvents” and therefore does not involve a generalization beyond the solvents whose solvation properties were predicted here.

References

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