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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- Zhang, H. Z., Li, Y. Q., Xia, J. R., Davidovits, P., Williams, L. R., Jayne, J. T., Kolb, C. E., and Worsnop, D. R.: Uptake of gas-phase species by 1-octanol. 1. Uptake of α-pinene, γ-terpinene, p-cymene, and 2-methyl-2-hexanol as a function of relative humidity and temperature. J. Phys. Chem. A, 107, 6388–6397, 2003.
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- Wania, F., Lei, Y. D., Wang, C., Abbatt, J. P. D., Goss, K.-U.: Novel methods for predicting gas-particle partitioning during the formation of secondary organic aerosol. Atmos. Chem. Phys., 14, 13189–13204, 2014.

Response to Anonymous Referee #2

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 a still a highly 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.

We thank the reviewer for the favorable appraisal and for the thoughtful suggestion for improving the manuscript.

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?

The reviewer is raising an interesting point, although we suspect that non-phase separated aerosol is generally dominated by water and does rarely have equal parts water and organic matter. Whether a phase is considered mostly aqueous or mostly organic to some extent also depends on the way composition is defined: On a molar basis, even largely organic phases are made up mostly of water molecules (see e.g. Zuend and Seinfeld, 2012), although this does not imply that their solvation behavior is closer to water than to an organic solvent. Ultimately, it does not matter whether we call such an aerosol aqueous or organic. If its composition was known, we would be able to calculate the respective partitioning. Under typical atmospheric conditions it appears that phase separation is common, and that is why our calculations focus on this scenario. We will delete the word aqueous in the phrase "the possibility of the formation of a single condensed ~~aqueous~~ phase" and rephrase the sentence "all of the organic material present will be in a single~~, largely aqueous~~ condensed phase".

(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' graphical representation? Some discussion reconciling known observations with this theoretical representation would be warranted.

The excised portion (represented by the three dots) in the sentence on the partitioning properties of the oxidation products of the mono-aromatic hydrocarbons is "identified by Forstner et al. (1997)", which is a very important qualification. While we do not contest that there is evidence for sizable SOA yields from mono-aromatic oxidation, we would suggest that the compounds making up this SOA are unlikely to be those identified in Forstner et al. (1997). There is therefore no discrepancy. The reviewer quite rightly surmises that there might be higher generation oxidation products and products of oligomerisation reactions that are responsible for the SOA formation from mono-aromatics. We had previously encountered that the oxidation products identified in a study (e.g. monoterpene ozonolysis in Chen and Griffin (2005)) are too volatile to contribute notably to SOA formation. See discussion on this issue on page 13201 of Wania et al. (2014).

We will add the following sentence for clarification: "SOA formed during the oxidation of monoaromatics (Ng et al. 2007, Wyche et al. 2009) is therefore unlikely to be made up of the substances identified in Forstner et al. (1997) and displayed in Fig. 2."

> 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).

We have previously calculated SOA yields from the oxidation of *n*-alkanes of different chain length and compared those yields with the ones calculated by Jordan et al. (2008) and measured by Lim and Ziemann (2014). This comparison is described in section 4.2 (pages 13200-13201) of Wania et al. (2014).

> (3) At various points throughout the manuscript, I find the discussion of water effects on partitioning muddied 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 ug/m^3, as is more typical of ambient aerosols near the ground.

The application of the term liquid water content (LWC) is not limited to aerosol but is also applied to clouds. To prevent confusion we will now avoid the phrases "low LWC" and "high LWC" and refer more explicitly to "low LWC typical of aerosol" and "high LWC typical of clouds" in the section 26565-66. We will also qualify the statement "analysis of phase partitioning that ignores liquid water in the atmosphere can lead to erroneous conclusions, **especially in the presence of clouds**".

> (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.

We believe that our paper indeed explores the impact of functionalization of α-pinene in the partitioning space. This is done implicitly in Figure 6 and explicitly in Figure 11. Figure 6 displays the location of various products of α-pinene oxidation in the partitioning space and while they are not explicitly identified as being part of a specific reaction sequence, they clearly have different levels of oxidation (note that the oxidation products are represented by differently coloured lines depending on the number of oxygen atoms) and thus belong to multiple generations of oxidation products. In Figure 11, the red cone on the left side of the diagram explicitly envelopes the products formed during the oxidation of α-pinene (and was derived from the placement of chemicals in Figure 6).

> It is not clear that a-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.

According to our predicted partition coefficients, the slope in the partitioning space is very similar for α-pinene and *n*-alkane oxidation products, i.e., the two cones in Figure 11 are parallel to each other. Also, in both cases nitration leads more to a 1:1 decrease in $K_{W/G}$ and $K_{WIOM/G}$ than addition of a oxygen containing functional group, where $K_{W/G}$ tends to increase more rapidly than $K_{WIOM/G}$. In fact, we would not really expect widely different effects on $K_{W/G}$ and $K_{WIOM/G}$ depending on whether the functional group is added to an aliphatic or an unsaturated alicyclic compound.

We appreciate being made aware of the recent paper by Hodzic et al. (2014), which displays log *H*-log *C** relationships for atmospheric oxidation products of different SOA precursor compounds in diagrams (Figure 1 in Hodzic et al.) that are quite similar to the partitioning space plots in our manuscript. We will now reference that paper in the introduction (by adding the sentence: "Recently, Hodzic et al. (2014) placed SOA compounds in a two-dimensional space defined by saturation concentration and effective Henry's law constant in order to observe and derive relationships between these two parameters for different groups of SOA compounds").

We also compared the findings of Hodzic et al. with our observations. Among the commonalities are:

Wania et al.	**Hodzic et al.**
The red cones in Fig. 11 enveloping the oxidation products of α-pinene and the C17 *n*-alkane have similar slopes in the partitioning space.	"Similar dependencies between *H* and *C** are observed for products of major biogenic and anthropogenic precursors"
In Fig. 11, the cone enveloping the oxidation products of α-pinene is below (i.e. at a higher $K_{W/G}$ indicating stronger preference for the aqueous phase) the cone enveloping the oxidation products of the C17 *n*-alkane.	"the oxidation products of biogenic precursors are typically more soluble than those of anthropogenic precursors (the intercept for terpenes is larger by two orders of magntitude than that of toluene)"
The nitrated products of α-pinene and C17 *n*-alkane tend to fall along the upper edge of the cones in Fig. 11, implying that they have a relatively lower $K_{W/G}$ (weaker preference for the aqueous phase) compared to the oxygenated products.	"An increase in *H* up to an order of magnitude in the intercept is generally observed for lower NO_x, indicating that the products formed are typically more water soluble."

The discrepancy is the one identified by the reviewer:

Functionalization of precursor compounds tends to increase $K_{W/G}$ twice as fast as $K_{WIOM/G}$	"The slope of the linear regression [between $\log_{10}H$ and $\log_{10}C^*$] varies between -0.5 and -0.9."

We have to presume that this discrepancy has its root in the differences in the prediction of *H* and *C** on one hand and $K_{W/G}$ and $K_{WIOM/G}$ on the other. We make two observations:

- The faster increase in $K_{W/G}$ than $K_{WIOM/G}$ upon precursor functionalization was observed when predictions are made with SPARC, ppLFER and COSMOtherm (Compare e.g. Figs. 6A, 6B and Fig. S2).
- In Hodzic et al. (2014), both *C** and *H* were predicted with group contribution methods (Raventus-Duran et al., 2010, Nanoolal et al., 2008), which have unknown and possibly quite larger uncertainties for substances that are dissimilar (e.g. have a much larger number of functional groups) from the training data set (which encompasses largely hydrocarbons and monofunctional substances).

We will include sentences that comment on these commonalities and discrepancies, specifically in section 3.5 we will add: "Hodzic et al (2014) also noted that the relationships between effective Henry's law constant and saturation concentration were similar for the products of different precursors" and "Incidentally, this is different from what Hodzic et al. (2014) noted for the oxidation products of different precursors: for a one log unit change in saturation concentration, the effective Henry's law constant only changed by 0.5 to 0.9 log units" and "This is in agreement with Hodzic et al. (2014), who noted that products formed during low NO_x conditions are predicted to be more soluble."

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.

We will rephrase the first sentence of the Introduction to: "The phase distribution of oxidized organic compounds between the gas phase and the condensed phases present in the atmosphere, and how that distribution is affected by atmospheric and chemical variables, is central to the understanding and quantification of the formation of secondary organic aerosol."

(6) Page 26548 line 20-21: Include a reference for the sentence "lower tempetatures shift the gas/aqueous phase equilibrium of volatile substances, such as a-pinene and n-alkanes, to the gas phase", as this is counterintuitive.

This sentence will be deleted in response to a comment by anonymous referee #1.

(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.

We will now also cite here the papers suggested by the reviewer.

(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.

The sentence will be rephrased as suggested and the following phrase will be added: "and typically derived from saturation vapour pressure"

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

"Partitioning coefficient" will be replaced with "partition coefficient" throughout.

(10) Page 26550 line 25: missing the word "is" after $K_{X/Y}$.

The three words "has units of" got lost during type setting and will be added again.

(11) Page 26553 line 26-29: a bit more discussion of the central region is warranted. While the white triangle is clear 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.

We will add the sentence: "Finally, the two triangular areas with bow-shaped flanks, surrounding the white triangle and being delineated by dashed lines, encompass properties of chemicals that partition mostly in one phase, with the remainder split between the other two phases."

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

We will add a reference to Hilal et al. 2004.

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

We will add the phrase: "with 8 to 17 carbons"

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

We agree. This issue is discussed in more detail in section 3.4 with respect to α-pinene oxidation products. While these substances not necessarily exist in all three states at the same time, they can occur in all three states depending on the prevailing atmospheric conditions (temperature, LWC, OAL, salinity, etc.). We will add the following sentence: "Figure 4 reveals that higher generation oxidation products of monoterpenes and mono-aromatic hydrocarbons fall mostly into the SV-OOC category in the centre of the partitioning space, indicating that they may partition to a significant extent into gas, aqueous and WIOM phase depending on the prevailing atmospheric conditions. This also means that their exact placement in the space is important, because it will affect the predicted phase distribution."

(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 $K_{X/Y}$, thus, "prediction of $K_{WIOM/G}$ appear to be generally biased low relative to SPARC predictions and the $K_{W/G}$ 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 $K_{W/G}$ and a lower value in $K_{WIOM/G}$, 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 ppLFER value in 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.

The reviewer is correct and we appreciate their very careful reading of our manuscript. We had erroneously labeled Figure S3: the origin of the arrows corresponds to the ppLFER predictions and the tip of the blue arrows corresponds to the SPARC predictions. In other words, the descriptions in the text were correct, but the figure was not. We will correct Figure S3 accordingly and also add labels to identify compounds that are explicitly mentioned in the text.

(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 exists (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.

SPARC in this case was used to predict solvation in pure organic solvents, not in complex, potentially multiphase, ambient aerosol. Based on data in Park et al., 1987, the activity coefficient in different organic solvent can indeed vary widely (by about two orders of magnitude), but not as widely as predicted here by SPARC. We thus still believe that the range of $K_{Solvent/G}$ predicted by SPARC is implausible.

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

We agree.

(18) Page 26567 line 27: "functionalization roughly increases the $K_{W/G}$ by two log units for every log unit increase in log $K_{WIOM/G}$". 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.

Based on Table 1 in Hodzic et al. (2014), the relationship between the effective Henry's law constant H and the saturation concentration C^* for the oxidation products of the C-18 *n*-alkane under low NO_x conditions is: $\log_{10}(H) = -0.51 \log_{10}(C^*) + 6.43$.

In other words for a one log unit change in C^*, H changes by half a log unit. Surprisingly this is the opposite of what we observed: $K_{W/G}$ changes by two log units for every one log unit change in $K_{WIOM/G}$. We have no explanation for this discrepancy, but point out that the trend we observed was obtained using ppLFER, SPARC and COSMOtherm predictions. We also believe our results to be more plausible: functional groups that result from oxidation should increase the interactions with water more than the interactions in the pure phase, i.e., should affect the Henry Law constant to a larger extent than the saturation concentration in the gas phase.

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

During typesetting, the words "has units of" was deleted from line 25 of page 26550. $K_{X/Y}$ is therefore not defined as "m^3 of phase Y per m^3 of phase X", but merely has units of "m^3 of phase Y per m^3 of phase X".

When Figure 1 is first referenced on line 8 of page 26551 ("In Fig. 1a, log$K_{W/G}$ and log$K_{WIOM/G}$ are used to define such a space.") it is only to introduce the two axes and no reference is made to what is displayed in the coordinate system. At this point it is not necessary to understand the entire figure.

The caption to Figure 1 is already very long and we are reluctant to add more text. It has a focus on describing what is being displayed and not on how it is being constructed (i.e. the underlying equations) and we are doubtful that it would be feasible to write a caption that would allow a complete understanding of the figure without also reading the main text.

Unfortunately, we do not understand the comment on adding axes.

(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.

We will add labels identifying the C-8 and C-17 compound among the *n*-alkanes, as well as the precursors.

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

We will add the following sentence to the caption of Figure 6: "The red lines encircle regions where chemicals fall whose contribution to SOA formation would not be considered, if the aqueous phase in an aerosol (solid line) or in a cloud (dashed line) were ignored."

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