Response to Anonymous Referee #1

Uncertainties in the prediction of the gas-particle partitioning equilibrium of organic compounds during SOA formation arise primarily from the difficulties in the measurement or estimation of vapor pressures and activity coefficients. In most current SOA predictive models, activity coefficients are simply assumed to be unity, which could lead to the overestimation of saturation concentration by assuming ideal condensed phase behavior. A number of approaches, such as group contribution methods, have been developed to estimate vapor pressures, although predictions from different methods are not in good agreement.

Wania et al. employ three well-established methods, i.e., 'ppLFER', 'SPARC', and 'COSMO-RS', to calculate the partitioning coefficient directly, as opposed to combining the activity coefficient and vapor pressure of individual compounds via Raoult's law. This new approach, if demonstrated as less error prone than the traditional methods, is indeed worth being introduced to and adopted by the SOA community. It is necessary to establish that this new approach reduces uncertainties below those of the traditional methods. In addition, there are some minor issues that require clarification before publication, which are discussed below.

We appreciate the thoughtful review and the recognition of the potential merits of the approach we present.

Major Comments:

1. The authors choose the chamber-generated SOA yields from photooxidation of alkanes under high NO conditions as a 'standard' for comparing different methods and find that this new approach can reproduce the chamber data as well as or better than the traditional approach. The use of chamber-derived SOA yields as a 'standard' to evaluate different methods for the prediction of partitioning coefficients has one drawback: SOA yields are potentially underestimated due to deposition of organic vapors on the chamber walls.

We agree with the reviewer that agreement, or lack thereof, between SOA yields measured in chamber experiments and such yields predicted based on different methods should be interpreted carefully, because of the potential for wall sorption artifacts. We have expressed this caution in section 4.2. Despite those reservations, we wanted to include this comparison, because empirical data for directly evaluating the predicted partition coefficients are missing. Note that in response to a comment from reviewer 2, we have rephrased statements concerning the comparison of predicted and measured yields more cautiously.

A potential alternative approach, for example, is to estimate the vapor pressures of organic compounds based on the calculated partitioning coefficient using the three approaches, 'ppLFER', 'SPARC', and 'COSMO-RS', and then compare the estimated vapor pressures with those measured experimentally for a variety of compounds or estimated by the vapor pressure prediction models. Compounds with multi-functionalities and known vapor pressures are the best candidates. Uncertainties in the vapor pressure estimation will arise from the value assigned to the activity coefficient. Can any of the three models predict the activity coefficient as well? Can a value between 0.8 and 10, as stated in the draft, be assigned to the activity coefficient for all compounds?

While we appreciate the desire of the reviewer to aid us in identifying means of evaluating our predictions of partition coefficients $K_{i,WIOM}$ with empirical data, we feel that the idea of estimating vapour pressures $p_{i,L}$ from $K_{i,WIOM}$ by assuming a certain range of activity coefficients γ_i runs counter to the very essence of what we are trying to do, namely advocate the use of $K_{i,WIOM}$ **INSTEAD** of $p_{i,L}$ and γ_i.

Furthermore, the availability of reliable measured $p_{i,L}$ data for highly multi-functional compounds is only very marginally better than the availability of measured $K_{i,WIOM}$. As we had written in the Introduction of the original submission (page 21345 line 24 to page 21346, line 2: "Although evaluation … organic aerosol.")

2. The authors need to address the influence of particle-phase chemical composition on the estimation of partitioning coefficients. Four aerosol samples collected from urban and rural sites at different seasons, four organic compounds, and a mixture of alkane photoxodiation products are used as the possible surrogates for the solvents (particle phase).

What are the chemical properties of these surrogates that could potentially affect the predicted values of partitioning coefficients? In addition, sensitivity tests using varying solvents are necessary to be carried out. These tests can give insights into the choice of SOA composition for the prediction of gas-particle partitioning of products from the photochemistry of a variety of VOC systems.

While physical chemists have identified cohesion and the ability to act as H-bond acceptor and/or donor as the main determinants of a solvent's properties, aerosols had never been characterized for these properties. The strategy of Arp et al. (2008) was to characterize aerosols from different locations and time of the year in this regard.

We are not entirely sure what the reviewer is requesting, because in our opinion the manuscript already includes a "sensitivity test using varying solvents". Section 3.1.2 and Figure 6, in fact, compare the predicted partition coefficients into five different solvents. While we conclude from this comparison that solvent polarity has the potential to notably "affect the predicted values of partitioning coefficients", the predicted *K*s for relatively non-polar solvents are very similar.

When formulating our overall conclusion from the comparison of predicted *K*s (page 21359 line 23 to page 21360 line 2: "In general, it appears as if …. treat the WIOM phase"), we are also careful to not extend it to a "variety of VOC systems", but limit it to the *n*-alkane oxidation products.

In Wania et al. (2014), we calculated $K_{i,WIOM}$ for a number of oxidation products of α-pinene using three surrogate solvents of variable polarity to represent WIOM. In that case, SPARC and COSMOtherm disagreed how strongly $K_{i,WIOM}$ is affected by the choice of solvent. For more detail we refer to the discussion on page 26565 of Wania et al. (2014).

Minor revisions:

1. Page 21349, Line 18: What are the general properties of the solvent, single species or a mixture of compounds? If the solvent is a mixture of organic compounds, which is mostly the case for SOA, how could one represent the particle phase using solely molecular structure as input?

This sentence read: "All three methods thus can be used to predict the partitioning equilibrium between WIOM and the gas phase at any temperature using only molecular structure as input." Molecular structure here refers to the compound for which the partitioning equilibrium between WIOM and gas phase is to be predicted and not to how the particle phase is represented. In order to make this clear we have rephrased the sentence to: "All three methods thus can be used to predict an organic chemical's partitioning equilibrium between WIOM and the gas phase at any temperature based solely on its molecular structure."

The issue of the representation of the particle phase had already been addressed on page 21347 lines 11-13: "All three methods require information about the sorbing SOA phase either in the form of one or more representative molecular structures (COSMOtherm and SPARC) or in the form of a calibrated equation (ppLFER approach)."

2. Page 21350, Line 11: This sentence is not exactly correct. First, the cyclization of hydroxycarbonyl occurs on the surface or in the bulk phase of particles, producing hydroxyhemiacetal, which then loses water forming substituted dihydrofuran. Second, the vapor pressure of hydroxycarbonyl is relatively low and its partitioning into the particle phase can't be ignored, especially for long chain alkanes and under high SOA loadings.

Jordan et al. (2008) give a more detailed explanation why they did not consider the contribution of hydroxycarbonyls to the SOA yield. They wrote: "Hydroxy-carbonyls are not permitted to exist in the aerosol-phase. Laboratory studies indicate that they are converted to dihydrofurans via a heterogeneous process of cyclization and dehydration on the order of 10 min (Atkinson et al., 2008; Lim and Ziemann, in preparation). The vapor pressures of the dihydrofurans are sufficiently high that they return to the gas-phase from the particle. Because of the rapid nature of this process, the model treats the conversion of hydroxycarbonyls to dihydrofurans as if it occurred in the gas-phase."

Based on the reviewer's comment, we have rephrased the sentence to: "Partition coefficients for three δ-hydroxycarbonyls (RP21, AP14, AP16) were not included, because their rapid conversion into dihydrofurans should prevent them from making a significant contribution to the SOA yield (Jordan et al., 2008)"

3. Page 21350, Line 20-25: What are the general properties, such as average carbon oxidation state and molecular weight, of the four aerosol samples given by Arp et al. (2008b)? The authors calculated the partitioning coefficients for the alkanes and their oxidation products using these four aerosol samples as the absorbing phase and the calculated $K_{i,WIOM}$ values seem to agree with each other, as shown in Figure 5. Since the four aerosol samples as the solvent are the only variables in the calculation, what is the effect of their chemical properties on the calculated $K_{i,WIOM}$ values? Can the authors explain why the calculated partitioning coefficients are consistent with each other, although the four aerosol samples were collected at different seasons and places and might have very different characteristics?

Arp et al. (2008) recorded only a limited number of characteristics of the four ambient aerosol samples that formed the basis of the four ppLFER equations used in our study (for detail see response to point 5 below). Average carbon oxidation state and molecular weight were not determined. Because the aerosol samples from those studies no longer exist, retrospective characterization is neither possible.

We therefore do not know whether the similarity of the solvation properties of the four aerosol samples were the result of (i) a similar oxidation state (and therefore phase polarity) of the sampled aerosol, despite the differences in the type of locale and the season of sampling, or (ii) whether most ambient aerosol have similar solvation properties, despite differences in oxidation state.

4. Page 21351, Line 15: Please state why octan-1-ol was chosen as the solvent surrogate since its vapor pressure at room temperature is pretty high and as a result, a large fraction of this compound should be in the gas phase at typical aerosol mass loading, i.e., < 50 µg/m3.

Octan-1-ol was not chosen as a surrogate because it might resemble compounds found in organic aerosol. In fact, we agree with the reviewer that it is more volatile (and likely also considerably less oxidized) than compounds typically found in organic aerosol. As explained on page 21351 line 11 ("Following earlier work that has suggested that the solvation characteristics of the organic matter found in atmospheric aerosol resemble those of octan-1-ol (Finizio et al., 1997; Pankow, 1998)"), it was primarily chosen because it had previously been proposed as a surrogate solvent to represent organic aerosol. It is also routinely used in the prediction of the gas/particle partitioning of hazardous organic trace compounds (e.g. Kaupp & McLachlan, 1999; Lohmann & Lammel, 2004). One of the advantages of octan-1-ol is that because of its half century of use as a surrogate in pharmacology, a multitude of experimental solvation data and numerous predictions techniques for solvation into octan-1-ol exist.

5. Page 21355, Section 3.1.2: The authors compared the calculated partitioning coefficients by the 'SPARC' approach using different surrogate solvents, as shown in Figure 6. There seems to be a large impact of the choice of surrogate solvents on the calculated K_i values. This is not consistent with predictions by the 'ppLFER' approach, which indicate that the predicted K_i values are in general independent of the properties of the aerosol samples. I wonder how important the particle-phase characteristics is in determining the partitioning coefficient? It would be very useful if the authors can give a table, listing the properties of all the particle phase makeups, including aerosol

samples and surrogate solvents, and illustrate the impact of the particle phase characteristics on the predicted partitioning coefficients.

We agree with the reviewer that it would have been useful to have a detailed characterization of the four ambient aerosol samples. As mentioned in response to point 3, however, only a limited number of measurements had been performed on those samples. Data on mass concentration and the mass fraction of elemental and organic carbon from Table 1 in Arp et al. (2008) are given here:

	Berlin Winter	Aspvreten	Dubendorf Winter	Roost
Average PM_{10}	30 μg/m^3	8 μg/m^3	22 μg/m^3	nd
f_{EC}	0.14±0.03	0.04	0.16±0.03	0.15±0.03
f_{OC}	0.22±0.05	nd	0.24±0.05	0.29±0.07

We believe that the information in this table is too limited to draw meaningful conclusions regarding a relationship between the characteristics and solvation properties of the aerosol.

As for the characteristics of the surrogate solvents, we list their O:C ratio and average carbon oxidation state in the text (bottom half of page 21531). However, we fail to observe a clear relationship between those two parameters and the predicted solvation properties, which is discussed on page 21365, line 2 ("Interestingly, our study suggests … widely different oxidation states.")

In other words, it does not appear as if there is an obvious relationship between easily obtained characteristics of the solvents (and of ambient organic aerosol samples), such as O:C ratio and average carbon oxidation state, and their solvation properties.

6. Page 21357, Section 3.1.5: Would it be a better constraint to use the same surrogate solvent, in order to compare predictions by the three different approaches?

No, because predictions for the same surrogate solvent had already been compared and discussed in section 3.1.4. The three methods compared in 3.1.5 were selected with a view to have conceptually widely different approaches represented (as explained in page 21357 line 9-15), i.e. we deliberately avoided the use of the same surrogate.

7. Page 21358, Line 4: Are the SOA yields the maximum, or measured after a certain amount of OH exposure? Please specify.

The yields are those recorded at the end of the experiments lasting one hour. The sentence on line 4 of page 21358 was amended as follows: "SOA yields **corresponding to the end of** the chamber experiments of Lim and Ziemann (2005) were calculated".

8. Page 21362, Line 14-20: A recent study by Ehn et al. (2014) reported the formation of extremely low volatility compounds from the ozonolysis of alpha-pinene. If the authors use one of these ELVOC compounds as the particle phase surrogate, how would the predicted SOA yield change?

We would expect that the SPARC-predicted solvation properties of the highly oxidized ELVOCs would be quite different from those we predicted for the relatively non-polar surrogates (WIOM B, octanol, most abundant oxidation product). As such, we suspect that a SOA yield estimate based on partitioning to an ELVOC phase would show larger discrepancies from the measured yields (compare e.g. the poor yield estimates obtained with the polar surrogate MBTCA and MT in the middle panel in Fig. S2).

The experiments by Lim & Ziemann (2005) included only *n*-alkanes as VOC precursors and no terpenes, such as α-pinene. There is no compelling reason to believe that ELVOCs originating from the oxidation of α-pinene are a good surrogate for the solvation properties of SOA formed exclusively from the oxidation of *n*-alkanes. They are, however, an obvious surrogate to consider when the objective is to predict the partitioning behaviour of α-pinene oxidation products. We refer to our recent submission (Wania et al. 2014), which explicitly deals with the latter. Although this study does not consider an ELVOC as described in Ehn et al. (2014) as a potential surrogate solvent, it employs a highly oxidized α-pinene oxidation product (5-hydroperoxy-4-(hydroxymethyl)-5- methyl-2-oxohexanoic acid, designated as C813OOH in the Master Chemical Mechanism model) as a surrogate solvent.

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Response to Anonymous Referee #2

General Comments

This manuscript deals with the description and evaluation of a group of alternative approaches to determining the equilibrium partitioning of organic compounds in the dry (non-aqueous) organic aerosol phase – authors refer to this as water insoluble organic matter (WIOM). Thorough comparison of the three techniques for a case study of OH-oxidation of n-alkanes is presented. The partitioning coefficients ($K_{\mathrm{i,WIOM}}$ per the authors' notation) are calculated for each of the oxidation products for the n-alkane reactions using the different techniques and are shown to compare quite well despite the differences in the underlying calculations. Of particular interest are their results demonstrating assuming a single surrogate compound for the WIOM phase and using a less computationally intensive approach seems to reproduce the results of a more fundamental calculation.

The work is certainly relevant and of great interest to the SOA community, as it proposes what amounts to a paradigm shift in the approach to determining the gas-particle particle partitioning of organic compounds in the ambient environment.

We appreciate the very thorough and detailed review as well as the recognition of the potential relevance of the presented material.

The authors point out the lack of available data to assess vapor pressure predictions and do, to their credit, not ignore the same fact for their own proposed alternative approaches. If an experimental method were to be established for the direct measurement of $K_{\mathrm{i,WIOM}}$, then the accuracy of their approaches could be assessed alongside vapor pressure estimation techniques and could feasibly be of great importance to the SOA community.

We note that $K_{\mathrm{i,WIOM}}$ has been measured directly for a large number of organic chemicals using an experimental method (inverse gas chromatography), and these data have already been used to evaluate the three estimation techniques we use. This work has been described in a series of papers by Arp et al. (2008a, 2008b, 2009). What is missing for the evaluation of **both** vapor pressure **and** partitioning coefficient estimation techniques are experimental data for chemicals with multiple functional groups within the volatility range relevant for SOA formation.

However, it will almost certainly be received critically as a result of the manuscript's overall tone. Additionally, the quantification of the extent to which the authors' methods are more precise than those typically used in the SOA community is questionable, and despite the authors' own caution against over-interpretation, these case-study results appear to be overgeneralized in a few places throughout the document.

Our response to specific issues the reviewer raises is given below.

Specific Comments

While the first 3 paragraphs recapitulate the authors' argument quite well, the remainder of the introduction is spent thoroughly repudiating the typical vapor pressure estimation techniques in the SOA community, which is not altogether surprising considering the aim of this manuscript. However, this sets the tone of the paper, which potentially undermines its reception amongst the target audience.

Surprised by the comment, we reread the entire manuscript and specifically the Introduction, but could not find anything unprofessional, inappropriate or unduly harsh. Obviously, we try to be persuasive, because we want to convince the SOA community to reconsider the use of an approach that it has been employing for a long time. This involves the need to highlight the shortcomings of that approach.

The subtle differences between the ppLFER, SPARC and COSMO-RS results (through 3.1.3) provide great insight into these alternative approaches, but it is noted earlier that they are "not really new" and that they have just "yet to be discovered and adopted by the wider SOA community" (pg. 21346, Ln. 24). Referring to these described methods as "novel" in the title, therefore, seems to suggest something that is not the case. The authors' own words also support this interpretation: pg. 21347, ln 2: ". . . we apply them here illustratively to the products of the OH-initiated oxidation of normal alkanes in the presence of NOx. . ." Why not use a re-wording of that as the paper title since it is more representative of the content? This change would also help soften the perceived tone of the manuscript.

The manuscript title does not claim that we introduce "Novel methods for predicting gas-particle partitioning", but "Novel methods for predicting gas-particle partitioning during the formation of secondary organic aerosol". We think this is entirely appropriate representation of the content of the paper. Even though the methods we use have been introduced by one of us five years ago, to the best of our knowledge they have not been used in the wider SOA community. This is the first paper to apply these methods in the context of SOA formation.

Our primary interest with this paper is not the modeling of SOA formation during *n*-alkane oxidation, but demonstrating to the SOA community the feasibility and benefits of alternative approaches to quantifying gas-particle partitioning.

Additionally, the predicted SOA yields by these methods are referred to as being both "as good or better" (in abstract and Pg. 21358, Ln. 13) and "for the most part better" than the vapor pressure estimation methods discussed (e.g. Jordan et al., 2008). Whereas this comparison was qualified elsewhere, it ought to be qualified in the conclusions section as well – particularly for readers that may skim more than others, so as not to mislead. Perhaps the conclusion and abstract should be re-worded, as this has not been demonstrated to be a general result.

As suggested by the reviewer, abstract and conclusion section have been rephrased. In the abstract, we now write: "Furthermore, these partitioning coefficients $K_{i,WIOM}$ predicted SOA mass yields in agreement with those measured in chamber experiments of the oxidation of normal alkanes." In the conclusion section, it now reads: "For one case study, namely the oxidation of *n*-alkanes, we have shown that the use of $K_{i,WIOM}$ predicts SOA yield in agreement with experimental results obtained in chamber experiments."

The primary assertion of this manuscript is that $K_{i,WIOM}$ can be predicted with "much greater precision" (Pg. 21364, Ln. 2) than vapor pressures for individual compounds. This does appear to be true based on the MAD (also known as mean average error, MAE in other contexts) values calculated between the different $K_{i,WIOM}$ predictions here when compared against their selected literature values. However, it could be argued to be a tenuous conclusion for the following reasons.

Clearly, the quantitative comparison of the uncertainty in the prediction of $p_{i,L}$ and $K_{i,WIOM}$ is fraught with many potential problems. The reviewer deserves credit for highlighting some of these issues, which include:

- MD and MAD are imperfect criteria, especially because they depend on how many and which methods are included in the comparison (point [1] below),
- $p_{i,L}$ and $K_{i,WIOM}$ do not express exactly the same quantity (point [2] below),
- Ideally, predictions for exactly the same set of semi-volatile compounds should be compared (also part of point [2] below).

Another issue is that precision does not necessarily imply accuracy. Even if several methods come up with very similar predictions, they can be inaccurate.

On the following pages we concede that the comparison of prediction uncertainty in section 4.1 is afflicted by all of these problems. However, we maintain that the weight of evidence is so overwhelming, that the conclusion that $K_{i,WIOM}$ can be predicted with much greater precision than $p_{i,L}$ is still valid.

[1]: The authors' logic appears to be: typical vapor pressure estimation methods have an expected MAD > 2 (Pg. 21346, Ln. 15), so as long as the alternative methods have MAD < 2, then they are more precise. The premise to that argument, though, is loosely defined as there are plenty of examples (in this paper's references no less) where different vapor pressure estimation techniques have MAD values on the order of those for the approaches advocated in this manuscript. If this "2 log unit" uncertainty comparison were to be made convincing, perhaps a different metric than the MAD should be used that better encapsulates the impact of outliers (like RMSE) despite the fact that MAD/MAE are often used to assess the performance of vapor pressure prediction techniques elsewhere in the

literature.

The MD and MAD that are found between different predictions depend on (i) the number and type of prediction methods and (ii) the type and diversity (and possibly the number) of chemicals, that are included in the analysis. This is, however, the case for all other measures that could be used to quantify agreement, including the RMSE. As such, quantitative measures of prediction discrepancy should only be compared in a very general sense and with these limitations in mind.

In the present context, we feel strongly that the comparison of prediction uncertainty is strongly biased against $K_{i,WIOM}$ and in favour of $p_{i,L}$ (for several reasons, see also response to [2] below). The $p_{i,L}$ methods for SOA compounds that are generally compared (e.g. in Valorso et al., 2011) are conceptually similar (i.e. are group contribution methods) and rely on essentially the same set of empirical data for calibration. The $K_{i,WIOM}$ approaches we include in our comparison are based on widely different conceptual approaches and rely to a varying extent on calibration data and these calibration datasets are different for different methods. That the (admittedly imperfect) measures of discrepancy indicate better agreement for the three dissimilar $K_{i,WIOM}$ predictions than for the three similar $p_{i,L}$ predictions makes in our opinion a strong case for the better precision of the $K_{i,WIOM}$ prediction.

Clearly, the more volatile the substances, the better the agreement between different $p_{i,L}$ prediction methods can be expected to be, because the set of calibration data encompasses mostly relatively volatile substances. Figure 4 on page 6899 of Valoroso et al. (2011) illustrates very well how the agreement between $p_{i,L}$ predictions deteriorates with decreasing volatility. Therefore, the comparison of prediction uncertainty has to apply to the same volatility range (see point [3] below).

[2]: In another sense, the two quantities $K_{i,WIOM}$ and vapor pressure do not have the same physical meaning, so should their variation be related in such a way? For instance, the activity coefficient and molecular weight variability between compounds is implicitly considered in the value of $K_{i,WIOM}$ but not of vapor pressure alone.

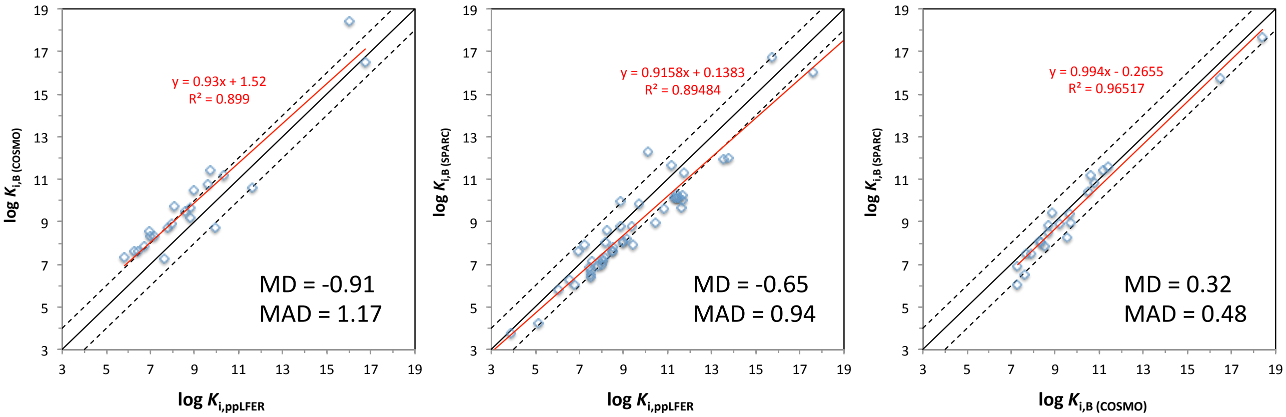
Predicting gas/particle partitioning via vapour pressure and activity coefficient requires the prediction of two different processes and thus has two sources of error. Instead we directly predict the partitioning free energy for the process of transferring a molecule between air and WIOM. This does not - **also not implicitly** - require the activity coefficient (which is related to the intermolecular interactions or a chemical within its own liquid phase, a situation that is of no relevance in the context of SOA formation).

In other words, the reviewer is somewhat correct in suggesting that it is not entirely valid to directly compare the variation in predicted $p_{i,L}$ and in predicted $K_{i,WIOM}$. This is the second reason why the comparison is “rigged” in favor of the $p_{i,L}$-based prediction, because it ignores the additional variation introduced by the estimation of activity coefficients.

As another example, the manuscript cites Valorso et al., 2011 (pg. 21360, ln. 7) in its discussion. This study and the cited material consider different SOA systems and perhaps even different ranges of volatilities – something the authors should directly address in the manuscript. To that end, it would be interesting to see similar results for the alpha pinene system mentioned elsewhere in the paper.

We agree with the reviewer that it is not entirely valid to compare the variation in the prediction of $p_{i,L}$ of α-pinene oxidation products with the variation in the prediction of $K_{i,WIOM}$ of *n*-alkane oxidation products. However, the two groups of oxidation products are similar in terms of the molecular size, functional groups and volatility range (see also response to point [3] below).

A comparison of $K_{\mathrm{i,WIOM}}$ predictions with the three methods (ppLFERs, SPARC, COSMOtherm) for a number of α-pinene oxidation products is shown in the figure below (data taken from Wania et al., 2014). This figure is similar to Figure 10, except that the COSMOtherm and SPARC predictions both use structure B as a surrogate solvent. Please note that the number of compounds varies in the three sub-plots, because COSMOtherm predictions were only made for a small set of substances.



This figure reveals that the discrepancies between the three prediction techniques for the α-pinene oxidation products, when expressed as MDs and MADs, are of a similar size (in the case of the comparisons involving the SPARC predictions) or slightly larger (in the case of the COSMOtherm vs. ppLFER comparison) than those discrepancies for the *n*-alkane oxidation products. In particular, the mean difference is smaller than one log unit in all three cases.

[3]: Regarding the range of aerosol volatility: how is the 'atmospherically relevant' range of $K_{\mathrm{i,WIOM}}$ determined?

In Wania et al. (2014), we describe in more detail, how the atmospherically relevant $K_{\mathrm{i,WIOM}}$ range is derived. The lower threshold is determined when 1 % of a compound with a log $K_{\mathrm{i,WIOM}}$ of 8 is sorbed to aerosol under high organic aerosol load conditions (100 μg/m^3). The upper threshold of log $K_{\mathrm{i,WIOM}}$ of 14 corresponds to a 1 % gas phase distribution at low organic aerosol conditions (defined as 1 μg/m^3). The atmospheric phase distribution of compounds with a log $K_{\mathrm{i,WIOM}}$ in this range (which we call semi-volatile) is dependent on knowing the accurate value of $K_{\mathrm{i,WIOM}}$.

Using the manuscript's supplemental information and converting the units of $K'_{\mathrm{i,p}}$ to m^3 μg^{-1} (i.e. K_p of Pankow 1994, Atmos. Environ., 28, 185-188), the following equation for an equivalent (approximately) saturation mass concentration (in μg m^{-3}) can be obtained:

$$C^* = 1 / K_p = \rho_{\mathrm{aerosol}} / (K_{\mathrm{WIOM}}\, 10^{-6}) = 10^{12} / K_{\mathrm{WIOM}}$$

Where the density of aerosol is in units of g m^{-3} (using a value of 10^6 as in the manuscript, pg. 21353, ln. 15) would suggest that for $\log(K_{\mathrm{i,WIOM}}) = \{\sim 9.5, 15\}$ (e.g. Figure 5), the equivalent $C^* = \{\sim 300, 10^{-3}\}$. This is consistent with the typical range of ambient organic aerosol and in the range of what are referred to by some as SVOCs and LVOCs (Pandis et al., Faraday Discuss., 2013,165,9-24). The authors may wish to clarify this otherwise in the text if this explanation is not satisfactory.

Yes, this derivation appears correct. A log $K_{\mathrm{i,WIOM}}$ of 8 and 14 would correspond to a saturation mass concentration of approximately 1000 and 0.01 μg/m^3, respectively.

Note: these C* values equate to, when roughly converted (assuming ideal gas and Mw = 0.2 kg mol^{-1}), log(P, atm) of about −5 and −10. This range is not the same as presented in Valorso et al. (−13 to −5), and perhaps more interestingly the domain of their investigated log(P, atm) was −30 to 0 while the equivalent range for this study would be (if calculated as above) −11 to 3, potentially calling into question the values cited on pg. 21360, ln. 12 as incomparable.

The reviewer is correct in pointing out that the range of $p_{i,L}$ "of particular interest for atmospheric applications" highlighted in Figure 4 in Valorso et al. (2011) is not exactly the same as the "atmospherically relevant" $K_{i,WIOM}$ range highlighted in our illustrations, although they essentially overlap. It is also correct that the entire range of volatilities compared in Figure 4 of Valorso et al. (2011) is larger than that shown in our figures.

Because Valorso et al. (2011) report discrepancies between three different $p_{i,L}$ predictions resolved by the number of functional groups per molecule, we also calculated MD and MAD between the $K_{i,WIOM}$ predictions for the *n*-alkane oxidation products (the data displayed in Figure 10) this way. The results are given in the Table below:

	1 functional group	2 functional groups	3 functional groups	>3 functional groups
n	10	30	40	52
$MAD_{ppLFER/COSMO}$	0.42	0.72	0.74	0.55
$MD_{ppLFER/COSMO}$	-0.35	-0.60	-0.73	-0.47
$MAD_{ppLER/SPARC}$	0.59	0.93	0.74	1.06
$MD_{ppLFER/SPARC}$	-0.59	-0.93	-0.74	-1.06
$MAD_{COSMO/SPARC}$	0.32	0.73	0.64	0.62
$MD_{COSMO/SPARC}$	-0.24	-0.33	-0.01	-0.59

A comparison of these discrepancies with those reported in Table 2 on page 6900 of Valorso et al. (2011) shows that the MAD and MD between the predictions for compounds with:

- one and two functional groups are similar for $p_{i,L}$ and $K_{i,WIOM}$
- three functional groups are slightly larger for $p_{i,L}$ than for $K_{i,WIOM}$
- more than three functional groups are much larger for $p_{i,L}$ than for $K_{i,WIOM}$

In other words, in the atmospherically relevant range, which encompasses compounds with two to five functional groups, the three $K_{i,WIOM}$ predictions agree much better with each other than the three $p_{i,L}$ predictions.

There are still two limitations to this comparison:

- Valorso et al. (2011)'s data set is considerably larger than ours by three orders of magnitude (>100 vs. >100000)
- We compare predictions for $p_{i,L}$ of the oxidation products of α-pinene with predictions for $K_{i,WIOM}$ of the oxidation products of *n*-alkanes. These products have similar functional groups and molecular size, but *n*-alkane products are obviously more aliphatic than alicyclic when compared to the α-pinene products.

We have revised section 4.1 to make the comparison of MADs and MDs between the three $p_{i,L}$ predictions in Valorso et al. (2010) and our three $K_{i,WIOM}$ predictions more meaningful. Namely, we now explicitly compare prediction discrepancies for compounds with the same number of functional groups: "The most noteworthy aspect of the comparison of the $K_{i,WIOM}$ data sets (excluding the two assuming an unrealistically polar organic matter phase) is that the MADs are always less than 0.85 log units. MADs and MDs for groups of *n*-alkane oxidation products with the same number of functional groups are reported in Table S2 in the Supplement. Discrepancies between different $p_{i,L}$* predictions for multifunctional chemicals of relevance in the context of SOA formation tend to be much larger (Camredon and Aumont, 2006, Valorso et al., 2011). For example, Valorso et al. (2011) noted MADs between three commonly used methods of 1.27, 1.31, and 0.57 for the $p_{i,L}$ of oxidation products of α-pinene with 3 functional groups and MADs of 3.6, 2.23, and 1.52 log units for products with more than 3 functional groups. This contrasts with MADs of 0.74, 0.74 and 0.64 the log $K_{i,WIOM}$ of oxidation products of *n*-alkanes with 3 functional groups, and MADs of 0.55, 1.06 and 0.62 for those with four and five functional groups. The same holds for the mean bias: Valorso et al. (2011) reported MDs of -1.14, -1.23 and -0.09 between log $p_{i,L}$ predictions of compounds with three functional groups and MDs of -3.59, -2.2 and 1.39 for those with more than three functional groups. Here the mean bias ranged from -0.01 to -0.74 for compounds with three functional groups and from -0.47 to -1.06 for those with four and five functional groups. Clearly, whereas the discrepancy between the $p_{i,L}$* predictions generally increases rapidly with increasing number of functional groups, and therefore relevance to gas particle partitioning, no such deterioration in the agreement of $K_{i,WIOM}$ predictions was observed."

We also added the table above in the Supplement as Table S2.

Of course, the authors could point out that a proportional relationship between vapor pressure and $K_{i,WIOM}$ does not necessarily exist given potential variation in the activity coefficient for different compounds in the WIOM phase. Although, such an argument would lend credence to the previous point [2].

See our response to point [2] above.

A final note regarding the manuscript is its generalizability, as this manuscript presents only one case study. The proposed alternative approaches are indeed presented in an appealing fashion, and although the authors may be leaving this to a follow up manuscript, they mention additional calculations carried out on the alpha pinene SOA system using Chen & Griffin (2005) oxidation products as a starting point that are not shown – for good reason of course (pg. 21362). It would support the methods' generalizability to see a similar analysis as the case study presented here done for the alpha pinene system using the products from Valorso et al. (2011) or a contemporary. It may also help justify the choice of the MAD values the authors' use for comparison in section 4.1.

We refer to our response regarding α-pinene oxidation products above and to our recent submission (Wania et al., 2014).

Technical Comments

In general, there is an odd word choice throughout the document (e.g. "eschew") that would not aid non-native English speakers in interpreting the contents of the manuscript. The authors may wish to adjust the text to account for this.

This comment is rather amusing, considering that the main author and three of four co-authors are themselves non-native English speakers. In our experience the use of unusual words is hardly ever a stumbling block to a non-native speaker's understanding and interpreting the contents of a manuscript, if these words have a precise and unequivocal meaning. Most of them relish the opportunity to expand their vocabulary. Nevertheless, we have replaced "eschew" with more commonly used words.

Pg. 21342, Ln. 17: "… .vapor pressure estimates, the predictions between the $K_{i,WIOM}$ estimates do not deteriorate. . ." Subject/verb agreement & sentence fragment.

The sentence has been rephrased: "Also, in contrast to the agreement between vapour pressure estimates, **the agreement** between the $K_{i,WIOM}$ estimates does not deteriorate with increasing number of functional groups."

Last sentence of abstract: Remove the phrase "or the assignment of SOA-forming molecules to volatility basis sets." This point is not mentioned in the manuscript. If the authors would rather elaborate on this topic, it should be separate from the discussion of predicting vapor pressures, as that is not the goal of the VBS approach.

As suggested, we have deleted the phrase "or the assignment of SOA-forming molecules to volatility basis sets."

Pg. 21344, Ln. 8: "In particular..." – sentence is difficult to follow due to wording. Consider rewording for readability.

The sentence has been split in two and rephrased: "In particular, partitioning of a chemical between gas phase and WIOM is broken up into its partitioning between WIOM and its pure liquid phase and between its own pure liquid phase and the gas phase. The former is described by the activity coefficient of the chemical in WIOM, the latter by its saturation vapour pressure (Fig. 1)."

Pg. 21344, Ln. 22: Could the authors clarify what it means to be "more accurately accessible?" This is related to the discussion of accuracy vs precision above.

Accuracy and precision are both relevant, so we rephrased this sentence: "Use of the thermodynamic cycle is justified if $p_{L,i}^*$ and $\gamma_{i,WIOM}$ can be predicted more accurately and precisely than $K_{i,WIOM}$ itself."

Pg. 21348, Ln. 3: Typo? Change "Eq. (1)" to "Eq. (3)"

Yes. This has been corrected.

Pg. 21348, Ln. 16: Very long direct quote regarding SPARC. Suggest summarizing.

This use of this long quote is quite deliberate, as the inner workings of SPARC are not entirely transparent. In order to avoid misrepresenting what SPARC does, we prefer to let its developers summarise it.

Pg. 21348, Ln. 27: For readers unfamiliar with SMILES, perhaps it would be better to introduce this material, or at least define the acronym and provide a citation for background.

We now define SMILES (simplified molecular-input line-entry system) and added a reference to Weininger (1988).

Pg.21353, Ln. 18: Modify equation numbers from "(2) and (3)" to "(4) and (5)" as the reference here is incorrect.

Yes. This has been corrected.

Pg. 21355, Ln. 10: "Table S2" should be "Table S1" – I assume, as there is only one table in the supplement.

Yes. This has been corrected.

Pg. 21356, Ln. 10-12: Remove sentence beginning "Considering the uncertainty. . ." or provide some supporting quantification of the inherent uncertainty.

We have added a reference to Stenzel et al. (2014), who sought to quantify the prediction uncertainty of the three methods.

Pg. 21356, Ln. 12-19: Whereas KOAWIN in EPISuite relies on a relationship between the air-water-octanol partitioning of a substance, this study does not take into account the possible existence of an aqueous phase. Could the way that the octanol-air partitioning coefficients are calculated therefore be inherently different so as to preclude a direct comparison?

The calibration data set upon which KOAWIN is build includes many values that are not empirically determined partition coefficients between octanol and the gas phase ($K_{i,O}$), but are estimated from partition coefficients between water and octanol ($K_{i,OW}$) and between gas phase and water ($K_{i,AW}$), using the relationship (Meylan and Howard, 2005):

$$K_{i,O} = K_{i,OW} / K_{i,AW} \qquad (1)$$

Strictly speaking, these three partition coefficients do however not form a thermodynamic triangle, because $K_{i,OW}$ describes equilibrium partitioning between octanol saturated with water and water saturated with octanol, whereas $K_{i,AW}$ and $K_{i,O}$ refer to the pure water and pure octanol phase, respectively (Goss, 2004). In other words, equation 1 is only correct if (i) the solvation properties of the aqueous phase are not affected by the presence of octanol, and (ii) the solvation properties of the octanol phase are not affected by the presence of water. The reviewer is therefore correct that a KOAWIN predicted K_{OA}-value may not be directly comparable to a K_{OA} predicted using SPARC or COSMOtherm (although this has nothing to do with whether our study takes into account the possible existence of an aqueous phase).

In Beyer et al. (2002) (Figure A1 page 952), we have shown that the limitation of equation (1) become severe for hydrophobic substances with a high $K_{i,OW}$. Figure S1 demonstrates that the largest discrepancies between the $K_{i,O\ (EPIsuite)}$ and the $K_{i,O\ (SPARC)}$ and $K_{i,O(COSMO)}$ occurred for involatile substances (log $K_{i,O} > 9$). These substances have multiple highly polar functional groups and thus are not hydrophobic. The mutual solubility of octanol and water should therefore have a minor effect on their solvation in octanol and water. In other words, it is very unlikely that the discrepancies displayed in Figure S1 are due to the limitations of equation (1).

Pg. 21356, Ln. 15: Figure S1 in supplement only shows comparison between SPARC and EPISuite, not ppLFER.

Yes, but since SPARC and COSMOtherm gave essentially identical predictions of $K_{i,O}$, a second figure showing a comparison between $K_{i,O}$ predictions by COSMOtherm and EPISuite is redundant. The main text now is more specific: "Fig. S1 in the Supplement **compares EPISuite and SPARC predictions**".

The last two paragraphs of section 4.1 are somewhat redundant and could be condensed/combined with the approach description in the methods section.

We disagree, as these two paragraphs are part of the answer to the question: "What is at the root of the different performance of $p_{L,i}^*$ and $K_{i,WIOM}$ predictions methods?" and thus could not be integrated into the methods section earlier in the paper, when the different performance had not been established.

Pg. 21361, Ln. 23: Comma splice at . . . "here is promising, but should"

No, it is not a comma splice, because two independent clauses ("The agreement is promising." and "The agreement should be interpreted with caution.") are joined by a coordinating conjunction ("but").

Pg. 21363, Ln. 1: Reword the sentence for clarity & grammar . . . "make to the formation of SOA"

We believe this sentence to be grammatically correct, but have rephrased it: "There is now also experimental evidence that much less volatile oxidation products contribute significantly to the SOA formed during the oxidation of α-pinene"

Pg. 21363, Ln.12: What does the phrase "conceptually simpler and therefore more elegant" add to the value of the discussion of these alternative approaches?

We agree that "elegant" may not be the most appropriate word, but this argument essentially relates to the principle of parsimony (Occam's razor). Applied in the present context, it implies that the simpler of two alternative approaches is preferable. We rephrased the sentence: "Predicting the partitioning equilibrium of interest directly rather than through a thermodynamic triangle is conceptually simpler and therefore **preferable**."

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