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 $K_{\mathrm{i,WIOM}}$ with empirical data, we feel that the idea of estimating vapour pressures $p_{\mathrm{i,L}}$ from $K_{\mathrm{i,WIOM}}$ 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 $K_{\mathrm{i,WIOM}}$ **INSTEAD** of $p_{\mathrm{i,L}}$ and γ_{i}.

Furthermore, the availability of reliable measured $p_{\mathrm{i,L}}$ data for highly multi-functional compounds is only very marginally better than the availability of measured $K_{\mathrm{i,WIOM}}$. 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 $K_{\mathrm{i,WIOM}}$ 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 $K_{\mathrm{i,WIOM}}$ 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.

References

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