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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Novel methods for predicting gas-particle partitioning during the formation of secondary organic aerosol" *by* F. Wania et al.

Anonymous Referee #1

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Uncertainties in the prediction of the gas-particle partitioning equilibirum 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

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'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.

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. 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?

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

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(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.

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?

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.

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 Ki,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 Ki,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?

4. Page 21351, Line 15: Please state why octan-1-ol was chosen as the solvent surro-

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gate 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.

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 Ki values. This is not consistent with predictions by the 'ppLFER' approach, which indicate that the predicted Ki 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.

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?

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

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?

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 21341, 2014.