

Supporting Information for

Novel methods for predicting gas-particle partitioning during the formation of secondary organic aerosol

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Different Definitions of the Equilibrium Partition Coefficient between Gas and Particle Phase

Following Mackay (2001), we define the equilibrium partition coefficient of a compound i between particles and gas phase as:

$$K_{i,P}(\text{m}^3 \text{ gas}/\text{m}^3 \text{ particles}) = \frac{C_{i,P}(\text{mol}/\text{m}^3 \text{ particles})}{C_{i,G}(\text{mol}/\text{m}^3 \text{ gas})}$$

Note that $C_{i,P}$ is the concentration of i in a volume of particles and not in a volume of air. Strictly speaking, the partition coefficient $K_{i,P}$ is thus not dimensionless, but has units of $\text{m}^3 \text{ gas}/\text{m}^3 \text{ aerosol}$. The volume of aerosol is not as easily determined as its mass. Therefore, when measuring partitioning from the gas phase to aerosol in the laboratory, Arp et al. (2008) defined $K'_{i,P}$ as:

$$K'_{i,P}(\text{m}^3 \text{ gas}/\text{g particles}) = \frac{C'_{i,P}(\text{mol}/\text{g particles})}{C_{i,G}(\text{mol}/\text{m}^3 \text{ gas})}$$

1 $K'_{i,P}$ thus has units of $\text{m}^3 \text{ gas/g particles}$, and is convertible to $K_{i,P}$ using the density of aerosol d_p :
 $K_{i,P}(\text{m}^3 \text{ gas/m}^3 \text{ particles}) = K'_{i,P}(\text{m}^3 \text{ gas/g particles}) \times d_p(\text{g particles/m}^3 \text{ particles})$

2 We estimate d_p using:

$$d_p = f_{OM} \times 1,000,000 \text{ g/m}^3 + (1 - f_{OM}) \times 2,400,000 \text{ g/m}^3$$

3 where f_{OM} is the volume fraction of the particles made up of organic matter.

4 Pankow (2003) uses the same definition of the gas-particle partition coefficient as Arp et al.
 5 (2008), except that he uses mass concentrations instead of molar concentrations and expresses
 6 $C'_{i \text{ Aerosol}}$ in units of mass per μg of particles instead of per g of aerosol.

7 Multiplication of $K'_{i,P}$ with the concentration of the total suspended particulate matter TPM in
 8 g/m^3 yields the ratio of the mass (or molar) amounts of compound i in the sorbed and gaseous
 9 states (Pankow, 2003):

$$\frac{F_i}{A_i} = K'_{i,P}(\text{m}^3 \text{ gas/g particles}) \times TPM(\text{g particles/m}^3 \text{ gas})$$

10 Even though F_i/A_i is dimensionless, it is not the same as, and should not be confused with, $K_{i,P}$.
 11 Both can be used to estimate the mass or molar fraction of i that is in the particle phase \emptyset is:

$$\emptyset = \frac{F_i/A_i}{1+F_i/A_i} = \frac{K'_{i,P} \times TPM}{1+K'_{i,P} \times TPM} = \frac{K_{i,P} \times (V_P/V_G)}{1+K_{i,P} \times (V_P/V_G)}$$

13 Where V_P/V_G is the volume fraction of particles in the atmosphere:

$$V_P/V_G (\text{m}^3 \text{ particles/m}^3 \text{ gas}) = \frac{TPM(\text{g particles/m}^3 \text{ gas})}{d_p(\text{g particles/m}^3 \text{ aerosol})}$$

14 Note that some authors refer to this fraction \emptyset as a “partition coefficient” (e.g. Donahue et al.,
 15 2006).

16 References

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Table S1 Most abundant alkane oxidation product in SOA used as “solvent” surrogate in the calculation of $K_{\text{prev/G}}$ using SPARC. The most abundant oxidation product at each chain length was determined from the calculated SOA composition when $K_{\text{B/G (SPARC)}}$ was used.

Carbon chain length	Most abundant alkane oxidation product in SOA	
	Code	Name
C8	UR38	4-hydroxyoctane-1,7-diyl_dinitrate
C9	UR38	5-hydroxynonane-2,8-diyl_dinitrate
C10	UR38	5-hydroxydecane-2,6-diyl_dinitrate
C11	UR38	5-hydroxyundecane-2,7-diyl_dinitrate
C12	UR40	4-oxobutan-2-yl-4-(nitrooxy)octanoate
C13	AP12	5-hydroxytridecan-2-yl_nitrate
C14	UR36	4-oxobutan-2-yl_decanoate
C15	UR36	4-oxobutan-2-yl_undecanoate
C16	UR36	4-oxobutan-2-yl_dodecanoate
C17	UR36	4-oxobutan-2-yl_tridecanoate

Table S2 Mean difference (MD) and mean absolute difference (MAD) between $K_{\text{i,WIOM}}$ for *n*-alkane oxidation products with variable number of functional groups when predicted by ppLFER (average of four aerosol), SPARC (using structure B as a surrogate solvent) and COSMOtherm (using the actual mix of oxidation products). Data underlying this analysis are displayed in Figure 10.

	1 functional group	2 functional groups	3 functional groups	>3 functional groups
<i>n</i>	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 _{ppLFER/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

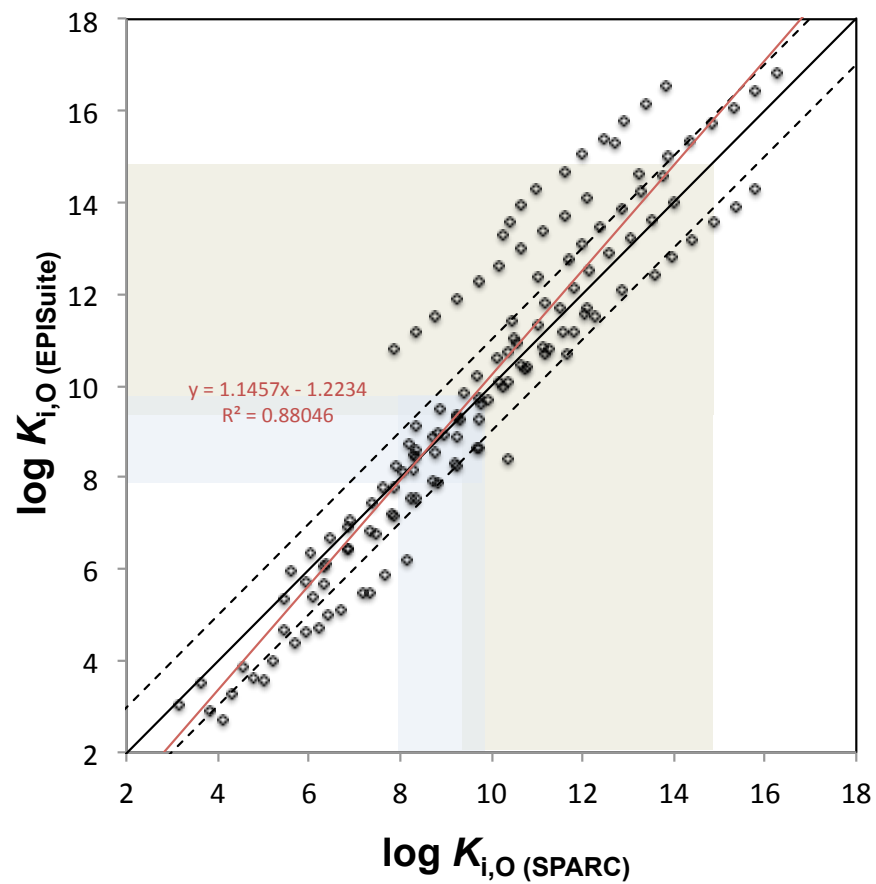


Figure S1 Plot comparing the partition coefficients at 25 °C of alkanes and their oxidation products between octan-1-ol and the gas phase predicted with SPARC and EPISuite.

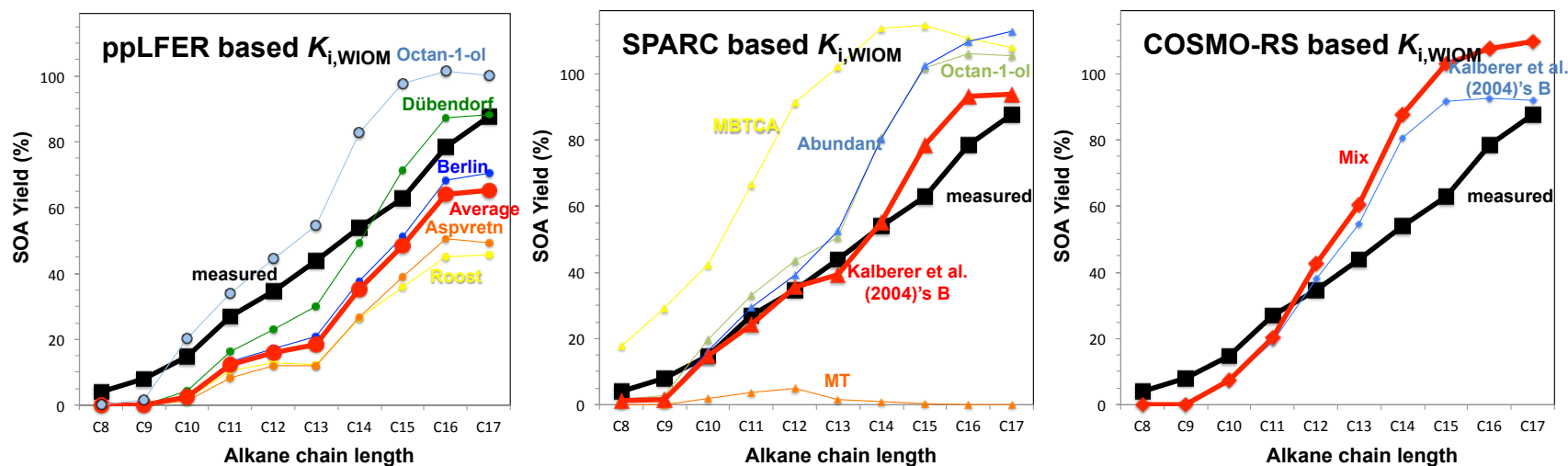


Figure S2 SOA yield from chamber experiments (black squares and line) compared to simulated results using the 14 different $K_{i,WIOM}$ data sets. Yields were calculated using partitioning data obtained by polyparameter linear free energy relationships (left), SPARC (middle) and COSMO-RS (right). The thick curves in red are those included in Fig. 11 in the main text and rely on the estimation methods compared in Sect. 3.1.5. For nomenclature of the different $K_{i,WIOM}$ estimates refer to Table 1.

Comparison of Predicted and Measured SOA Composition

We also predicted the composition of the SOA formed in the chamber experiments for each *n*-alkane chain length using the three sets of $K_{i,WIOM}$ considered in Sect. 3.1.5. These three predictions were compared with the compositions calculated by Jordan et al. (2008) and measured by Lim and Ziemann (2005). Although Lim and Ziemann (2005) could not quantify the exact composition of the SOA formed in their experiments, there are some pieces of empirical information: the parent *n*-alkanes and the carbonyl esters (UR36, UR40, UR43) were absent, and the contribution of AP11 and AP12 could be determined. All four predicted compositions are summarized in Fig. S3, as are the measured contributions of AP11 and AP12.

In agreement with the measurements, the use of $K_{i,B}$ (SPARC) and $K_{i,ppLFER}$ gives negligible contributions of the parent *n*-alkanes to the SOA. Jordan et al. (2008) had to increase the product of vapour pressure and activity coefficient by an order of magnitude to prevent the longer chain *n*-alkanes to partition to the particle phase. When using $K_{i,Mix}$ (COSMO) the C16 and C17 alkanes also partition somewhat to the SOA. All predictions agree with the measurements in indicating the presence of AP11 and AP12 in the SOA for the longer alkanes (C13 to C17), although they tend to overpredict the contribution of AP11. The $K_{i,ppLFER}$ dataset predicts a contribution of AP11 and AP12 to the SOA, which is in best agreement with the measurements. All predicted compositions indicate a very substantial contribution of the three carbonyl esters (UR36, UR42, UR43) to the SOA, even though they could not be detected in the SOA. As Jordan et al. (2008) discuss, this is not because of erroneous prediction of the partitioning between gas and particle phase, but because of unknown chemistry not included in CACM at the time.

References

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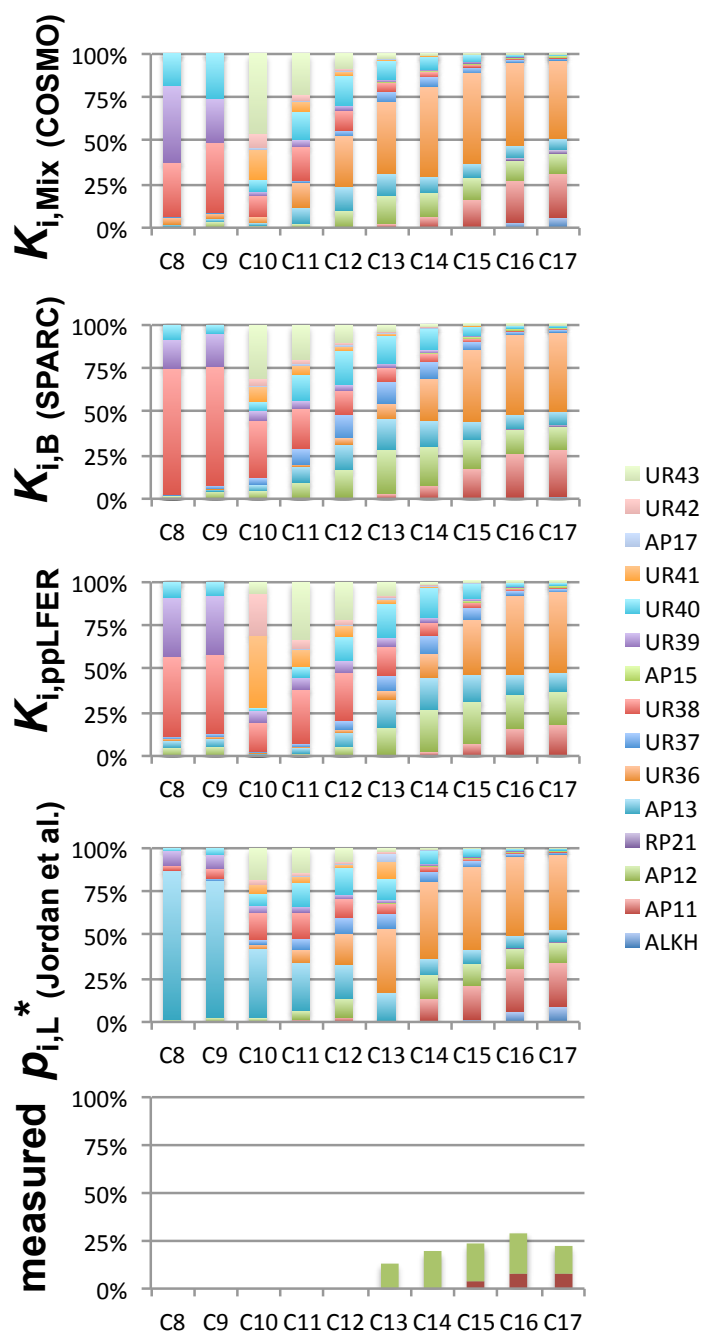


Figure S3 Predicted and measured composition of the secondary organic aerosol formed in chamber experiments of the OH-initiated reaction of *n*-alkanes in the presence of NO_x. All predictions use a CACM-calculated total concentration, but differ with respect to the set of $K_{i,WIOM}$ used to describe gas-particle partitioning. For comparison Jordan et al. (2008)'s vapour pressure based prediction is also shown.