1 **Uncertain Henry's Law Constants Compromise Equilibrium**

2 **Partitioning Calculations of Atmospheric Oxidation Products**

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Abstract

Gas-particle partitioning governs the distribution, removal and transport of organic compounds in the atmosphere and the formation of secondary organic aerosol. The large variety of atmospheric species and their wide range of properties make predicting this partitioning equilibrium challenging. Here we expand on earlier work and predict gas-organic and gas-aqueous phase partitioning coefficients for 3414 atmospherically relevant molecules using COSMOtherm, SPARC and poly-parameter linear free energy relationships. The Master Chemical Mechanism generated the structures by oxidizing primary emitted volatile organic compounds. Predictions for gas-organic phase partitioning coefficients ($K_{WIOM/G}$) by different methods are on average within one order of magnitude of each other, irrespective of the numbers of functional groups, except for predictions by COSMOtherm and SPARC for compounds with more than three functional groups, which have a slightly higher discrepancy. Discrepancies between predictions of gas-aqueous partitioning ($K_{W/G}$) are much larger and increase with the number of functional groups in the molecule. In particular, COSMOtherm often predicts much lower $K_{W/G}$ for highly functionalized compounds than the other methods. While the quantum-chemistry based COSMOtherm accounts for the influence of intramolecular interactions on conformation, highly functionalized molecules likely fall outside of the applicability domain of the other techniques, which at least in part rely on empirical data for calibration. Further analysis suggests that atmospheric phase distribution calculations are sensitive to the partitioning coefficient estimation method, in particular to the estimated value of $K_{W/G}$. The large uncertainty in $K_{W/G}$ predictions for highly functionalized organic compounds needs to be resolved to improve the quantitative treatment of SOA formation.

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Introduction

Volatile organic compounds (VOCs) emitted to the atmosphere are oxidized to form secondary products. These products tend to be more oxygenated, less volatile and more water-soluble than their parent compounds, and thus have higher affinity for aerosol particles and aqueous droplets. Equilibrium partitioning coefficients are often needed to assess the distribution of these oxidized compounds among different phases in the atmosphere such as aerosol particles, fog and cloud droplets. In particular, the partitioning between gas and organic phase and between gas and aqueous phase is required for the evaluation of an organic compound's contribution to secondary organic aerosol (SOA) formation, its transport, removal and lifetime. Experimentally determined partitioning coefficients are rarely available for the oxidation products of VOCs due to the difficulties in making the measurements and obtaining chemical standards. Furthermore, the number of organic species in the atmosphere is in the hundreds of thousands, if not higher. Their gas-particle partitioning is therefore usually predicted. Reliable estimation methods for gas-organic and gas-aqueous partitioning should be applicable to a wide range of organic compounds, especially to multifunctional species generated during the multi-step atmospheric oxidation of precursor VOCs.

Current approaches for predicting partitioning into non-aqueous organic aerosol phases almost exclusively rely on predictions of vapor pressure. These predictions have large uncertainties; comparison among different vapor pressure prediction methods suggest increasing discrepancies with increasing numbers of functional groups in an organic compound (Valorso et al., 2011;Barley and McFiggans, 2010;McFiggans et al., 2010). This uncertainty matters, because it is the multi-functional oxidation products that can occur in either gas or condensed phases in the atmosphere. Instead of relying on predictions for vapor pressures, Wania et al. (2014) proposed using three alternative methods for direct gas-particle partitioning prediction: poly-parameter linear free energy relationships (ppLFERs), the on-line calculator of SPARC Performs Automated Reasoning in Chemistry (SPARC) and the quantum-chemistry based program COSMOtherm. Wania et al. (2014) found that partitioning coefficients predicted for the oxidation products of n-alkanes are within one order of magnitude, and mutual agreement

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66   does not deteriorate with increasing number of functional groups. Because of the relatively

67   small number of oxidation products in that study, the reliability of these prediction methods for

68   other organic compounds requires further evaluation.

69   While more experimental data exist for the Henry's law constant of atmospherically relevant

70   compounds than gas-organic phase partitioning coefficients (Sander, 2015), data are not usually

71   available for VOC oxidation products, which potentially have a higher affinity for atmospheric

72   aqueous phases. Currently available prediction methods for the air-water partitioning

73   coefficient include GROup contribution Method for Henry's law Estimate (GROMHE) (Raventos-

74   Duran et al., 2010), SPARC (Hilal et al., 2008), HENRYWIN in EPI suite (US EPA, 2012), and

75   ppLFERs (Goss, 2006). Sander (2015) provides a more comprehensive list of websites as well as

76   quantitative structure-property relationships for Henry's law constants. Hodzic et al. (2014)

77   developed a method to predict Henry's law constant from a molecule's volatility to be

78   implemented in atmospheric models. COSMOtherm can also predict gas-aqueous phase

79   partitioning of organic compounds, including VOC oxidation products (Wania et al., 2015).

80   Though many different methods are available for Henry's law constant prediction, they have

81   not been systematically evaluated for a large set of organic compounds of atmospheric

82   relevance. An exception is the comparison of GROMHE, SPARC and HENRYWIN predictions for

83   488 organic compounds bearing functional groups of atmospheric relevance (Raventos-Duran

84   et al., 2010).

85   The objective of this paper was to compare and evaluate gas-particle partitioning predictions

86   for a large number of organic compounds of atmospheric interest using ppLFER (in combination

87   with ABSOLV-predicted solute descriptors), SPARC and COSMOtherm. While all three methods

88   are able to estimate both gas-organic and gas-aqueous partitioning, they are based on different

89   principles: ppLFERs are empirically calibrated multiple linear regressions, SPARC contains

90   solvation models based on fundamental chemical structure theory (Hilal et al., 2004), and

91   COSMOtherm combines quantum chemistry with statistical thermodynamics (Klamt and Eckert,

92   2000). This study thus expands earlier work (Wania et al., 2014) to a much larger number of

93   compounds and to aqueous phase partitioning. As such, it includes quantum-chemistry based

94   predictions for an unprecedented number of atmospherically relevant compounds.

Method

96   The Master Chemical Mechanism (MCM v3.2, http://mcm.leeds.ac.uk/MCM) a near-explicit

97   chemical mechanism, was used to generate 3414 non-radical species through the multi-step gas

98   phase oxidation of 143 parent VOCs (methane + 142 non-methane VOCs). Reactions of the

99   parent VOCs with O_3, OH and NO_3 are included in the MCM mechanism whenever such

100   reactions are possible. The details about the studied compounds are given in the supporting

101   information (Excel spreadsheet), including the compounds' MCM ID, SMILES, precursors (i.e.

102   the parent VOC), molecular weight, molecular formula, elements, generation of oxidation,

103   number and species of functional groups, O:C ratio, and average carbon oxidation state ($\overline{OS}_C$)

104   (Kroll et al., 2011).

105   Three prediction methods are used to estimate the equilibrium partitioning coefficients

106   between a water-insoluble organic matter phase (WIOM) and the gas phase ($K_{WIOM/G}$) at 15 °C in

107   unit of m^3 (air)/m^3 (WIOM) as well as the equilibrium partitioning coefficients between water

108   and gas phase ($K_{W/G}$) at 15 °C in unit of m^3 (air)/m^3 (water). The two partitioning coefficients are

109   defined as:

110   $K_{WIOM/G} = C_{WIOM}/C_G$ (1)

111   $K_{W/G} = C_W/C_G$ (2)

112   C_{WIOM}, C_W and C_G (mol/m^3) are equilibrium concentrations of an organic compound in WIOM,

113   water, and gas phase, respectively. Partitioning between gas and aqueous phase can be

114   significantly influenced by the presence of inorganic salts (i.e. the salt effect) (Endo et al.,

115   2012;Wang et al., 2016;Wang et al., 2014;Waxman et al., 2015), the hydration of carbonyls (Ip

116   et al., 2009) and the dissociation of organic acids (Mouchel-Vallon et al., 2013), particularly in

117   the aqueous phase of aerosols. However, in this study only the partitioning between gas and

118   pure water, i.e. the Henry's law constant, is predicted, and no hydration, salt effect or acid

119   dissociation is considered. Conversion of partitioning coefficients $K_{W/G}$ to Henry's constant (K_H)

120   in unit M/atm or $K_{WIOM/G}$ to saturation concentration (C^*, µg/m^3) is provided in the supporting

121   information.

122   Wania et al. (2014) describe each prediction method in detail. In brief, ppLFER-based

123   predictions rely on solute descriptors for the 3414 compounds generated with ABSOLV

124   (ACD/Labs, Advanced Chemistry Development, Inc., Toronto, Canada) as well as system

125   parameters for water-air partitioning from Goss (2006) and organic aerosol-air partitioning

126   from Arp et al. (2008). As described in Wania et al. (2014), the latter is the average $K_{WIOM/G}$

127   predicted for four different organic aerosols. For the calculations of $K_{WIOM/G}$ by SPARC and

128   COSMOtherm, the phase WIOM is represented by the surrogate structure "B" as proposed by

129   Kalberer et al. (2004) and adopted previously by Arp and Goss (2009) and Wania et al. (2014).

130   SPARC calculations were carried out using the on-line calculator (http://archemcalc.com/sparc-

131   web/calc), with SMILES (simplified molecular-input line-entry system) strings as input.

132   COSMOtherm predicts a large variety of properties based on COSMO-RS (conductor-like

133   screening model for real solvents) theory, which uses quantum-chemical calculations and

134   statistical thermodynamics (Klamt and Eckert, 2000;Klamt, 2005). First, TURBOMOLE (version

135   6.6, 2014, University of Karlsruhe & Forschungszentrum Karlsruhe GmbH, 1989–2007,

136   TURBOMOLE GmbH, since 2007 available from www.turbomole.com) optimizes the geometry

137   of the molecules of interest at the BP-TZVP level. COSMOconf (version 3.0, COSMOlogic) then

138   selects a maximum of ten lowest energy conformers for each calculated molecule and

139   generates COSMO files. Calculations with TURBOMOLE and COSMOconf were performed on the

140   General Purpose Cluster (GPC) supercomputer at the SciNet HPC Consortium at University of

141   Toronto (Loken et al., 2010). Finally, COSMOtherm (version C30_1501 with BP_TZVP_C30_1501

142   parameterization, COSMOlogic GmbH & Co. KG, Leverkusen, Germany, 2015) calculates

143   partitioning coefficients from the selected COSMO files at 15 °C.

144   In order to compare different predictions numerically, we calculated the mean difference (MD)

145   and the mean absolute difference (MAD) for each pair of $K_{WIOM/G}$ or $K_{W/G}$ sets:

146    $$\text{MD}_{XY} = \frac{1}{n}\sum_i \left(\log_{10} K_{i,CP/G\ X} - \log_{10} K_{i,CP/G\ Y} \right) \qquad (3)$$

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147 $$\text{MAD}_{XY} = \frac{1}{n}\sum_i \left| \log_{10} K_{i,\text{CP/G X}} - \log_{10} K_{i,\text{CP/G Y}} \right| \tag{4}$$

148 where CP ("condensed phase") stands for either WIOM or water and X and Y represents two

149 prediction techniques.

Results

The Range of Estimated Partitioning Coefficients

152 Partitioning coefficients predicted for each compound with different methods are given in an

153 Excel spreadsheet as Supporting Information. All three methods predicted the log $K_{\text{WIOM/G}}$ for

154 these organic compounds to range from approximately 0 to 15 (Figure 1 (a)-(c)). Hodzic et al.

155 (2014) predicted a log C^* in the range of -8~12 (at 25 °C) for oxidation products of different

156 VOCs (including n-alkanes, benzene, toluene, xylene, isoprene and terpenes), corresponding to

157 a log $K_{\text{WIOM/G}}$ range of approximately 0 and 20 (see conversion in Supporting information), i.e.

158 their data set included higher $K_{\text{WIOM/G}}$ values than those generated here, even though $K_{\text{WIOM/G}}$

159 value are lower at higher temperature.

160 The log $K_{\text{W/G}}$ range predicted for the studied compounds by the three methods is more variable

161 (Figure 1 (d)-(f)), with the ABSOLV/ppLFER predictions covering a wider range (-1.4 to 21.3) than

162 either SPARC (-2.7 to 17.2) or COSMOtherm (-2 to 13.8). Hodzic et al. (2014) predicted a log K_H

163 (at 25°C in M/atm) in the range of -4 and 16 (at 25 °C), corresponding to log $K_{\text{W/G}}$ between -2.6

164 and 17.4. The wider range of the ABSOLV/ppLFER predictions is due to much higher predicted

165 $K_{\text{W/G}}$-values for compounds with the highest affinity for the aqueous phase.

Comparison between Different Prediction Methods

167 The discrepancies between different predictions (MAD and MD) are given in Table 1. The

168 agreement between the $K_{\text{WIOM/G}}$ predictions by COSMOtherm, SPARC and ABSOLV/ppLFER was

169 reasonable (Figure 1 (a)-(c)). In particular, the MAD between $K_{\text{WIOM/G}}$ predictions is less than 1

170 log units (Table 1) and therefore similar to what had been previously found for a much smaller

171 set of n-alkane oxidation products (Wania et al., 2014). The $K_{\text{WIOM/G}}$-values predicted by SPARC

172 tend to be higher than those predicted by COSMOtherm and ABSOLV/ppLFER (MD of -0.64 and

173   -0.79 in log units, respectively), whereas the latter two predictions have a slightly better

174   agreement, with a MD of 0.15 log units (Figure 1 (c) and Table 1). Overall, the agreement in the

175    $K_{WIOM/G}$ predicted with these three methods, which are based on very different theoretical

176   foundations, is much better than that between different vapor pressure estimation methods

177   commonly used for gas-particle partitioning calculations (Valorso et al., 2011).
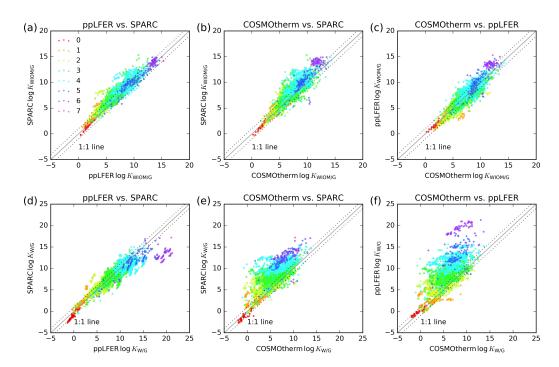

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Figure 1   Comparison of the $K_{WIOM/G}$ (upper panel) and $K_{W/G}$ (lower panel) predicted using

COSMOtherm, SPARC and ABSOLV/ppLFERs. The differently colored dots indicate the

number of functional groups in the molecules. The solid line indicates a 1:1 agreement.

The dotted lines indicate a deviation by ±1 log unit.

183   The $K_{W/G}$ predicted by ABSOLV/ppLFER and SPARC differ from COSMOtherm predictions

184   substantially, on average by more than two orders of magnitude. In Figure 1 (e) and (f),

185   predictions are more scattered (indicating a larger MAD) and most markers are located above

186   the 1:1 line, indicating that $K_{W/G}$ predicted by COSMOtherm are mostly lower than those

187   predicted by SPARC and ABSOLV/ppLFER, with a MD of -2.06 and -2.42 log units, respectively.

188   These discrepancies tend to increase with the $K_{W/G}$. Raventos-Duran et al. (2010) also showed

189   that the reliability of $K_{W/G}$ estimates made by GROMHE, SPARC and HENRYWIN decreases with

190   increasing affinity for the aqueous phase. $K_{W/G}$ predictions by SPARC and ABSOLV/ppLFER are

191   more consistent (with a MAD around 1 log units, see Figure 1 (d)). The largest discrepancies

192   between ABSOLV/ppLFER and SPARC (and also between ABSOLV/ppLFER and COSMOtherm)

193   occur for compounds with the highest $K_{W/G}$ as predicted by ABSOLV/ppLFER (purple markers in

194   Figure 1 (d) and (f)). Further analysis indicates that these compounds have the largest number

195   of functional groups (≥6) and oxygen (9~12 oxygen) in the molecule; this will be discussed in

196   detail below.

197   **Table 1**   Mean absolute differences (MAD) and mean differences (MD) between SPARC,

198   ABSOLV/ppLFER and COSMOtherm predictions for compounds with different numbers

199   of functional groups

Number of Functional Groups			0	1	2	3	4	5	>5	All
Number of Compounds			63	372	1179	1064	565	111	60	3414
$\log K_{WIOM/G}$	ppLFER vs. SPARC	MAD	0.24	0.70	0.95	0.93	1.08	0.75	0.54	0.91
		MD	0.05	-0.70	-0.91	-0.81	-0.83	-0.24	-0.30	-0.79
	COSMOtherm vs. SPARC	MAD	0.36	0.48	0.80	0.94	1.42	1.22	2.11	0.94
		MD	0.29	-0.19	-0.55	-0.57	-1.21	-0.78	-1.83	-0.64
	COSMOtherm vs. ppLFER	MAD	0.32	0.67	0.63	0.74	0.89	0.93	1.72	0.73
		MD	0.24	0.51	0.36	0.24	-0.38	-0.54	-1.53	0.15
$\log K_{W/G}$	ppLFER vs. SPARC	MAD	0.75	0.57	0.84	1.08	1.48	1.53	5.78	1.10
		MD	0.74	-0.09	-0.15	0.38	0.87	1.45	5.76	0.36
	COSMOtherm vs. SPARC	MAD	0.51	0.86	1.61	2.31	3.78	4.34	4.55	2.23
		MD	0.48	-0.59	-1.44	-2.18	-3.74	-4.04	-4.36	-2.06
	COSMOtherm vs. ppLFER	MAD	0.40	1.16	1.64	2.63	4.62	5.55	10.09	2.64
		MD	-0.26	-0.50	-1.29	-2.56	-4.61	-5.50	-10.05	-2.42

200   **Dependence of Partitioning Coefficients on Attributes of the Compounds**

201   The equilibrium partitioning coefficients depend on molecular attributes. Here we explored this

202   dependency on the number of functional groups, molecular mass, generation of oxidation,

203   number of oxygens and O:C ratio.

204   Previous work observed that discrepancies between vapor pressure predictions by different

205   methods increased with the number of functional groups in atmospherically relevant organic

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206   compounds (Valorso et al., 2011;Barley and McFiggans, 2010). For instance, the MAD between

207   different vapor pressure predictions increased from 0.47 to 3.6 log units when the number of

208   functional groups in the molecules increased from one to more than three (Valorso et al., 2011).

209   In order to explore if the partitioning coefficients predicted with SPARC, ABSOLV/ppLFER and

210   COSMOtherm show the same dependence on the number of functional groups, we counted the

211   number of hydroxyl (ROH), aldehyde (RCHO), ketone (RCOR'), carboxylic acid (RCOOH), ester

212   (RCOOR'), ether (ROR'), peracid (RCOOOH), peroxide (ROOH, ROOR'), nitrate (NO3), peroxyacyl

213   nitrate (PAN), nitro (NO2) groups, halogen (Cl, Br), and sulphur (S) in the 3414 molecules. About

214   two thirds (2243) of the compounds contain two or three functional groups (Table 1). 736

215   compounds contain more than three functional groups and the rest contains just one or no

216   functional group. In Figure 1 the compounds are colored according to the number of functional

217   groups in a molecule and Table 1 lists the MAD and MD between predictions based on the

218   number of functional groups. The predicted partitioning coefficients (both $K_{WIOM/G}$ and $K_{W/G}$)

219   generally increase with the number of functional groups (Figure 1 and Figure S1). Compounds

220   with no functional groups are the precursor compounds, which generally have a smaller

221   discrepancy among different prediction methods.

222   The boxplots in Figure 2 show the difference in SPARC, ABSOLV/ppLFER and COSMOtherm

223   predictions for compounds having different number of functional groups. The mean absolute

224   difference in predicted log $K_{WIOM/G}$ is almost always smaller than one log unit for compounds

225   with up to seven functional groups (Table 1). There is a slightly larger discrepancy in the

226   predicted log $K_{WIOM/G}$ values for compounds with more than three functional groups. The

227   agreement among different methods does not deteriorate as much with increasing number of

228   functional groups as that among vapor pressure predictions. The largest MADs of 1.72 and 2.11

229   between COSMOtherm and ABSOLV/ppLFER, and between COSMOtherm and SPARC,

230   respectively, for compounds with >5 functional groups (Table 1) are still much lower than

231   discrepancies reported between different vapor pressure prediction methods (Valorso et al.,
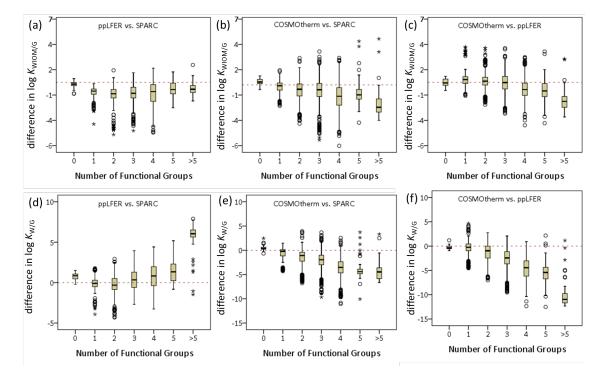
232   2011).

Figure 2   Boxplot of difference in SPARC, ABSOLV/ppLFER and COSMOtherm predictions for compounds with different number of functional groups. The line inside each box shows the median difference for log $K_{WIOM/G}$ or log $K_{W/G}$ for different categories of compounds. The marker circle and star indicates possible outliers and extreme values, respectively.

Different from the predictions for $K_{WIOM/G}$, the discrepancy between COSMOtherm and SPARC and between COSMOtherm and ABSOLV/ppLFER in the predicted $K_{W/G}$ increases significantly with the number of functional groups (Figures 1 and 2), from less than one order of magnitude for compounds with no functional groups to up to five orders of magnitude for compounds with more than three functional groups (Table 1). In addition, the MD in Table 1 and Figure 2 indicate that the discrepancies are almost always in one specific direction, i.e. a lower value of $K_{W/G}$ estimated by COSMOtherm. This is evidenced by the almost identical absolute values of MAD and MD between COSMOtherm and ABSOLV/ppLFER and between COSMOtherm and SPARC for compounds with more than three functional groups (Table 1). The uncertainty of the SPARC, ABSOLV/ppLFER and COSMOtherm predictions of $K_{W/G}$ tends to increase with the

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248   number of functional groups. Clearly, the reliability of $K_{W/G}$ estimates for multifunctional

249   compounds needs further assessment.

250   It is also possible to explore the dependence of the prediction discrepancy on other molecular

251   attributes, such as molecular mass (Figures S2 and S3), the number of oxygen in the molecule

252   (Figures S4 and S5), the O:C ratio (Figure S6), the number of oxidation steps a molecular has

253   undergone (oxidation generation, Figure S7), or the number of occurrences of a specific type of

254   functional group, e.g. hydroxyl, in a molecule (Figure S8). The prediction discrepancies become

255   larger with an increase in each of these parameters, especially for $K_{W/G}$. This is not surprising as

256   these molecular attributes all tend to be highly correlated, i.e. with each oxidation step a

257   molecule becomes more oxygenated, has a large molar mass, a larger number of oxygen, a

258   higher O:C ratio, and a larger number of functional groups.

Discussion

260   We believe there are primarily two factors that are contributing to errors in the prediction of

261    $K_{CP/G}$ for the SOA compounds. One is the lack of experimental data for compounds that are

262   similar to the SOA compounds, which implies that prediction methods relying on calibration

263   with experimental data are being used outside their applicability domain. The other is the

264   failure of some prediction methods to account for the various conformations that compounds

265   with multiple functional groups can undergo due to extensive intra-molecular interaction

266   (mostly internal hydrogen bonding, see Figure S9 for example). The two factors are related: in

267   some instances a prediction method cannot account for such conformations precisely because

268   the calibration data set does not contain compounds that undergo such intra-molecular

269   interactions.

270   SPARC relies to some extent on calibrations with empirical data. While the experimental data

271   underlying SPARC have not been disclosed, it is highly unlikely that they include multifunctional

272   compounds of atmospheric relevance (e.g. compounds containing multiple functional groups,

273   including peroxides, peroxy acids etc.), simply because such empirical data do not exist. It is

274   therefore safe to assume that many of the 3414 SOA compounds will fall outside of the domain

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275 of applicability of SPARC. It is also likely that SPARC can only account for intra-molecular

276 interactions and conformations to a limited extent, if at all.

277 In the case of ppLFER, there are actually two predictions that rely on calibration with empirical

278 data, the prediction of solute descriptors and the prediction of $K_{CP/G}$. The solute descriptors are

279 predicted with ABSOLV, because experimentally measured descriptors are unavailable for

280 multifunctional atmospheric oxidation products. ABSOLV relies on a group contribution

281 approach (Platts et al., 1999) complemented by some other, undisclosed procedures that make

282 use of experimental partition coefficients between various phases (ACD/Labs, 2016). Again,

283 those experimental data do not comprise compounds structurally similar to the multifunctional

284 atmospheric oxidation products considered here. As a group contribution method, which adds

285 up the contributions of different functional groups to a compound's property, ABSOLV

286 therefore cannot, or only to a limited extent, consider the interactions between different

287 functional groups in a molecule.

288 Ideally, when supplied with well-characterized solute descriptors, ppLFERs should be able to

289 consider the influence of both intra-molecular interactions and the interactions a molecule has

290 with its surroundings, i.e. the involved partitioning phases. Even if a molecule has different

291 conformations in different phases, i.e. if the solute descriptors for a compound are phase

292 dependent, it is possible to derive well-calibrated "average" descriptors to use in a ppLFER

293 (Niederer and Goss, 2008). However ABSOLV cannot correctly predict such "average"

294 descriptors and our ppLFER predictions therefore cannot account for the influence of

295 conformations.

296 In the case of the actual ppLFER prediction of $K_{W/G}$ and $K_{WIOM/G}$, the empirical calibration

297 datasets are public (Goss, 2006;Arp et al., 2008) and do not comprise compounds that are

298 representative of the 3414 SOA compounds in terms of the number of functional groups per

299 molecule or the range of K-values. For instance, the log $K_{W/G}$ of the 217 compounds Goss (2006)

300 used for the development of a ppLFER ranged from -2.4 to 7.4, i.e. the highest $K_{W/G}$ predicted

301 here is almost 14 orders of magnitude higher than the highest $K_{W/G}$ included in the calibration.

302 Similarly, Arp and Goss (2009) developed the ppLFERs for atmospheric aerosol from an

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303   empirical dataset of 50~59 chemicals, whose log $K_{WIOM/G}$ ranged from approximately 2 to 7. The

304   highest $K_{WIOM/G}$ predicted here is eight orders of magnitude higher. Predictions for compounds

305   outside of the calibration domain may introduce large errors and the high $K_{W/G}$ and $K_{WIOM/G}$

306   values estimated by ppLFER can thus be expected to be highly uncertain. Overall, however, we

307   expect the uncertainty of the ABSOLV-predicted solute descriptors to be larger than the

308   uncertainty introduced by the ppLFER equation, especially for the relatively well-calibrated

309   water/gas phase partition system.

310   In contrast to the other methods, COSMOtherm relies only in a very fundamental way on some

311   empirical calibrations (and these calibrations are not specific for specific compound classes or

312   partition systems) and it considers intra-molecular interactions and the different conformations

313   of a molecule. As such, COSMOtherm is not constrained by the limitations the other methods

314   face, namely the lack of suitable calibration data, which necessitates extreme extrapolations

315   and predictions beyond the applicability domain, and the failure to account for the effect of

316   intra-molecular interactions and conformations on the interactions with condensed phases.

317   Because intra-molecular interactions are likely to reduce the potential of a compound to

318   interact with condensed phases (i.e. the organic and aqueous phase), ignoring them can be

319   expected to lead to overestimated partitioning coefficients $K_{CP/G}$ and to underestimated vapor

320   pressures (P_L). This is consistent with COSMOtherm-predicted $K_{WIOM/G}$ and $K_{W/G}$-values for

321   multifunctional compounds that are lower than the SPARC and ABSOLV/ppLFER predictions (i.e.

322   MD<0 in Table 1), because the latter do not account for the influence of intra-molecular

323   interactions. Kurtén et al. (2016) similarly found that COSMOtherm-predicted saturation vapor

324   pressures for most of the more highly oxidized monomers were significantly higher (up to 8

325   orders of magnitude) than those predicted by group-contribution methods. The wider range on

326   the higher end of the log C^* values estimated by Hodzic et al. (2014) is possibly due to the large

327   uncertainties associated with vapor pressure estimation (likely underestimation) for low volatile

328   compounds. Valorso et al. (2011) also found group contribution methods to underestimate the

329   saturation vapor pressure of multifunctional species.

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330 Compared to $K_{WIOM/G}$, P_L and C^*, ignoring intra-molecular interaction is likely even more

331 problematic in the case of $K_{W/G}$ prediction. Intra-molecular interactions mostly affect the ability

332 of the molecule to undergo H-bonding with solvent molecules. The system constants describing

333 H-bond interactions (a and b) are larger in the ppLFER equations for $K_{W/G}$ than in the one for

334 $K_{WIOM/G}$ (Arp et al., 2008;Goss, 2006), indicating a stronger effect of H-bonds on water/gas

335 partitioning than WIOM/gas partitioning. This likely is the reason why the COSMOtherm-

336 predicted $K_{W/G}$ are so much lower than the $K_{W/G}$ predicted by the other two methods, whereas

337 the difference is much smaller for the $K_{WIOM/G}$ (Table 1). It likely also explains why the

338 discrepancies among the predicted $K_{W/G}$ increase with the number of functional groups. It is

339 more difficult to predict $K_{W/G}$ than $K_{WIOM/G}$, because the free energy cost of cavity formation in

340 water is influenced more strongly by H-bonding and therefore much more variable than in

341 WIOM. Certainly, the activity coefficient in water (γ_W) is much more variable than the activity

342 coefficient in WIOM (γ_{WIOM}) for the investigated substances. log γ_{WIOM} predicted by

343 COSMOtherm at 15 °C varies from -3.8 to 1.8 (with an average of 0.04, indicating a γ_{WIOM} close

344 to unity, and a standard deviation of 0.5, 94 % of the compounds have a log γ_{WIOM} between -1

345 and 1), whereas γ_W ranges from -2.3 to 8.9 (with an average of 2.7 and a standard deviation of

346 1.4) (Supporting information Excel spreadsheet and Figure S10).

347 In the absence of experimental data for multi-functional SOA compounds, we do not know

348 whether COSMOtherm-predicted $K_{W/G}$ and $K_{WIOM/G}$ values are any better than the other

349 predictions. For example, two earlier studies suggested that COSMOtherm might be

350 overestimating vapor pressures of multi-functional oxygen-containing compounds (Kurtén et al.,

351 2016;Schröder et al., 2016). However, we can infer that the:

352 - fact that COSMOtherm on the one hand and ABSOLV/ppLFERs and SPARC on the other hand

353   predict $K_{WIOM/G}$ that are on average within one order of magnitude for all studied

354   compounds, including highly oxygenated multifunctional organic compounds, lends

355   credibility to all three predictions and suggests that partly ignoring intra-molecular

356   interactions and extrapolating beyond the applicability domain incurs only limited errors in

357   the $K_{WIOM/G}$ prediction of ABSOLV/ppLFERs and SPARC. In addition, COSMOtherm and SPARC

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358   use a single surrogate molecule to represent the WIOM phase, while ppLFERs were

359   calibrated from atmospheric aerosols. The agreement among different methods suggests

360   that the surrogate suitably represents the solvation properties of organic aerosol.

361 -   generally better agreement between $K_{W/G}$ values predicted by ABSOLV/ppLFER and SPARC

362   (Figure 1 (d)) should not be seen as an indication that these methods are better at

363   predicting $K_{W/G}$. In fact, the lower $K_{W/G}$ values predicted by COSMOtherm have a higher

364   chance of being correct than the $K_{W/G}$ values predicted by ABSOLV/ppLFER and SPARC.

365   While ABSOLV/ppLFERs, SPARC and the group contributions methods currently used in the

366   atmospheric chemistry community are much more easily implemented for the large number of

367   compounds implicated in SOA formation, the current study demonstrates that the expertise

368   and time required to perform quantum-chemical calculations for atmospherically relevant

369   molecules should constitute but a minor impediment to a wider adoption of COSMOtherm

370   predictions. Here, we are not only compiling all the predictions we have made in the supporting

371   information file, we are also making available the cosmo-files (see Data Availability for details),

372   whose generation is the major time and CPU-demanding step in the use of COSMOtherm.

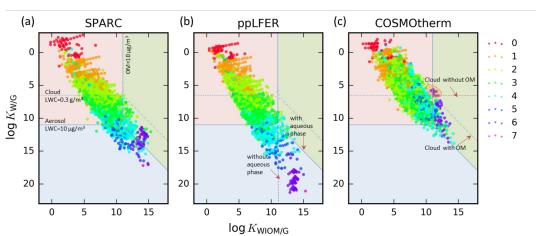373 **Atmospheric Implications**

374   The phase distribution of an organic compound in the atmosphere depends on its partitioning

375   coefficients. The two-dimensional partitioning space defined by log $K_{W/G}$ and log $K_{WIOM/G}$

376   introduced recently (Wania et al., 2015) is used here to illustrate the difference in the

377   equilibrium phase distribution of these compounds in the atmosphere that arises from using

378   partitioning coefficients estimated by different methods (Figure 3). A detailed description of

379   partitioning space has been provided by Wania et al. (2015), a brief explanation is given in the

380   supporting information (Figure S11). Briefly, the blue solid lines between the differently colored

381   fields indicate partitioning property combinations that lead to equal distributions between two

382   phases in a phase-separated aerosol scenario, with a liquid water content (LWC) of 10 $\mu g/m^3$

383   and organic matter loading (OM) of 10 $\mu g/m^3$. The purple dashed line in Figure 3 (b) shows an

384   aerosol scenario without an aqueous phase (see Figure S11 (c) for detail). The blue dotted lines

385   represent a cloud scenario where LWC is 0.3 g/m^3 and OM is either 10 $\mu g/m^3$ or non-existent

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386 because all of the OM is dissolved in the aqueous phase (illustrated by the red dashed lines in

387 Figure 3 (c), see also Figure S11 (d)). Compounds are located in the partitioning space based on

388 their estimated partitioning coefficients ($K_{WIOM/G}$ and $K_{W/G}$). Compounds on the boundary lines

389 have 50 % in either of the two phases on both sides of the boundary and are thus most

390 sensitive to uncertain partitioning properties. On the other hand, for substances that fall far

391 from the boundary lines indicating a phase transition (e.g. volatile compounds with two or less

392 functional groups), even relatively large uncertainties in the partitioning coefficients could be

393 tolerated, because they are inconsequential.

394

395 **Figure 3**   Partitioning space plot, showing in pink, blue and green the combinations of partitioning

396   properties that lead to dominant equilibrium partitioning to the gas, aqueous, and

397   WIOM phases, respectively. The blue solid and dotted lines are boundaries for an

398   aerosol scenario (LWC 10 µg/m^3, 10 µg/m^3 OM) and a cloud scenario (LWC 0.3 g/m^3, 10

399   µg/m^3 OM), respectively. The vertical purple dashed lines in Figure 3 (b) shows an

400   aerosol scenario without an aqueous phase (LWC 0 µg/m^3, 10 µg/m^3 OM). The

401   horizontal red dashed lines in Figure 3 (c) represent a cloud scenario where LWC is 0.3

402   g/m^3 and OM 0 µg/m^3. The differently colored dots indicate the number of functional

403   groups in the molecules.

404 When plotted in the chemical partition space, the 3414 chemicals occupy more or less the same

405 region as the much smaller set of SOA compounds investigated earlier (Wania et al., 2015).

406 When using predictions by COSMOtherm the SOA compounds cover a relatively smaller region

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407   as compared to ABSOLV/ppLFER and SPARC. With increasing number of functional groups

408   (Figure 3) or molecular weight (Figure S12), an increasing fraction of these compounds

409   partitions into the condensed phases, i.e. WIOM or water. In general, compounds with water or

410   WIOM as the dominant phase usually are multifunctional, i.e. contain more than two functional

411   groups. According to Figure S12, compounds with predominant partitioning into WIOM usually

412   have a molar mass in excess of 200 g/mol, while some compounds with molar mass less than

413   200 g/mol prefer the aqueous phase. Other than the water content and WIOM loadings

414   illustrated in Figure 3, in reality a compound's atmospheric phase distribution depends on other

415   factors such as the organic matter composition, salt content, pH, and temperature (Wania et

416   al., 2015;Wang et al., 2015).

417   Comparing the different panels of Figure 3 reveals that the atmospheric equilibrium phase

418   distribution of SOA compounds can be very different depending on which methods is used for

419   partitioning coefficient estimation. The difference is most striking when comparing the

420   placement of highly functionalized compounds (with more than 3 functional groups) based on

421   ABSOLV/ppLFER and COSMOtherm predictions. The large $K_{W/G}$ values estimated by

422   ABSOLV/ppLFERs lead to these compounds having a high affinity for aqueous aerosol. In

423   contrast, predictions by COSMOtherm suggest that only very few of them (and not even the

424   ones with the highest number of functional groups) prefer the aqueous aerosol phase; instead

425   most of them have either gas or WIOM as the dominant phase. SPARC predicts a slightly larger

426   preference of highly functionalized compounds for the aqueous phase than COSMOtherm.

427   In a cloud scenario with a much higher LWC (shown by the blue dotted boundary lines in Figure

428   3), the choice of $K_{W/G}$ prediction method also matters. Whereas with ABSOLV/ppLFER and

429   SPARC most of the highly functionalized compounds (i.e. 96 % or 97 % of the 736 compounds

430   with >3 functional groups) partitions into aqueous phase, only two-thirds (64 %) do so when the

431    $K_{W/G}$s predicted by COSMOtherm are used. Further, only COSMOtherm predicts that some of

432   the SOA compounds (circled in Figure 3(c)) would prefer to form a separate WIOM phase rather

433   than dissolve in the bulk aqueous phase.

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434   Table 2 summarizes the number and percentage of compounds that have dominant partitioning

435   (at least 50 %) into different phases, which shows the impact of using different prediction

436   techniques on phase distribution calculations in different atmospheric scenarios. In a para-

437   meterisation of SOA formation that includes an aqueous aerosol phase, use of $K_{W/G}$ predicted

438   by ABSOLV/ppLFERs (and probably also the commonly employed group contribution methods)

439   would lead to much higher SOA mass than use of $K_{W/G}$ predicted by COSMOtherm. For instance,

440   10 % and 17 % of the compounds predominantly partition into the aqueous phase when

441   predictions by SPARC and ABSOLV/ppLFER are used, in contrast to only 14 compounds (less

442   than 1 %) with COSMOtherm predictions (Table 2 scenario (a)). A large difference also occurs in

443   the cloud scenarios (Table 2 scenarios (b) and (d)), where SPARC and ABSOLV/ppLFER predict

444   twice as many compounds partitioning into the aqueous phase than COSMOtherm. Incidentally,

445   in a parameterization of SOA formation that does not account for an aqueous aerosol phase

446   (the scenario in Figure S11 (c) and Table 2 (c)), the impact of the choice of partitioning

447   prediction method is much smaller. The number of compounds on the right side of the purple

448   dashed boundary in Figure 3 (b) does not vary substantially with different predictions.

449   **Table 2**   Percentage and number of compounds with at least 50 % in gas, water or WIOM phase

450   under different aerosol and cloud scenarios predicted with SPARC, ABSOLV/ppLFER and

451   COSMOtherm. The four scenarios (a-d) correspond to the scenarios in Figure S11 (a-d) in

452   Supporting information.

aerosol scenarios	(a) (LWC=10 µg/m^3, OM=10 µg/m^3)			(c) without water phase (LWC=0 µg/m^3, OM=10 µg/m^3)	
	Φ_G>50 %[a]	Φ_W>50 %[a]	Φ_{WIOM}>50 %[a]	Φ_G>50 %	Φ_{WIOM}>50 %
SPARC	85 % (2892)[b]	10 % (352)	4% (134)	92 % (3132)	8 % (282)
ABSOLV/ppLFER	82 % (2804)	17 % (570)	1% (25)	96 % (3267)	4 % (141)
COSMOtherm	96 % (3268)	0 % (14)	3% (119)	96 % (3282)	4 % (131)

cloud scenarios	(b) (LWC=0.3 g/m^3, OM=10 µg/m^3)			(d) without WIOM phase (LWC=0.3 g/m^3, OM=0 µg/m^3)	
	Φ_G>50%	Φ_W>50 %	Φ_{WIOM}>50 %	Φ_G>50%	Φ_W>50 %
SPARC	36 % (1242)	64 % (2168)	0 % (0)	36 % (1242)	64 % (2172)
ABSOLV/ppLFER	35 % (1201)	65 % (2211)	0 % (0)	35 % (1203)	65 % (2211)
COSMOtherm	66 % (2258)	33 % (1137)	0 % (9)	66 % (2267)	34 % (1147)

453   [a] Φ_G, Φ_W and Φ_{WIOM} represent for fractions of compounds in gas phase, water phase and WIOM phase, respectively.
454   [b] number in brackets are number of compounds

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Conclusions

For compounds implicated in SOA formation, the prediction of $K_{W/G}$ is much more uncertain than the prediction of $K_{WIOM/G}$. This is true even if we consider that $K_{WIOM/G}$ will vary somewhat depending on the composition of the WIOM (Wang et al., 2015). In particular, the methods currently used for $K_{W/G}$ prediction of these substances have the potential to greatly overestimate $K_{W/G}$. This uncertainty is consequential, as the predicted equilibrium phase distribution in the atmosphere, and therefore also the predicted aerosol yield, is very sensitive to the predicted values of $K_{W/G}$: depending on the method used for prediction, the aqueous phase is either very important for SOA formation from the studied set of compounds or hardly at all. Isaacman-VanWertz et al. (2016) recently found the estimated phase distribution of 2-methylerythritol, an isoprene oxidation product (in Figure S6), highly dependent on the chosen method for predicting $K_{W/G}$. Here we show that this is a general issue potentially affecting a very large number of SOA compounds. In order to identify reliable prediction methods, it will be necessary to experimentally determine the phase distribution of highly functionalized, atmospherically relevant substances, whereby the focus should be on establishing their partitioning into aqueous aerosol.

Data Availability

COSMO files for the 3414 organic compounds can be accessed by contacting the corresponding author.

Supporting Information

The supporting information contains figures and text mentioned in the paper, including detailed information on the organic compounds, e.g. SMILES, molecular formula, molecular weight, functional groups, O:C ratios, predicted K-values, ABSOLV predicted solute descriptors, COSMOtherm predicted vapor pressures and activity coefficients in WIOM and water.

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