

Ionic Liquid Assisted Dissolution of Dissolved Organic Matter and PAHs from Soil Below the Critical Micelle Concentration

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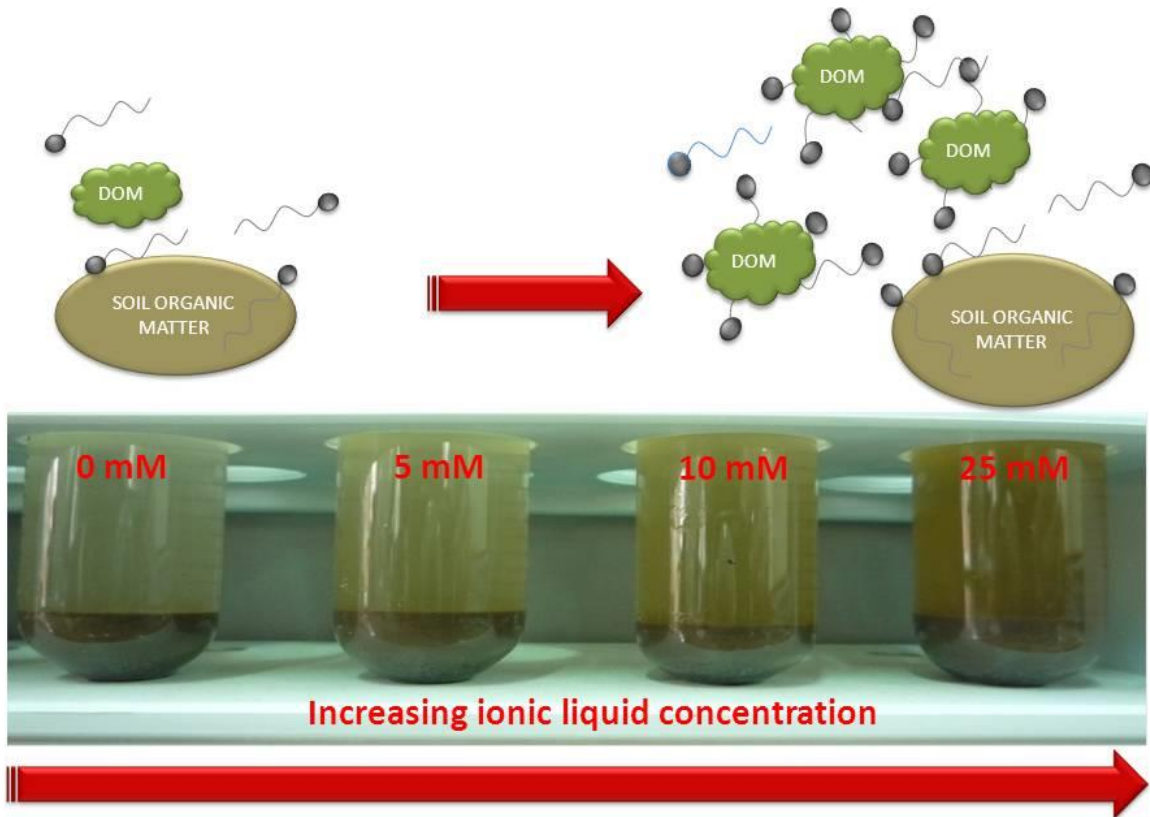
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13 **TABLE OF CONTENTS ART**



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17 **ABSTRACT**

18 Increased use and production of ionic liquids (ILs) may result in emissions into the environment.
19 Particularly vulnerable are industrial areas and landfills where ILs are utilized and ultimately
20 disposed of. This study investigates how IL contamination can affect soil properties and the
21 sorption of pre-existing contaminants. The commonly used IL 1-methyl-3-octyl imidazolium
22 chloride ([OMIM][Cl]) was added at various quantities to a landfill soil contaminated with
23 polycyclic aromatic hydrocarbons (PAHs). Subsequently, the release of PAHs and dissolved
24 organic matter (DOM) from this soil was thoroughly investigated. Two fractions of PAH release
25 into the porewater were measured, the freely-dissolved fraction (measured using a passive
26 sampler) and the total PAH concentration (which includes the freely-dissolved molecules as well
27 as those associated with colloids, micelles and DOM). As expected the highest levels of total
28 PAH porewater concentration occurred when the critical micelle concentration (CMC) of the IL
29 was exceeded. However, as we report here for the first time, enhanced amounts of freely-
30 dissolved PAHs were released by sub-CMC concentrations of IL. Additionally, enhanced levels
31 of DOM, due to dissolution of soil organic matter by IL, were also observed upon addition of
32 sub-CMC IL concentrations. Based on this, enhanced release of pre-existing contaminants and
33 DOM is suggested as a potential risk from IL emissions at trace concentrations well below the
34 CMC. Potential mechanisms of this sub-CMC release are discussed.

35

36 INTRODUCTION

37 For over a decade ionic liquids (ILs) have been gaining considerable industry attention, due to
38 their negligible volatility, high thermal, chemical and electrochemical stability, excellent
39 solvating properties and a multitude of tunable structures. The first commercial use was in 2002,
40 when the multi-ton commercial process (BASIL™ by BASF) employing ILs was launched.
41 Other applications include the dimerization of butenes, their use as liquid pistons, and as a
42 storage media for hazardous gases and dye-sensitized solar cells.¹ The most common ILs are
43 manufactured on a multi-ton scale.^{2, 3} To date no reports of ILs being found in the environment
44 are known. To prepare for possible emissions, recent efforts have been directed towards better
45 understanding of ILs' (eco)toxicity, biodegradability and their potential effects on the
46 environment. Efforts so far indicate that some ILs present a low to high hazard potential for man
47 and the environment, and that their "greenness" depends strongly on their structure.⁴ The fate
48 and effect that ILs have on soil, once emitted, is not yet understood. ILs can affect both soil and
49 soil sorption properties for other contaminants that may be present.^{5, 6}

50 Most ILs have organic ions, and many of them exhibit behavior similar to that of cationic
51 surfactants.⁷ In an aqueous environment, cationic surfactants exist as monomers only at low
52 concentrations, where they have a preference to sorb onto negatively charged solid surfaces by
53 electrostatic interactions.⁸ Aggregation in the aqueous phase occurs at a specific threshold
54 concentration known as the critical micelle or critical aggregate concentration (CMC and CAC,
55 respectively).^{9, 10} Though similar to cationic surfactants, there are some differences with ILs.
56 Firstly, ILs are not generally designed to be surfactants, though some such as imidazolium
57 homologues have CMCs lower than commercial cationic surfactants and only slightly higher
58 than anionic ones.¹¹ Secondly, in commercial applications, ILs are generally present as a free



59 phase (and not commonly as an emulsion). Finally, ILs in the pure state are liquid, have a larger
60 conductivity than surfactants, and a broad electrochemical window (the span of potentials
61 between which they are neither reduced nor oxidized).

62 Because the cores of surfactant or IL micelles are hydrophobic, hydrophobic organic
63 compounds (HOCs) can partition into them. This process is referred to as “solubilization”, as is
64 depicted in Figure S1 in the Supporting Information (SI). This is widely recognized, and for this
65 reason surfactants have been applied in so called surfactant enhanced remediation of soils
66 contaminated with HOCs.⁹ If ILs are released at levels exceeding their CMC in a soil-porewater
67 system, they could similarly solubilize hydrophobic compounds present. Below the CMC,
68 surfactants are generally considered to have a negligible impact on the sorption or release of
69 hydrophobic compounds.^{9, 12, 13}

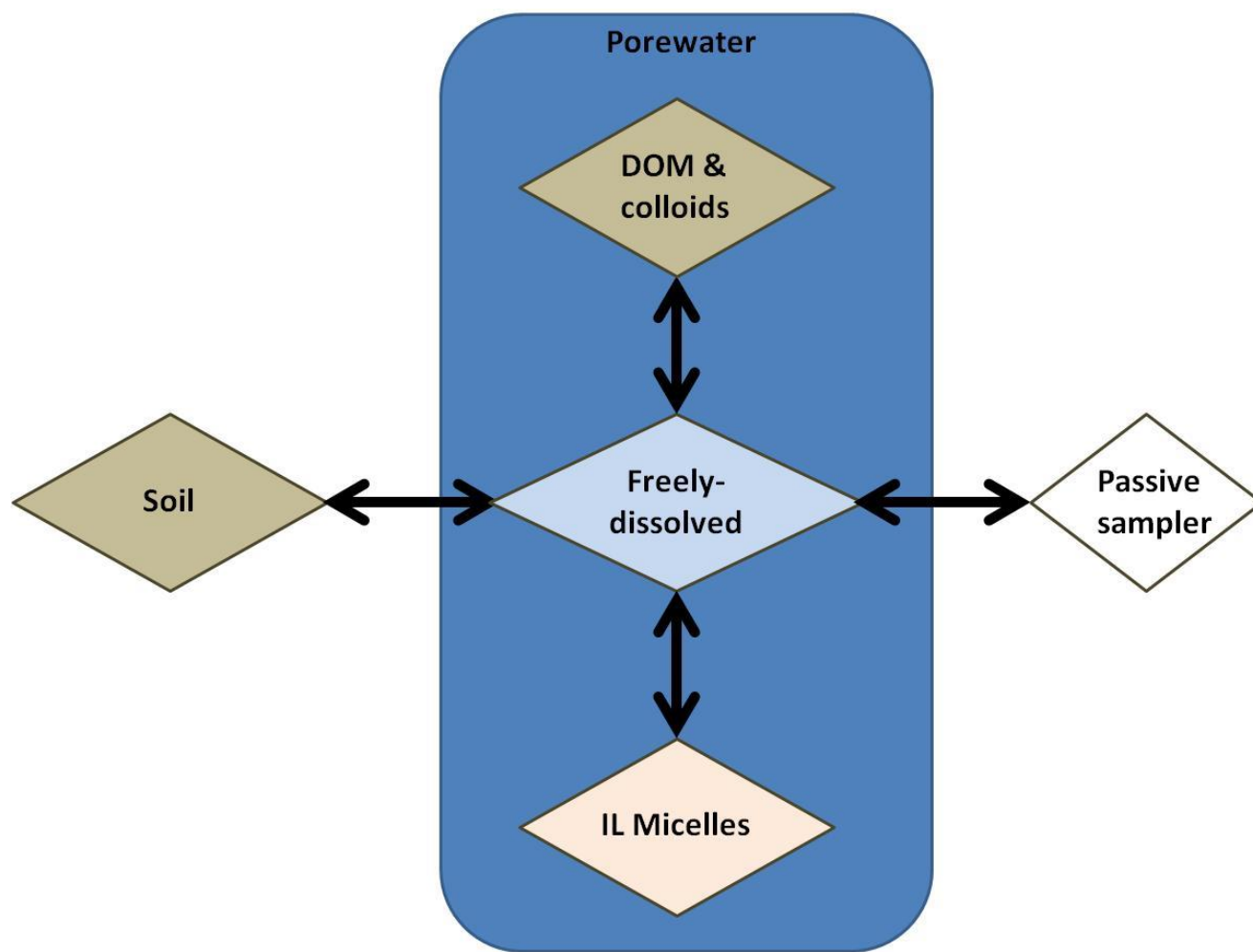
70 Whether an IL with an organic cation behaves like (cationic) surfactants, in that it enhances
71 release of HOCs above but not below the CMC, has not yet been tested. Herein, we conduct a
72 series of experiments to obtain a mechanistic understanding of how IL added at varying
73 concentrations can affect a contaminated soil by release of dissolved organic matter (DOM) and
74 pre-existing contaminants. Specifically, we focus on the dissolution and solubilization of DOM
75 and 16 PAHs listed in the initial US Environmental Protection Agency’s *Priority Pollutants List*
76 by the IL 1-methyl-3-octylimidazolium chloride [OMIM][Cl] below and above its CMC from a
77 polluted soil. As shown, contrary to what is commonly concluded for cationic surfactants, this IL
78 caused enhanced release of PAHs below the CMC.

79
80



81 **THEORETICAL BACKGROUND**

82 To conceptualize the mechanisms involved during HOC release in a soil-surfactant system, the
83 properties of soil and the aqueous porewater need to be considered. Porewater consists of various
84 phases including suspended colloids, dissolved organic matter (DOM) and any formed micelles.
85 HOC molecules that are “freely-dissolved”, i.e. completely solvated by water, can partition with
86 any of these other phases within the pore water, as shown in Figure 1.



87
88 **Figure 1. Partitioning processes for hydrophobic organic compounds (HOC) in a soil**
89 **porewater system containing ionic liquid (IL) micelles. The potential phases for the HOC to**
90 **exist are: soil sorbed, freely-dissolved (solvated by water), solubilized in an IL micelle,**
91 **DOM-sorbed and colloid-sorbed. When a passive sampler is introduced, some HOCs are**
92 **also in the passive-sampler sorbed phase. The arrows represent partitioning equilibria.**

93

94 The freely-dissolved state is the central phase through which an HOC molecule can transfer
95 between the soil, DOM, colloids and micelles. How much contaminant may be freely-dissolved
96 depends largely on the contaminant and solution chemistry of the porewater. For instance, pure
97 water can hold very low concentrations of HOCs, due to the H-bonding between water molecules
98 being more energetically favorable than solvation interactions between water and HOCs.
99 However, if there are other entities dissolved in the water that disrupt the H-bonding between
100 water molecules, such as organic molecules, DOM, ionic liquids or dissolved hydrophobic
101 moieties in general, H-bonding within the porewater phase would be reduced, and thus the
102 aqueous matrix could solvate more HOCs. These effects are described in the central text book by
103 Schwarzenbach et al. as “salting in” or cosolvency.¹⁴ HOCs entering (pore)water in the freely-
104 dissolved state is referred to as *dissolution*, which is in contrast to *solubilization* within micelles.
105 Compounds in the freely-dissolved phase are considered the most bioavailable to organisms.¹⁵

106 The other major factor that governs the freely-dissolved concentration in the porewater is the
107 sorption capacity of soils. For HOCs like PAHs, sorption to soil is generally attributed to the soil
108 organic matter (SOM) content; whereas the sorption capacity of cationic compounds like
109 [OMIM] is additionally attributed to interactions with pH dependant negative moieties in the
110 SOM (e.g. carboxyl, hydroxyl, phenolic functional groups) and minerals.¹⁶ Suspended, non-
111 dissolved colloids (such as black carbon colloids) may also be present and act as sorbents.¹⁷

112 DOM is considered anionic, like SOM. Negative charges present in both DOM and SOM
113 cause mutual repulsion, resulting in a certain amount of suspended DOM in the porewater.¹⁸⁻²⁰
114 Any intervention into porewater H-bonding or surface charges can shift this fine balance and
115 cause dissolution or precipitation of DOM. As explained above, increased dissolution of DOM



116 can increase dissolution of HOCs. Conversely, adsorption of cationic surfactants can precipitate
117 DOM and this in turn could cause simultaneous precipitation of HOCs.^{9, 12, 18, 21}

118

119 **MATERIALS AND METHODOLOGY**

120 **Chemicals.** [OMIM][Cl] was obtained from Merck KGa (Darmstadt, Germany). CaCl₂
121 anhydride was obtained from POCh Gliwice, Poland. Acetone and hexane used for extraction
122 and a mixture of deuterated PAH (including d8-naphthalene, d10-phenanthrene, d10-pyrene,
123 d12-benz(a)anthracene, d12-benzo(a)pyrene, d12-benzo(ghi)perylene) used as an extraction
124 efficiency standard were obtained from VWR International AS, Oslo, Norway. For preparation
125 of the HPLC mobile phase, HPLC-grade acetonitrile from Lab-Scan (Dublin, Ireland) and
126 spectrophotometric-grade trifluoroacetic acid (Sigma-Aldrich, Germany) were used.

127 **PAH Contaminated Soil.** Soil that was known to be contaminated with PAHs was used for all
128 experiments presented herein. Use of such a “real world” contaminated soil is deemed more
129 representative of an actual PAH contamination than pristine soil spiked with PAHs in the
130 laboratory. The soil was obtained from the Lindum landfill in Drammen, Norway, and is
131 identical to the “urban soil” presented in a previous study.²² The soil was sampled in 2007, and
132 stored at 4 °C in the dark until the presented analysis in 2010. Properties are presented in Table
133 S1 of the Supporting Information (SI).

134 **Dissolution-Solubilization Experiment.** 2 g (dry weight) of PAH contaminated soil were
135 weighed into each test vial. Then, 20 mL of [OMIM][Cl] solution in concentrations of 0mM, 2.5
136 mM, 10 mM, 25 mM, 50 mM, 100 mM, 250 mM, 300 mM, or 400 mM were added, together
137 with 200 mgL⁻¹ NaN₃ (to prevent microbial degradation) and 0.01M CaCl₂. All solutions were



138 prepared in duplicate, and the freely-dissolved total porewater concentrations (Figure 1) were
139 determined separately as described below.

140 **Freely-dissolved C_{pw} .** To detect the dissolution of freely-dissolved PAHs in the porewater
141 (C_{pw}) a passive sampler made of polyoxymethylene (POM) was introduced (Astrup AS, Norway)
142 into each vial. The working principle of the POM sampler for freely-dissolved PAH sampling is
143 described elsewhere.^{23, 24} In summary, once the POM sampler is in equilibrium with the
144 porewater, the POM is extracted, the PAH concentration within the POM is determined, C_{POM} ,
145 and the freely dissolved C_{pw} is derived by use of the POM-water partition coefficient, K_{POM} :

146

$$147 \quad \text{freely dissolved } C_{pw} = K_{POM} \cdot C_{POM}^{-1} \quad (1)$$

148

149 The POM C_{pw} extraction method used was adapted from Hawthorne et al.,²⁵ though here a 55-
150 μm POM strip was used instead of a 76- μm strip, also a different solvent extraction step and
151 different quantities of soil and POM were used (see below). The detection limits for this method
152 range from 1 ng/L for naphthalene to 1 pg / L for the 5,6-ring PAHs.²⁵ In brief, POM strips were
153 precleaned by shaking end-over-end for one day with heptane, one day with methanol, and five
154 days in Millipore water while changing the water periodically. To each vial, 0.1 g of pre-cleaned
155 POM was added. Samples were sealed, placed in dark container to prevent photolysis, and
156 shaken end-over-end at 8-10 rpm for 30 days, which is sufficient time for equilibration.²⁵ Then,
157 POM was removed, the sample vials centrifuged and remaining aqueous phase isolated for the
158 total C_{pw} extractions (see below). Visible particles on the POM surface were removed with a
159 tissue and gentle rinsing with deionized water. The POM was then placed in a new vial, and a 20
160 mL mixture of 80:20 hexane:acetone spiked with deuterated PAHs was added, the later to serve

161 as an extraction efficiency internal standard. The vials containing POM were then shaken end-
162 over-end in the dark for another 5 days, the hexane:acetone was collected and was quantified
163 using GC/MS²⁶ to determine C_{POM} (see the SI for the GC/MS method description). Freely-
164 dissolved C_{pw} was obtained by use of equation 1 and available K_{POM} values.²⁵

165 **Total C_{pw} .** The isolated aqueous phase obtained after POM removal was divided into two
166 fractions: 1 mL was used to measure the IL concentration by HPLC/UV analysis, and the
167 remainder was extracted to obtain the total C_{pw} of PAHs. For the latter, the aqueous phase was
168 extracted with three portions of 20 mL of hexane. Surrogate standards of deuterated PAHs were
169 added to the solvent. Solvent extracts were combined and then dried by adding sodium sulphate,
170 and quantified using GC/MS²⁶ (see the SI).

171 **Depletion Check.** To investigate if POM additions were depleting PAHs from soil to such an
172 extent that it could alter the equilibrium regime, two samples were prepared at 0 mM IL, one
173 with 0.1 g and the other with 0.5 g of POM, and compared. The differences were not substantial,
174 as described in the SI; thus the influence of depletion at 0.1 g of POM to 2 g of dry soil used here
175 is considered negligible.

176 **Influence of IL on POM Performance.** As ILs were previously never introduced into a
177 POM-type extraction, it was necessary to ensure there were no interactions between IL and POM
178 that would influence sorption into the POM, or that ILs themselves did not alter the solubility of
179 PAHs. To test this, sample vials were prepared containing 0.5 μ g of each PAH-16, 0.1 g of POM,
180 and different mixtures of pure water and IL to make a total volume of 10 mL. The concentrations
181 of IL added were 0, 2.5, 10, 25, 50, 100, 250, 300 or 400 mM. The mixtures were shaken and the
182 POM extracted as above.



183 **Ionic Liquid Analysis.** The amount of IL adsorbed by soil was calculated as the difference
184 between the initial concentration and concentration measured in the aqueous phase at the end of
185 experiment. The degradation of IL was assumed to be negligible since concentrations of
186 [OMIM][Cl] used here were too high to be biodegraded (unless the local microbial community is
187 adapted, which is unlikely), additionally a sterilizing agent was used (sodium azide).^{5,6} A Perkin
188 Elmer Series 200 HPLC consisting of a chromatographic interface (Link 600) binary pump,
189 UV/VIS detector, vacuum degasser and Rheodyne injection valve was used. For IL cation
190 separation a C₆-Phenyl (Phenomenex) 150×4.6 mm column was used in conjunction with
191 detection by UV adsorption at a wavelength of 218 nm. The sample injection volume was 10 µL
192 and the mobile phase applied was 27% acetonitrile/water + 0.1% (v/v) trifluoroacetic acid at a
193 flow rate of 0.8 mL min⁻¹.²⁷

194 **Organic Carbon Analysis.** Total organic carbon content of the soil solution was measured
195 using a LiquiTOC (Elementar, Germany) with a platinum catalyst. The aqueous phase was
196 diluted 1:100 with demineralized water and measured in duplicate. The contribution of IL (up to
197 75% of total TOC at 400 mM) and PAHs (fraction of a percent of total TOC) in solution was
198 deducted from the resulting value, leaving only TOC due to soil.

199 **Ionic Liquid Titrations.** Titrations to determine the IL-DOM interaction at micellar and
200 submicellar concentration were conducted automatically using the CerkoLab system
201 (CLS/M/07/06) autotitrator. For each titration 0.1 mg L⁻¹ humic acid (Sigma Aldrich, Germany)
202 was used as an analyte, and 1 mM [OMIM][Cl] as a titrant. The progress of the titration was
203 recorded with a Hydromet ERH-11s conductivity electrode that was previously calibrated with
204 five KCl solutions. The 2nd derivative was determined using OriginPro7.5 from the average of
205 two replicate measurements.

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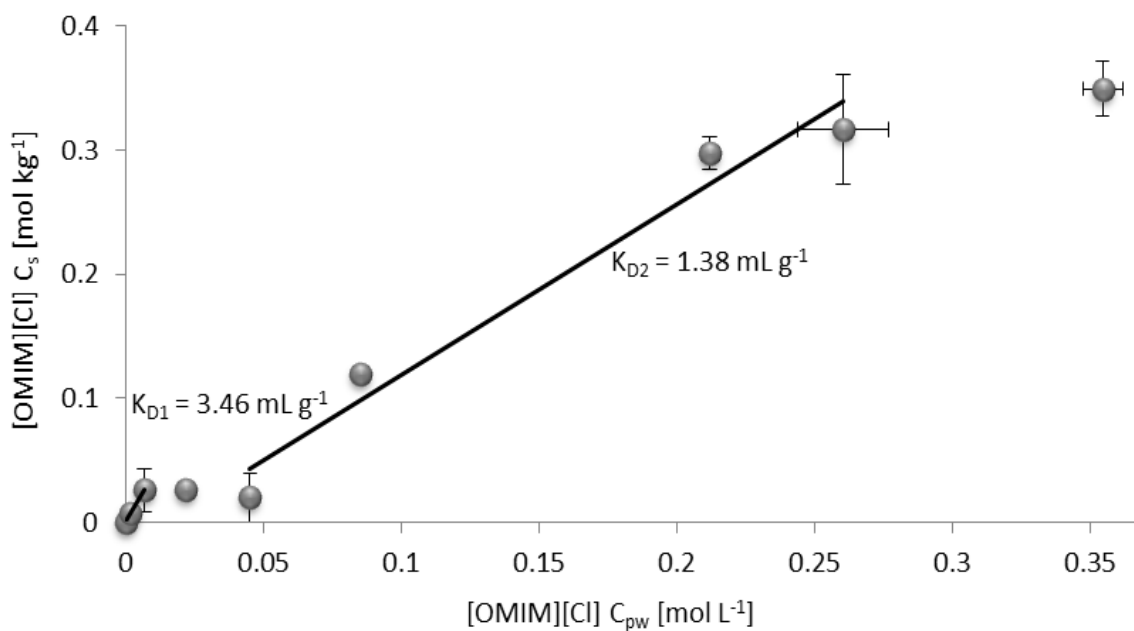


207 **RESULTS AND DISCUSSIONS**

208 The addition of [OMIM][Cl] resulted in a number of phenomena inside the soil and porewater.
209 In presenting the results we will first follow the behavior of the primary contaminant (IL), then
210 the fate of the secondary contaminants (PAHs), and finally that of DOM.

211 **IL Sorption.** The sorption isotherm for [OMIM][Cl] and the contaminated soil is shown in
212 Figure 2. The concentration of IL on the soil was determined by mass balance from the aqueous
213 equilibrium concentration determined by HPLC/UV.

214



215

216 **Figure 2. Sorption isotherm of [OMIM][Cl] to the sampled contaminated landfill soil (each**
217 **point is an average of two replicates, standard errors of both C_s and C_{pw} values are marked**
218 **with an error bar). The isotherm shows two plateau regions (between 0.01 - 0.05 M, and**
219 **0.25 - 0.04 M); K_{D1} and K_{D2} correspond to the two ascending regions.**

220 The isotherm shows two ascending regions and two plateau regions, which is characteristic for
221 surface active agents that modify the properties of surface on which they adsorb.²⁸ From the
222 ascending regions, two soil/porewater partition coefficients were calculated as slopes of linear,



223 ascending parts of the isotherm. It should be noted beforehand that the delineation and accuracy
224 of K_D values (ascending regions) and plateau regions are biased based on the concentrations
225 interval at which the isotherms were measured. The first K_D , K_{D1} , was extrapolated as 3.46 mL g^{-1}
226 ¹, and corresponds to the partitioning of IL between soil and solution (up to $\sim 0.01 \text{ mM}$), whereas
227 the second, K_{D2} , extrapolated as 1.38 mL g^{-1} , and describes the sorption of the second layer of IL
228 onto soil modified by the adsorption of the previous layer (between $\sim 0.04 \text{ mM}$ and 0.25 mM).
229 The first K_D is slightly larger than the second. The general justification for this is that the first K_D
230 accounts for both electrostatic and London dispersion interactions, and the second K_D only
231 accounts for the London dispersion interactions between already adsorbed IL molecules and IL
232 molecules forming the second layer.

233 **CMC.** In pure aqueous solution [OMIM][Cl] shows a detectable CMC at around 220 mM , and
234 in 10 mM CaCl_2 it is estimated to be approximately 175 mM .^{7, 29} The decrease in CMC in the
235 presence of salt is attributed to negatively charged chloride anions that allow for a closer
236 approach of IL head groups, thereby facilitating micelle formation. The difficulty in determining
237 the CMC in the current system is that some [OMIM][Cl] and CaCl_2 are adsorbed on the soil. The
238 exact concentration of [OMIM][Cl] at which micelles or aggregates form in the current system
239 can only be estimated based on the CMC in CaCl_2 solution and the K_D of [OMIM][Cl]. Assuming
240 CMC in 10 mM CaCl_2 to be 175 mM , and using the measured K_{D2} for [OMIM][Cl] of the tested
241 soil, it can be estimated that micellization with the present system occurs at an initial
242 concentration of approximately 250 mM [OMIM][Cl].

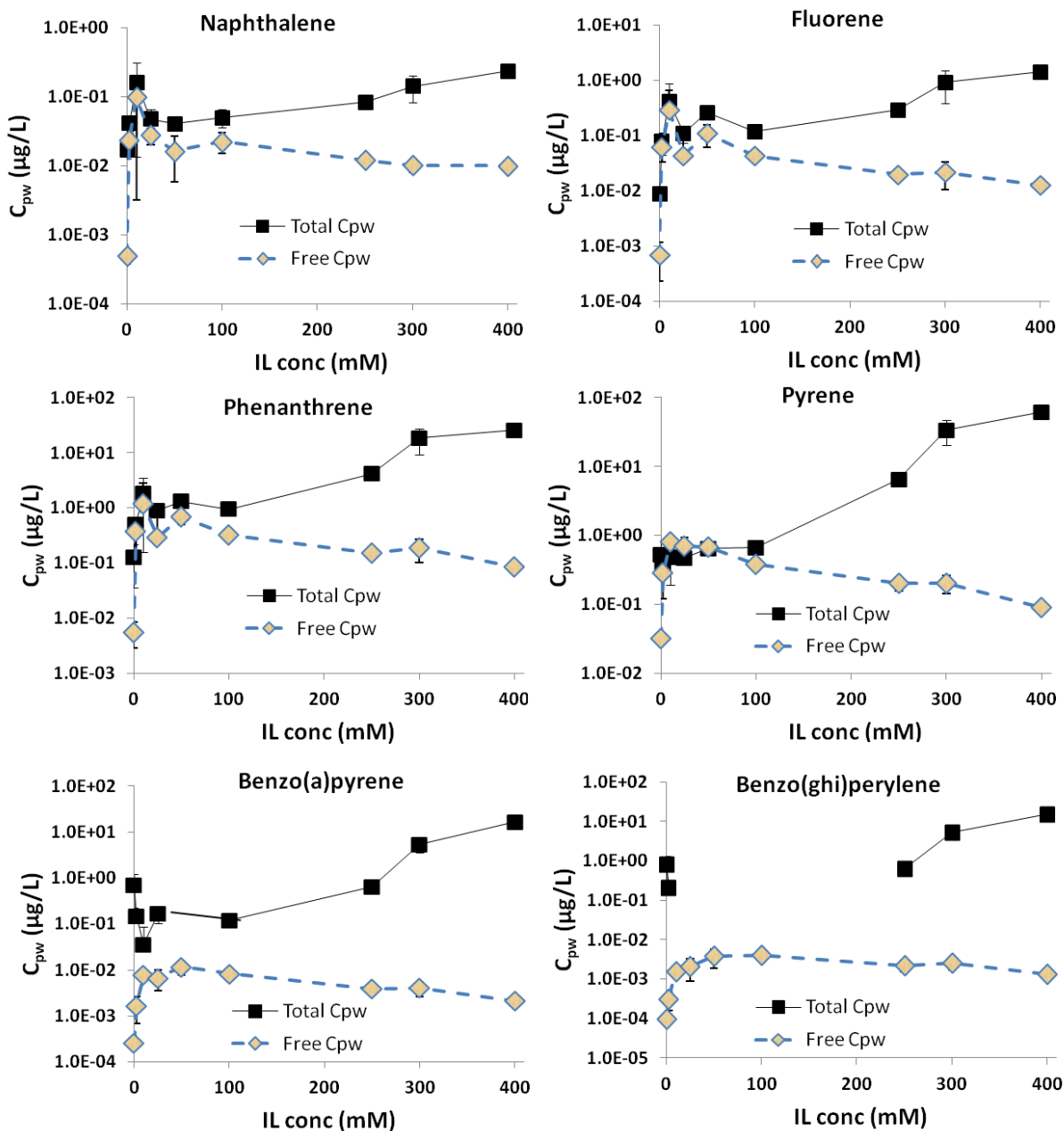
243 **Influence of IL on POM Performance.** For the batch systems containing POM and no soil,
244 no statistically significant change was observed in the final concentration of PAHs in the POM at
245 increasing IL concentrations until the CMC was exceeded (around 250 mM) (Figure S2 in the



246 SI). Above the CMC, the concentration in the POM dropped, indicating also a drop in the freely-
247 dissolved concentration. This is likely due to solubilization of PAHs from the POM and freely-
248 dissolved water phases into the IL micelles. No significant change in PAH concentration below
249 250 mM indicates that the presence of IL does not noticeably influence the sorption properties of
250 the POM or change the freely-dissolved solubility of PAHs in deionized water.

251 **PAHs in the Solid/IL Matrix.** Figure 3, Figures S3-5 (SI) and Tables S2-3 (SI) present the
252 freely-dissolved and total C_{pw} concentrations ($n = 2$) of PAHs in the soil-IL-POM systems. Note
253 that some total C_{pw} for the larger PAHs were below the detection limit, and ultimately only one
254 of the replicates was obtained for total C_{pw} at 50 mM IL. It is generally assumed that it is
255 necessary to exceed the surfactant's CMC to achieve enhanced HOC removal from a soil.^{12, 30} As
256 is evident from the obtained data, enhanced release of all PAHs into the total C_{pw} occurs above
257 the CMC, as expected. However, various trends are also evident at IL concentrations *below the*
258 *CMC*.

259



260

261 **Figure 3. Amount of total and freely-dissolved C_{pw} of PAHs from a contaminated soil in the**
 262 **presence of various initial $[\text{OMIM}][\text{Cl}]$ concentrations, showing results for two-ring**
 263 **(naphthalene, fluorene), three-ring (phenanthrene), four-ring (pyrene) and five-ring**
 264 **(benzo(a)pyrene) PAHs. Data are an average of two replicates, error bars are shown but**
 265 **generally are smaller than the label.**
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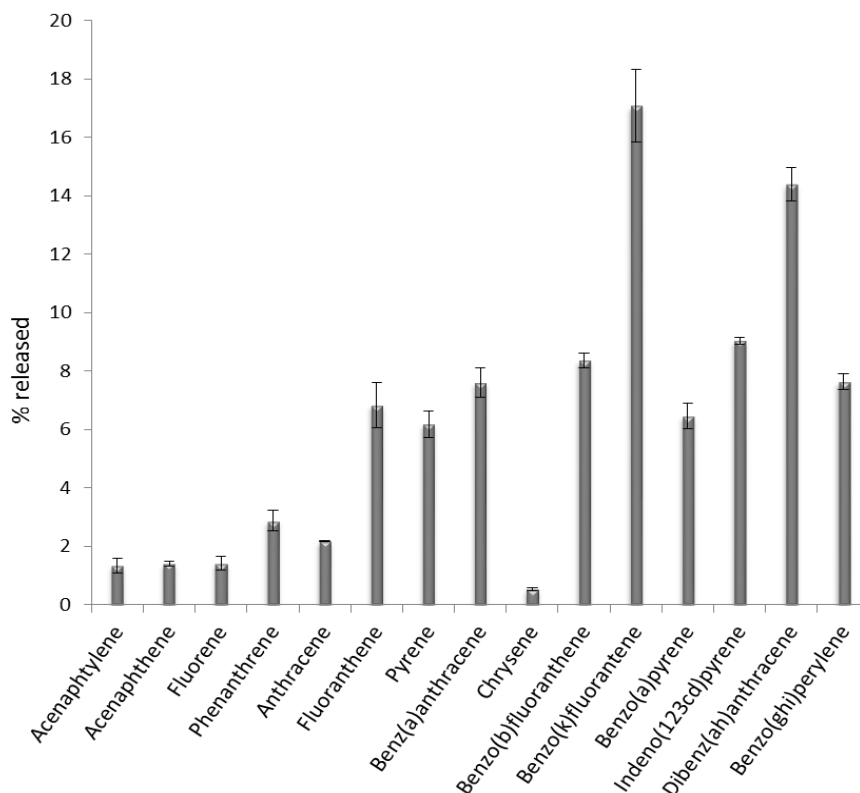
267 As evident in Figures 3 and Figures S3 - S5, the freely-dissolved C_{pw} of each PAH increases
 268 between 1 and 3 orders of magnitude as the IL concentration increases from 0 to 5 mM. For the

269 2-3 ring PAHs the freely-dissolved C_{pw} sharply peaks at 5 mM; for the 4-ring PAHs this peak at
270 5 mM is less sharp; the 5-ring PAHs exhibit a peak at 50 mM, and the 6-ring PAHs at 100 mM.
271 Above this peak, freely-dissolved C_{pw} gradually decreases with increasing IL. Comparing the
272 total and freely dissolved C_{pw} in these Figures, the two concentrations are the same at the 5 mM
273 IL peak for the 2-4 ring PAHs, implying that the freely-dissolved species is the main species in
274 porewater at this IL concentration. For the case of pyrene (Figure 3) and fluoranthene (Figure
275 S4), it appears that freely-dissolved C_{pw} is slightly greater than the total, which is impossible and
276 is attributed to analytical or extrapolation errors. For the 5-6 ring PAHs, the freely-dissolved C_{pw}
277 remains one to three orders of magnitude below the total C_{pw} , and thereby is likely only a minor
278 species (compared to e.g. colloid or DOM sorbed PAH species).

279 Looking just at the total C_{pw} , the two to three ring PAHs generally increase between 0 and 5
280 mM IL and remain more or less stable with increasing IL concentration until the CMC is
281 reached. Why the total C_{pw} remains more-or-less stable between 5 mM and the CMC, despite
282 decreasing freely-dissolved concentrations, may be due to increased association with suspended
283 DOM and colloids. For the 4-6 ring PAHs, no change in total C_{pw} is evident until the CMC is
284 exceeded, though PAHs associated with freely-dissolved C_{pw} and other porewater phases shifts
285 as described above.

286 The average percentage of PAHs released into the porewater in the presence of 400 mM IL
287 based on previously determined soil concentrations (Table S1) is presented in Figure 4. Note that
288 naphthalene in soil was not measured (due to high solvent blanks) and these percentages assume
289 that changes in total PAH concentration from analysis in 2007 to experiments here in 2010 were
290 negligible, thus may be underestimating the amount removed. The efficiency of release above
291 the CMC was substantially higher for the 4-6 ring PAHs. This is in agreement with previously

292 discussed findings by Liu *et al.*³¹. We propose that because smaller PAHs are more prone to
 293 dissolution (e.g. as seen in Figure 3), they could have been preferentially depleted in the
 294 environment, compared to the larger PAHs, before the soil was collected for analysis. This
 295 would cause the relative proportion of smaller PAHs remaining to be less prone to solubilization
 296 than the larger PAHs. Such trends have also been observed for PAH contaminated sediments.¹⁵
 297 Of the larger PAHs, chrysene was depleted noticeably the least. The reasons for this are unclear
 298 and may be unique to the present system; studies looking at removal of PAHs by use of
 299 surfactants do not find such outlying behavior for chrysene.^{32,33} How effective ILs (or
 300 surfactants) are at removing PAHs will likely depend on the history of pollution.
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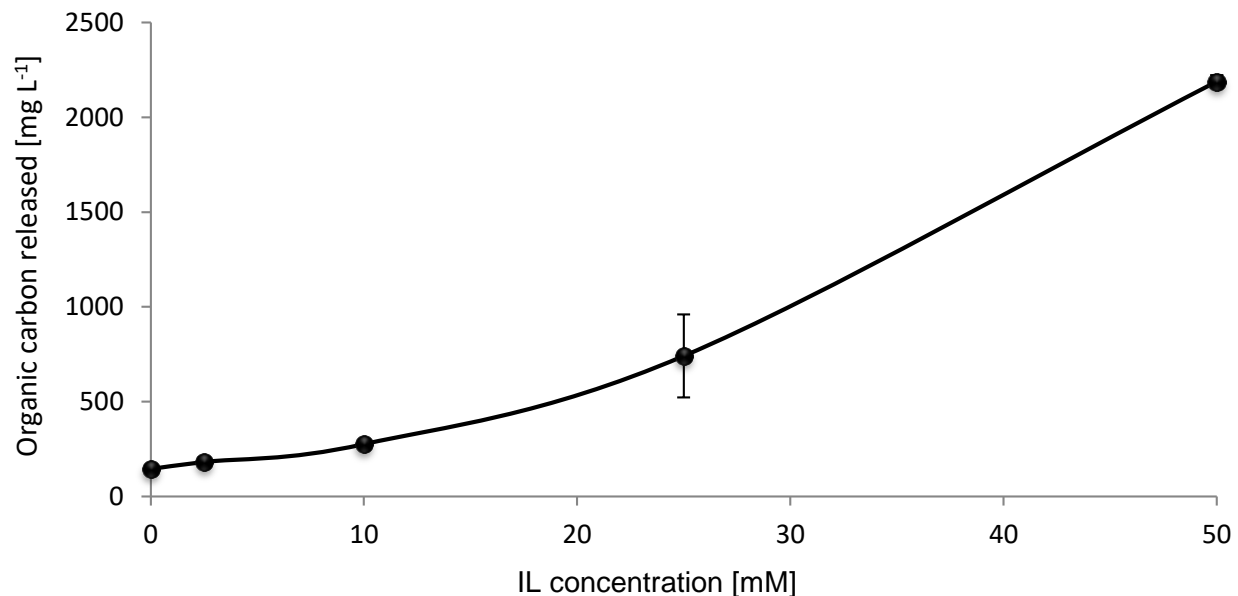


302
 303 **Figure 4. Percentage release of various PAHs from a contaminated landfill soil upon**
 304 **addition of 400 mM [OMIM][Cl]. Data are an average of two replicates, with error bars**
 305 **shown.**

306

307 **Release of DOM.** Because the addition of [OMIM][Cl] results in an overall release of PAHs
308 from the soil, an increase in dissolved organic matter (DOM) can be expected as well. This was
309 observed for [OMIM][Cl] additions from 10 to 50 mM, which are far below the CMC (Figure 5).

310



311

312 **Figure 5. Exponential release of organic carbon from soils under the influence of**
313 **[OMIM][Cl]. Initial IL concentrations are shown (average of two replicates, standard error**
314 **is marked with bars but generally smaller than markers)**

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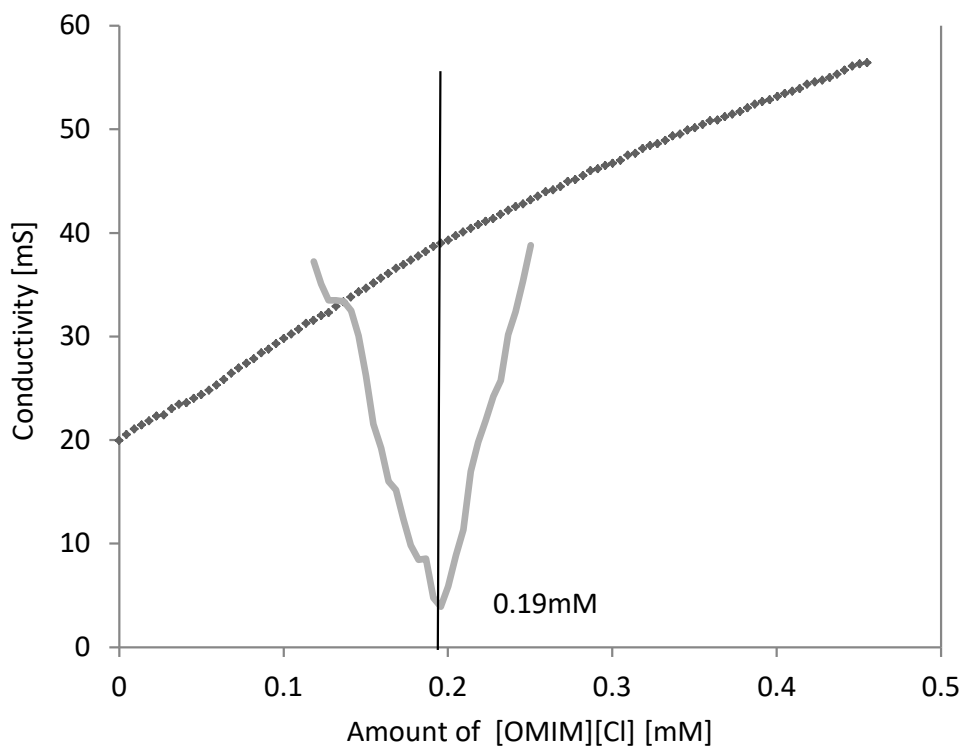
316 Visual examination of the test tube vials (Figure S6 in the SI as well as TOC art) also confirms
317 the increased release of DOM with IL concentrations below the CMC. When the IL content
318 approaches the CMC, the porewater solution becomes clear. This would indicate that at
319 concentrations just below the CMC the visible DOM precipitates out, likely due to a
320 neutralization of negative charges caused by adsorption of ILs. Colloidal systems are generally
321 stable when their zeta potential is smaller than -30mV or bigger than +30mV, outside of this
322 range repulsive forces between particles might be too weak and precipitation might occur.³⁴ We
323 have recently shown that adsorption of [OMIM][Cl] reverses the zeta potential of the minerals

324 quartz and kaolinite.³⁵ It is conceivable that a similar phenomenon, perhaps even more
325 pronounced, can occur for DOM as it too is a charged colloidal system that is capable of
326 interactions with ILs.

327 To verify a theory of solubilization/precipitation of DOM by [OMIM][Cl], an exemplary DOM
328 (in this case humic acid) was titrated with the ionic liquid and the conductivity was measured.
329 The results show that with added IL the conductivity increases up to a specific breakpoint
330 (Figure 6). After this breakpoint the slope of the curve decreases slightly. This phenomenon is
331 typical of surfactant micelle formation in solution, where the mobility of micelles is lower than
332 that of free ions, and thus a lowering of the conductivity is observed when micelle formation
333 occurs. However, in this case the concentration of [OMIM][Cl] at which the inflection of the
334 conductivity curve is observed is lower than the CMC. A viable justification for this is the
335 formation of IL-DOM complexes, as they have a lower ion mobility than the DOM by itself.

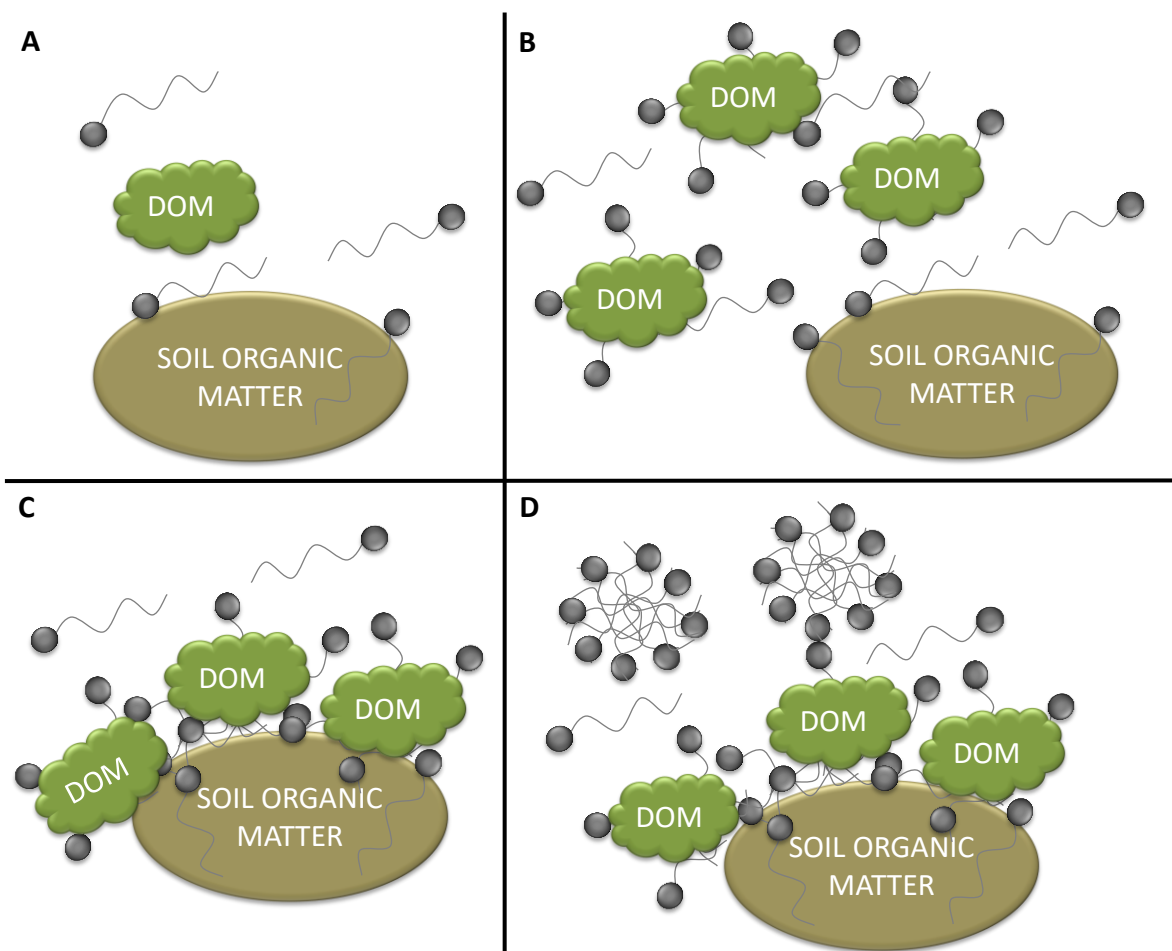
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339 **Figure 6. Conductivity titration curves of humic acid titrated with 1 mM [OMIM][Cl]. The**
340 **dotted line represents the 2nd derivative.**

341
342 **Proposed Mechanism.** Based on the observations of both freely-dissolved PAHs and DOM
343 increasing in the porewater with initial IL additions well below the CMC, there appears to be a
344 dissolution-type mechanism at play. One possibility is the formation of soluble complexes of IL
345 and soil components to form IL-DOM complexes, which can release PAHs by either
346 changing/breaking-up the (surface) structure of the SOM in a way that lowers affinity to soil, or
347 alternatively by decreasing H-bonding in the aqueous porewater mixture to facilitate dissolution
348 (e.g. by cosolvency or salting in effects¹⁴). An illustration of the above interpretation is presented
349 in Figure 7.



350

351 **Figure 7. Schematic representation of ILs' interactions with soil particles and dissolved**
 352 **organic matter (DOM) in four stages: A) initial IL addition in which DOM and SOM repel**
 353 **each other and the IL cations sorbs to some negatively-charged surfaces; B) IL-DOM**
 354 **complex formation at slightly elevated IL concentrations, increasing overall DOM and**
 355 **increasing freely dissolved PAH concentration by dissolution; C) some IL-DOM precipitate**
 356 **due to charge neutralization, however colloidal particles remain so that the total PAH in**
 357 **porewater remains the same though freely-dissolved PAH/dissolution slightly decreases; D)**
 358 **the CMC is exceeded and micelles form in the porewater, total PAH concentration**
 359 **increases though freely-dissolved concentration/dissolution continues to decrease with**
 360 **increasing IL.**

361
 362 The steps in Figure 7 are as follows, and are meant to be compared with the trends in Figures
 363 3, 5 and 6. Prior to addition of IL a certain amount of negatively charged DOM is present in the
 364 porewater, the negative charge causes the DOM aggregates and the soil to repel each other. The
 365 cation of the first IL molecules will sorb to the negative charges on soils and DOM (Figure 7A).

366 The first stage of extra PAH and DOM dissolution occurs as presented in Figure 7B, in which the
367 introduction of more IL causes additional DOM to be released into the solution, and the
368 formation of IL-DOM complexes. The presence of increased amount of IL-DOM complexes
369 leads to or coincides with increased freely-dissolved PAH dissolution, likely by lowering H-
370 bonding in the water solution¹⁴ or possibly by breaking up the soil and changing its properties to
371 sorb less effectively. Recall that the presence of the IL at low concentrations does not account for
372 this on its own (Figure S2). In Figure 7B, two to three ring PAHs are mainly present in the
373 porewater in freely-dissolved state, whereas 5-6 ring PAHs are mainly associated with other
374 porewater phases (colloids, DOM, IL-DOM complexes) (Figure 3). As the concentration of IL
375 increases, different species peak in concentration (Figure 6): first the freely-dissolved 2-4 ring
376 PAHs, then the 5-ring PAHs, followed by the 6-ring PAHs and the IL-DOM complexes. The
377 decrease in IL-DOM and DOM concentration is due to charge reversal (Figure 7C). The
378 presence of a peak in freely-dissolved PAH concentrations is likely due to a trade-off between
379 increased solubility in the porewater followed by increased sorption to suspended colloids
380 (though this sorption is weaker than to the native soil before adding IL). Meanwhile, the total
381 porewater concentration of PAHs does not change during the phase depicted at Figure 7C. . Then
382 at the CMC (Figure 7D), IL micelles substantially increase the solubilization of PAHs and
383 therefore the total C_{pw} of all ring sizes increases with increasing IL concentration, though
384 dissolution and therefore freely-dissolved C_{pw} decreases as more PAHs are present in micelles.

385 Because the increase in freely-dissolved concentrations is similar for all PAH ring sizes
386 (Figures 3, S3-S5), it cannot be accounted for by molecular volume or related factors (e.g. K_{ow}),
387 which is typically observed when adding completely miscible organic solvents to water (Figure
388 5.8 of Schwarzenbach et al. ¹⁴), or if the soil were to become less “hydrophobic”. Changes in



389 solubility not substantially related to the molecular volume could be indicative of a salting-in
390 type phenomena (e.g. PAH independent salting constant in Table 5.7 of Schwarzenbach et al. ¹⁴),
391 a polar interaction between the IL-DOM porewater and PAHs that is only weakly dependant on
392 PAH size (e.g. interactions of the pi electrons on the PAHs with electron accepting
393 functionalities in the IL-DOM-porewater matrix), or proportional changes regarding volume-
394 dependant interactions in the soil or water that are opposite to each other (e.g. a change in cavity
395 formation energy in the porewater or soil being approximately proportional and opposite to a
396 change in van der Waals interactions in the porewater or soil).

397 To verify or to acquire more information on the observed phenomena of increased
398 dissolution of PAHs and DOM in a contaminated soil below the CMC of an IL, further studies
399 using different soils, model humic acids, ILs and contaminants are recommended.

400

401 **SUPPORTING INFORMATION**

402 Detailed representation of release of all 16 PAHs form soil by [OMIM][Cl] as well as
403 other supporting data are included in Supporting Information. This material is available free of
404 charge via the Internet at <http://pubs.acs.org>

405

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