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

Marta Markiewicz[1], Christian Jungnickel[1], and Hans Peter H. Arp[2*]*

[1]Department of Chemical Technology, Chemical Faculty, Gdańsk University of Technology,

ul. Narutowicza 11/12, 80-233 Gdańsk, Poland

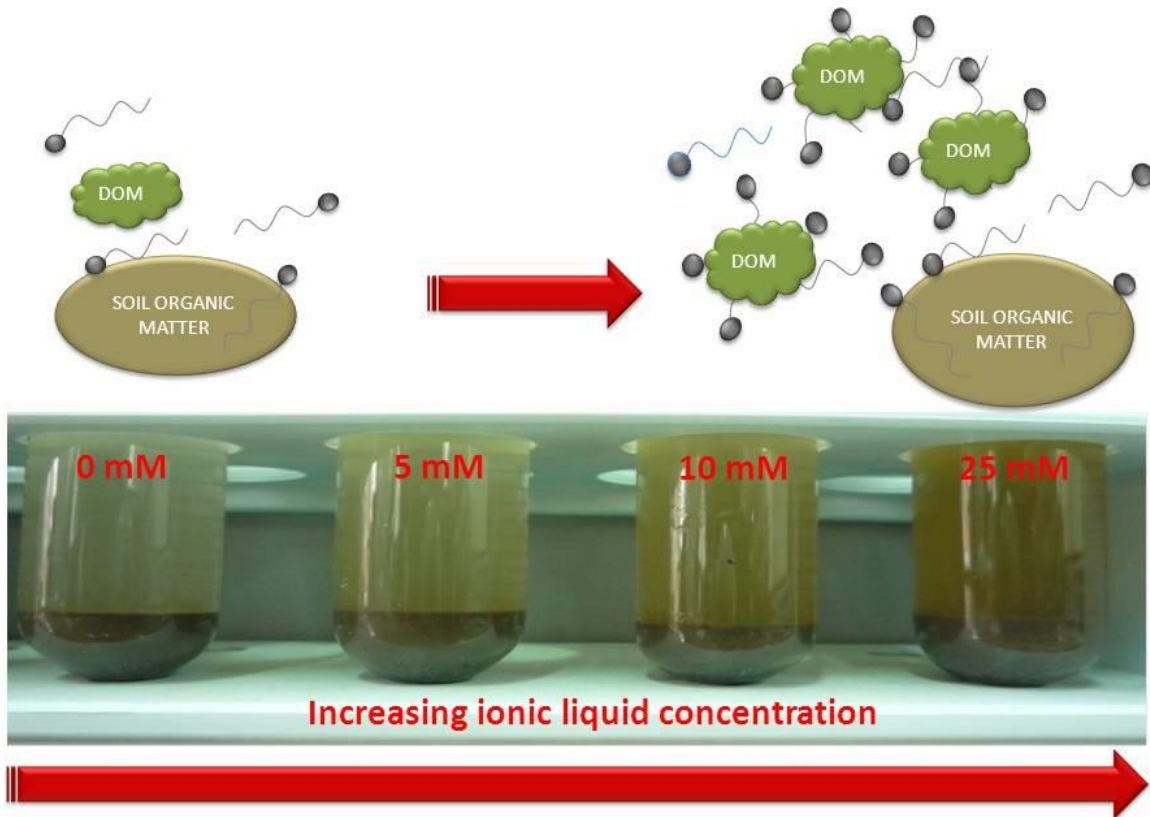[2]Norwegian Geotechnical Institute (NGI), Oslo, Norway

*corresponding authors

Phone: ++48 583471362;   Email: martam@chem.pg.gda.pl;

Phone: ++47 95020667;   Email: hpa@ngi.no

12
13   **TABLE OF CONTENTS ART**

14
15
16

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

INTRODUCTION

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

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

4

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

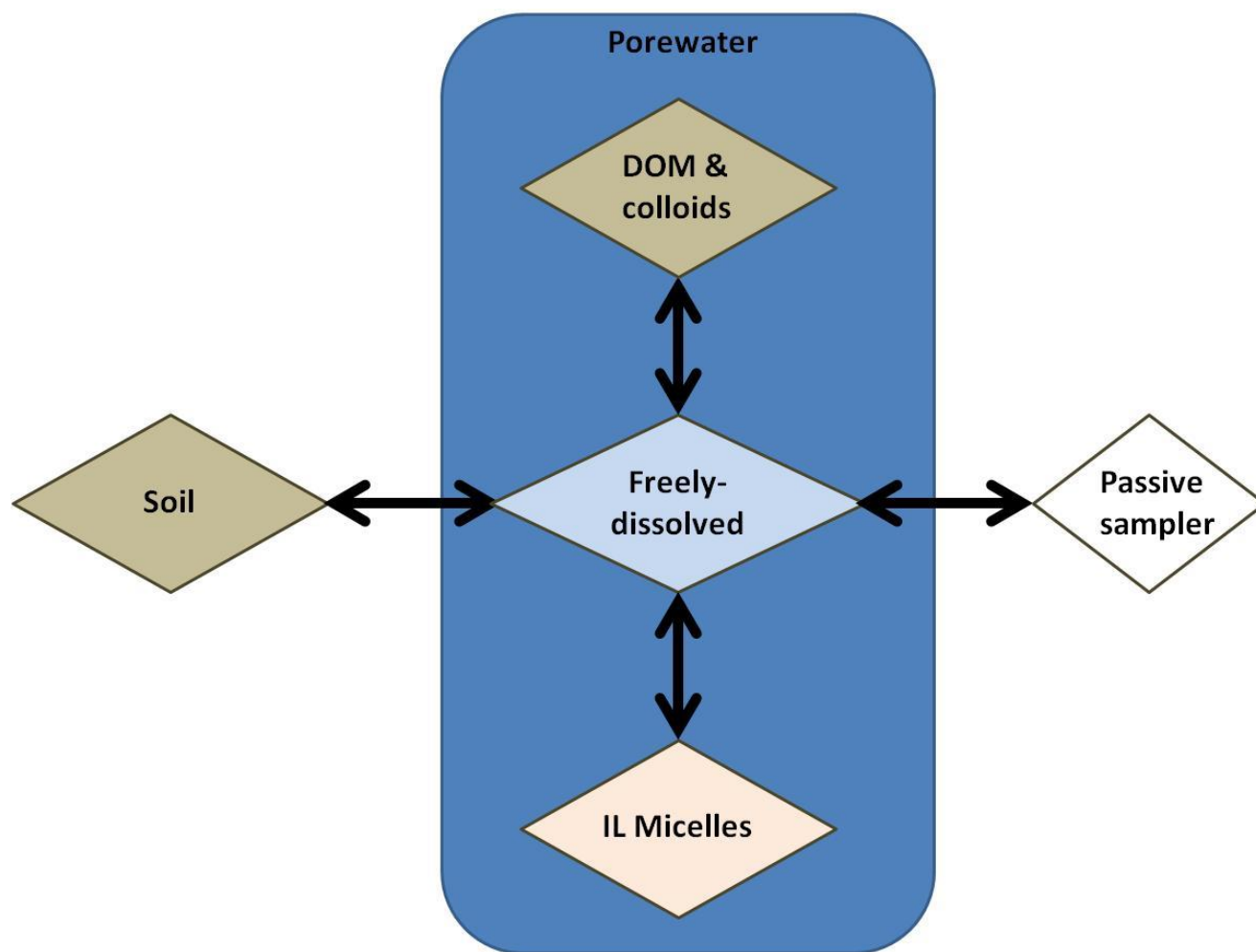69 hydrophobic compounds.[9, 12, 13]

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). $CaCl_2$

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} NaN_3 (to prevent microbial degradation) and 0.01M $CaCl_2$. All solutions were

8

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   *freely dissolved $C_{pw} = K_{POM} \cdot C_{POM}^{-1}$*   (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/MS[26] 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/MS[26] (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 μg 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 C_6-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

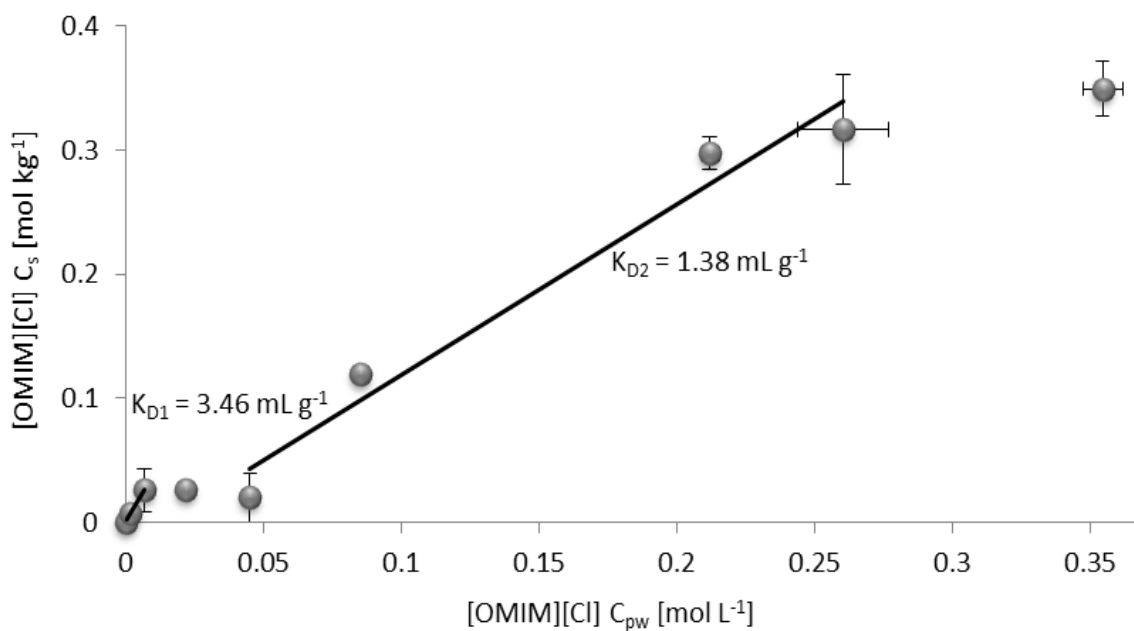205   two replicate measurements.

206

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

The chart shows the y-axis labeled [OMIM][Cl] C_s [mol kg^{-1}] ranging from 0 to 0.4, and the x-axis labeled [OMIM][Cl] C_{pw} [mol L^{-1}] ranging from 0 to 0.35. Two partition coefficients are marked: $K_{D1} = 3.46$ mL g^{-1} and $K_{D2} = 1.38$ mL g^{-1}.

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$^-$

226   ^{1}, and corresponds to the partitioning of IL between soil and solution (up to ~0.01 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~ 0.04 mM and 0.25mM).

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 10mM 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
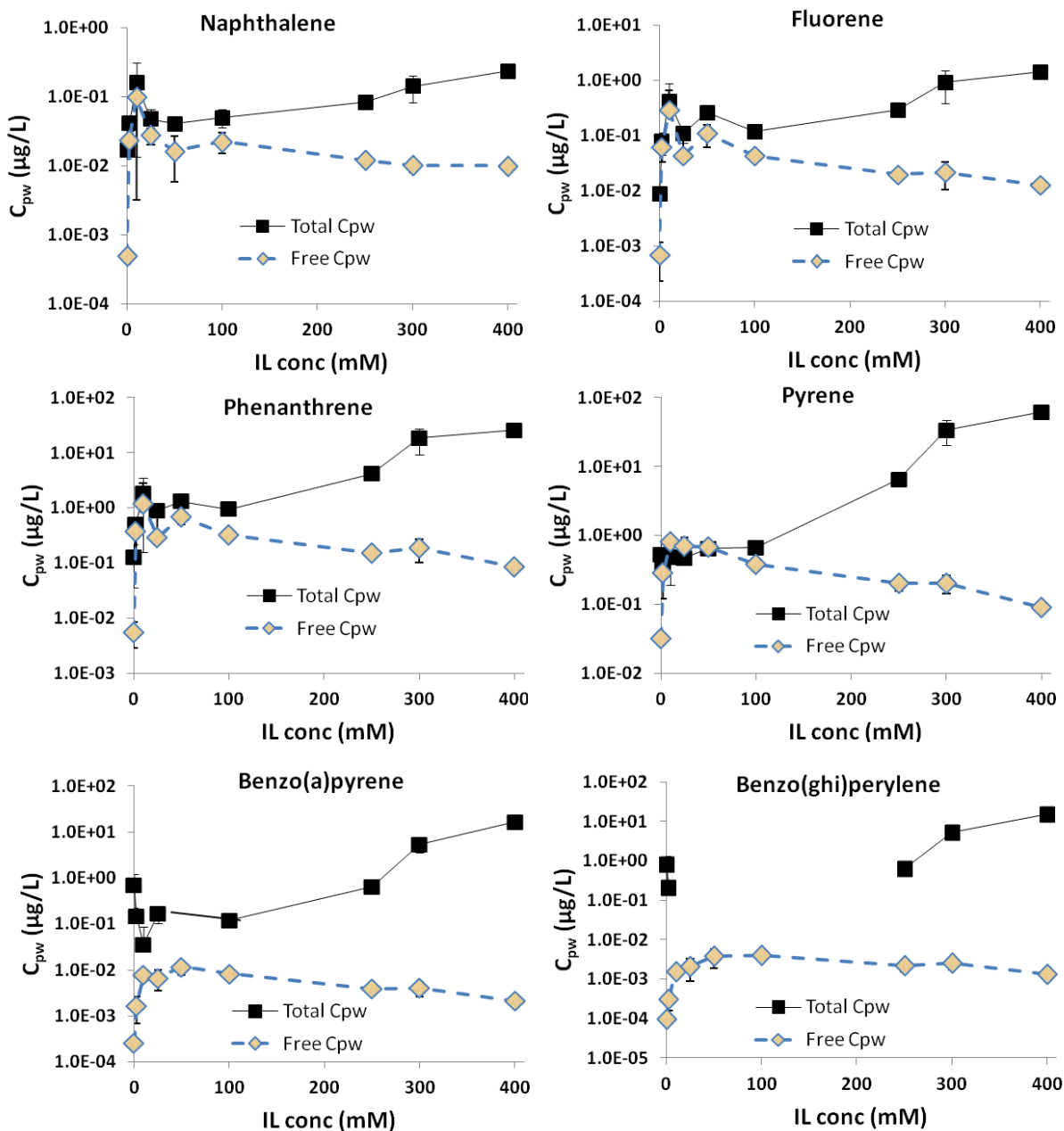
Figure 3. Amount of total and freely-dissolved C_{pw} of PAHs from a contaminated soil in the presence of various initial [OMIM][Cl] concentrations, showing results for two-ring (naphthalene, fluorene), three-ring (phenanthrene), four-ring (pyrene) and five-ring (benzo(a)pyrene) PAHs. Data are an average of two replicates, error bars are shown but generally are smaller than the label.

As evident in Figures 3 and Figures S3 - S5, the freely-dissolved C_{pw} of each PAH increases

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

16

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.

301
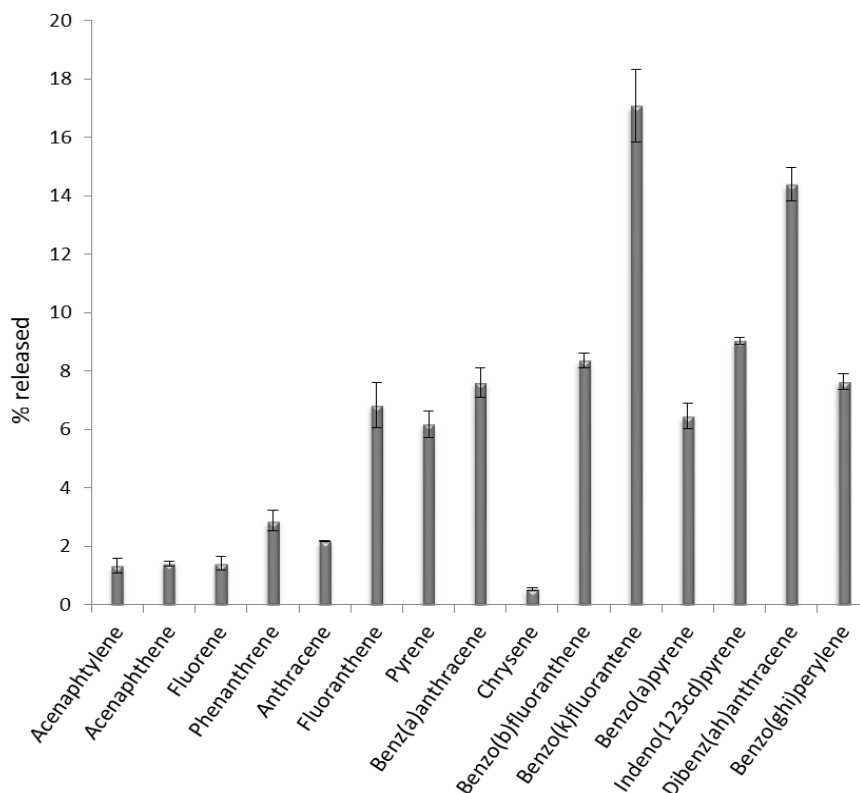
302

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.**

17

306

Release of DOM. Because the addition of [OMIM][Cl] results in an overall release of PAHs

from the soil, an increase in dissolved organic matter (DOM) can be expected as well. This was

observed for [OMIM][Cl] additions from 10 to 50 mM, which are far below the CMC (Figure 5).

310

311
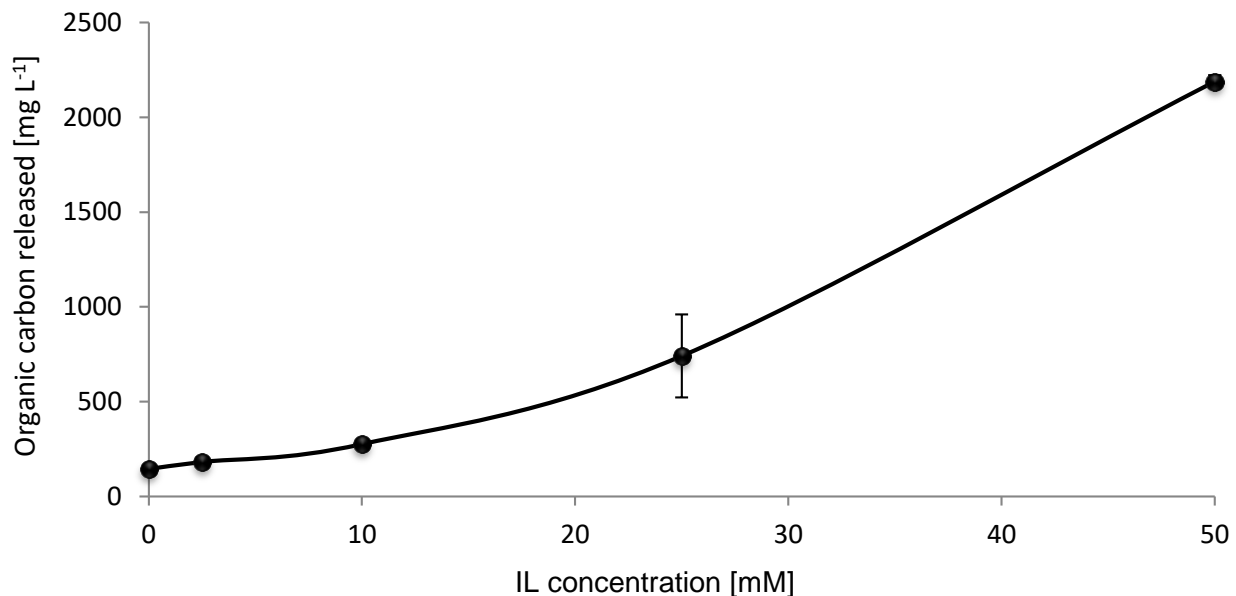
Figure 5. Exponential release of organic carbon from soils under the influence of [OMIM][Cl]. Initial IL concentrations are shown (average of two replicates, standard error is marked with bars but generally smaller than markers)

315

Visual examination of the test tube vials (Figure S6 in the SI as well as TOC art) also confirms

the increased release of DOM with IL concentrations below the CMC. When the IL content

approaches the CMC, the porewater solution becomes clear. This would indicate that at

concentrations just below the CMC the visible DOM precipitates out, likely due to a

neutralization of negative charges caused by adsorption of ILs. Colloidal systems are generally

stable when their zeta potential is smaller than -30mV or bigger than +30mV, outside of this

range repulsive forces between particles might be too weak and precipitation might occur.[34] We

have recently shown that adsorption of [OMIM][Cl] reverses the zeta potential of the minerals

18

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.

336

337

338
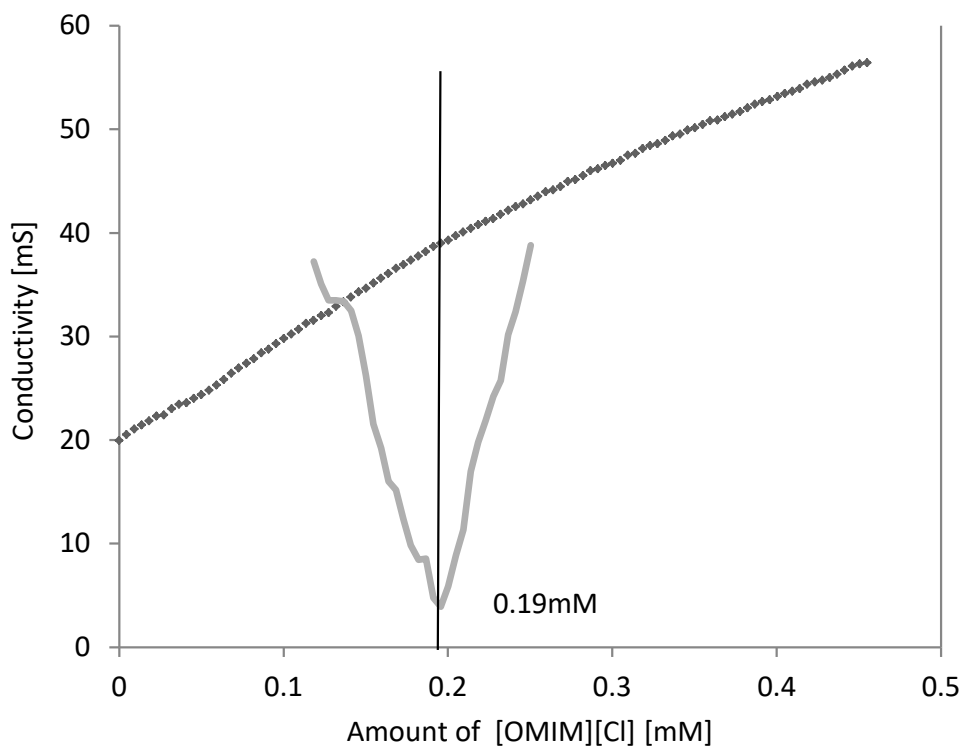
339 **Figure 6. Conductivity titration curves of humic acid titrated with 1 mM [OMIM][Cl]. The**
340 **dotted line represents the 2ⁿᵈ derivative.**

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 effects[14]). An illustration of the above interpretation is presented

349 in Figure 7.

20
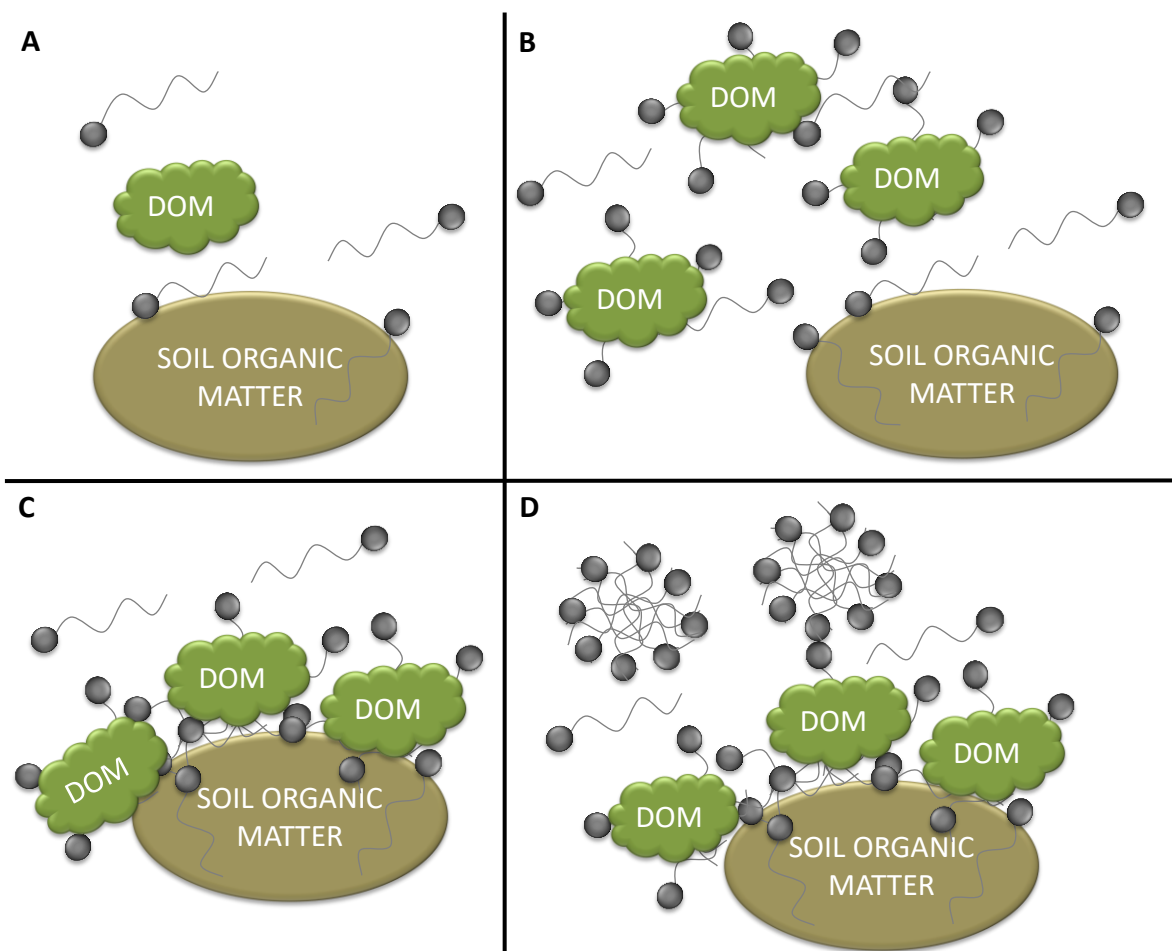
Figure 7. Schematic representation of ILs' interactions with soil particles and dissolved organic matter (DOM) in four stages: A) initial IL addition in which DOM and SOM repel each other and the IL cations sorbs to some negatively-charged surfaces; B) IL-DOM complex formation at slightly elevated IL concentrations, increasing overall DOM and increasing freely dissolved PAH concentration by dissolution; C) some IL-DOM precipitate due to charge neutralization, however colloidal particles remain so that the total PAH in porewater remains the same though freely-dissolved PAH/dissolution slightly decreases; D) the CMC is exceeded and micelles form in the porewater, total PAH concentration increases though freely-dissolved concentration/dissolution continues to decrease with increasing IL.

The steps in Figure 7 are as follows, and are meant to be compared with the trends in Figures 3, 5 and 6. Prior to addition of IL a certain amount of negatively charged DOM is present in the porewater, the negative charge causes the DOM aggregates and the soil to repel each other. The 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 solution[14] 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

22

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

406 **ACKNOWLEDGEMENTS**

REFERENCES

1.   Freemantle, M., *Introduction to Ionic Liquids*; RSC Publishing: 2009.

2.   Seddon, K. R., Ionic liquids: A taste of the future. *Nature Materials* **2003**, *2*, 363-365.

3.   Olivier-Bourbigou, H.; Favre, F., Ionic liquids in multiphasic reactions. In *Ionic liquids in synthesis*; Peter Wasserscheid, T. W., Ed. Wiley: 2008.

4.   Stolte, S.; Steudte, S.; Igartua, A.; Stepnowski, P., The Biodegradation of Ionic Liquids - the View from a Chemical Structure Perspective. *Curr. Org. Chem.* **2011**, *15*, (12), 1946-1973.

5.   Markiewicz, M.; Stolte, S.; Lustig, Z.; Łuczak, J.; Skup, M.; Hupka, J.; Jungnickel, C., Influence of microbial adaption and supplementation of nutrients on the biodegradation of ionic liquids in sewage sludge treatment processes. *J. Hazard. Mater.* **2011**, *195*, (15), 378-382.

6.   Markiewicz, M.; Jungnickel, C.; Markowska, A.; Szczepaniak, U.; Paszkiewicz, M.; Hupka, J., 1-Methyl-3-octylimidazolium Chloride—Sorption and Primary Biodegradation Analysis in Activated Sewage Sludge. *Molecules* **2009**, *14*, 4396-4405.

7.   Jungnickel, C.; Łuczak, J.; Ranke, J.; Fernández, J. F.; Müller, A.; Thöming, J., Micelle formation of imidazolium ionic liquids in aqueous solution. *Colloids Surf., A* **2008**, *316*, (1-3), 278-284.

8.   Łuczak, J.; Jungnickel, C.; Joskowska, M.; Thöming, J.; Hupka, J., Thermodynamics of micellization of imidazolium ionic liquids in an aqueous solution. *J. Colloid Interface Sci.* **2009**, *336*, 111-116.

9.   Haigh, S. D., A review of the interaction of surfactants with organic contaminants in soil. *Sci. Total Environ.* **1996**, *185*, 161-170.

10.   Atkin, R.; Craig, V. S. J.; Wanless, E. J.; Biggs, S., Mechanism of cationic surfactant adsorption at the solid–aqueous interface. *Adv. Colloid Interface Sci.* **2003**, *103*, 219-304.

11.   Pino, V.; Yao, C.; Anderson, J. L., Micellization and interfacial behavior of imidazolium-based ionic liquids in organic solvent–water mixtures. *J. Colloid Interface Sci.* **2009**, *333*, (2), 548–556.

12.   Laha, S.; Tansel, B.; Ussawarujikulchai, A., Surfactant-soil interactions during surfactant-amended remediation ofcontaminated soils by hydrophobic organic compounds: A review. *J. Environ. Manage.* **2009**, *90*, 95-100.

13.   Paria, S., Surfactant-enhanced remediation of organic contaminated soil and water. *Adv. Colloid Interface Sci.* **2008**, *138*, (1), 24-58.

14.   Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M., *Environmental Organic Chemistry*. 2 ed.; Wiley-Interscience: 2002.

15.   Arp, H. P. H.; Azzolina, N. A.; Cornelissen, G.; Hawthorne, S. B., Predicting Pore Water EPA-34 PAH Concentrations and Toxicity in Pyrogenic-Impacted Sediments Using Pyrene Content. *Environ. Sci. Technol.* **2011**, *45*, 5139-5146.

16.   Tan, K. H., Chapter 8: Cation exchange. In *Principles of soil chemistry*, 4th ed.; CRC Press: 2011; pp 205-224.

17.   Cornelissen, G.; Gustafsson, Ö.; Bucheli, T. D.; Jonker, M. T. O.; Koelmans, A. A.; vanNoort, P. C. M., Extensive Sorption of Organic Compounds to Black Carbon, Coal, and Kerogen in Sediments and Soils: Mechanisms and Consequences for Distribution, Bioaccumulation, and Biodegradation. *Environ. Sci. Technol.* **2005**, *39*, (18), 6881–6895.

18.   Moon, J.-W.; Mark N. Goltz; Kyu-Hong Ahn; Park, J.-W., Dissolved organic matter effects on the performance of a barrier to polycyclic aromatic hydrocarbon transport by groundwater. *J. Contam. Hydrol.* **2003**, *60*, 307- 326.

456   19.   Aboul-Kassim, T. A. T.; Simoneit, B. R. T., Interaction Mechanisms Between Organic
457 Pollutants and Solid Phase Systems. In *The Handbook of Environmental Chemistry.* Vol. 5E.;
458 Springer-Verlag: Berlin Heildelberg, 2001.
459   20.   Tan, K. H., Chapter 12: Chemistry of Soil - Organic Matter Interactions. In *Principles of*
460 *Soil Chemistry*; 2011; pp 293-309.
461   21.   Paria, S.; Khilar, K. C., A review on experimental studies of surfactant adsorption at the
462 hydrophilic solid–water interface. *Adv. Colloid Interface Sci.* **2004**, *110*, 75-95.
463   22.   Brändli, R. C.; Hartnik, T.; Henriksen, T.; Cornelissen, G., Sorption of native
464 polyaromatic hydrocarbons (PAH) to black carbon and amended activated carbon in soil.
465 *Chemosphere* **2008**, *73*, (11), 1805-1810.
466   23.   Jonker, M. T. O.; Koelmans, A. A., Polyoxymethylene Solid Phase Extraction as a
467 partitioning method for hydrophobic organic chemicals in sediment and soot. *Environmental*
468 *Science and Technology* **2001**, *35*, (18), 3742-3748.
469   24.   Hawthorne, S. B.; Miller, D. J.; Grabanski, C. B., Measuring Low Picogram Per Liter
470 Concentrations of Freely Dissolved Polychlorinated Biphenyls in Sediment Pore Water Using
471 Passive Sampling with Polyoxymethylene. *Anal. Chem.* **2009**, *81*, (22), 9472-9480.
472   25.   Hawthorne, S. B.; Jonker, M. T. O.; Heijden, S. A. v. d.; Grabanski, C. B.; Azzolina, N.
473 A.; Miller, D. J., Measuring Picogram per Liter Concentrations of Freely Dissolved Parent and
474 Alkyl PAHs (PAH-34), Using Passive Sampling with Polyoxymethylene. *Anal. Chem.* **2011**, *83*,
475 (17), 6754–6761.
476   26.   Arp, H. P. H.; Villers, F.; Lepland, A.; Kalaitzidis, S.; Christanis, K.; Oen, A. M. P.;
477 Breedveld, G. D.; Cornelissen, G., Influence of historical industrial epochs on pore water and
478 partitioning profiles of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in Oslo
479 Harbor, Norway, sediment cores. *Environ. Toxicol. Chem.* **2011**, *30*, (4).
480   27.   Nichthauser, J.; Mrozik, W.; Markowska, A.; Stepnowski, P., Analysis of residual ionic
481 liquids in environmental samples: Development of extraction methods. *Chemosphere* **2009**, *74*,
482 (4), 515–521.
483   28.   Jungnickel, C.; Mrozik, W.; Markiewicz, M.; Łuczak, J., Fate of Ionic Liquids in Soils
484 and Sediments. *Curr. Org. Chem.* **2011**, *15*, 1928-1945.
485   29.   Łuczak, J.; Markiewicz, M.; Thöming, J.; Hupka, J.; Jungnickel, C., Influence of the
486 Hofmeister anions on self-organization of 1-decyl-3-methylimidazolium chloride in aqueous
487 solutions. *J. Colloid Interface Sci.* **2011**, *362*, (2), 415-422.
488   30.   Prak, D. J. L.; Pritchard, P. H., Solubilization of polycyclic aromatic hydrocarbon
489 mixtures in micellar nonionic surfactant solutions. *Water Res.* **2002**, *36*, 3463-3472.
490   31.   Liu, J.-F.; Chi, Y.-G.; Peng, J.-F.; Jiang, G.-B.; Jonsson, J. A., Ionic Liquids/Water
491 Distribution Ratios of Some Polycyclic Aromatic Hydrocarbons. *J. Chem. Eng. Data* **2004**, *49*,
492 (5), 1422-1424.
493   32.   Tiehm, A.; Stieber, M.; Werner, P.; Frimmel, F. H., Surfactant-Enhanced Mobilization
494 and Biodegradation of Polycyclic Aromatic Hydrocarbons in Manufactured Gas Plant Soil.
495 *Environ. Sci. Technol.* **1997**, *31*, (9), 2570-2576.
496   33.   Deschenes, L.; Lafrance, P.; Villeneuve, J. P.; Samson, R., The effect of an anionic
497 surfactant on the mobilization and biodegradation of PAHs in a creosote-contaminated soil.
498 *Hydrological sciences journal* **1995**, *40*, (4), 471-484.
499   34.   Schramm, L. L., *Surfactants - Fundamentals and Application in Petroleum Industry*.
500 Cambridge University Press: 2000.

501   35.   Markiewicz, M.; Mrozik, W.; Rezwan, K.; Thöming, J.; Hupka, J.; Jungnickel, C.,
502   Changes in zeta potential of imidazolium ionic liquid modified minerals - implications for
503   determining the mechanism of adsorption. *Chemosphere* **2012,** *90*, (2), 706-712.

504

505