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

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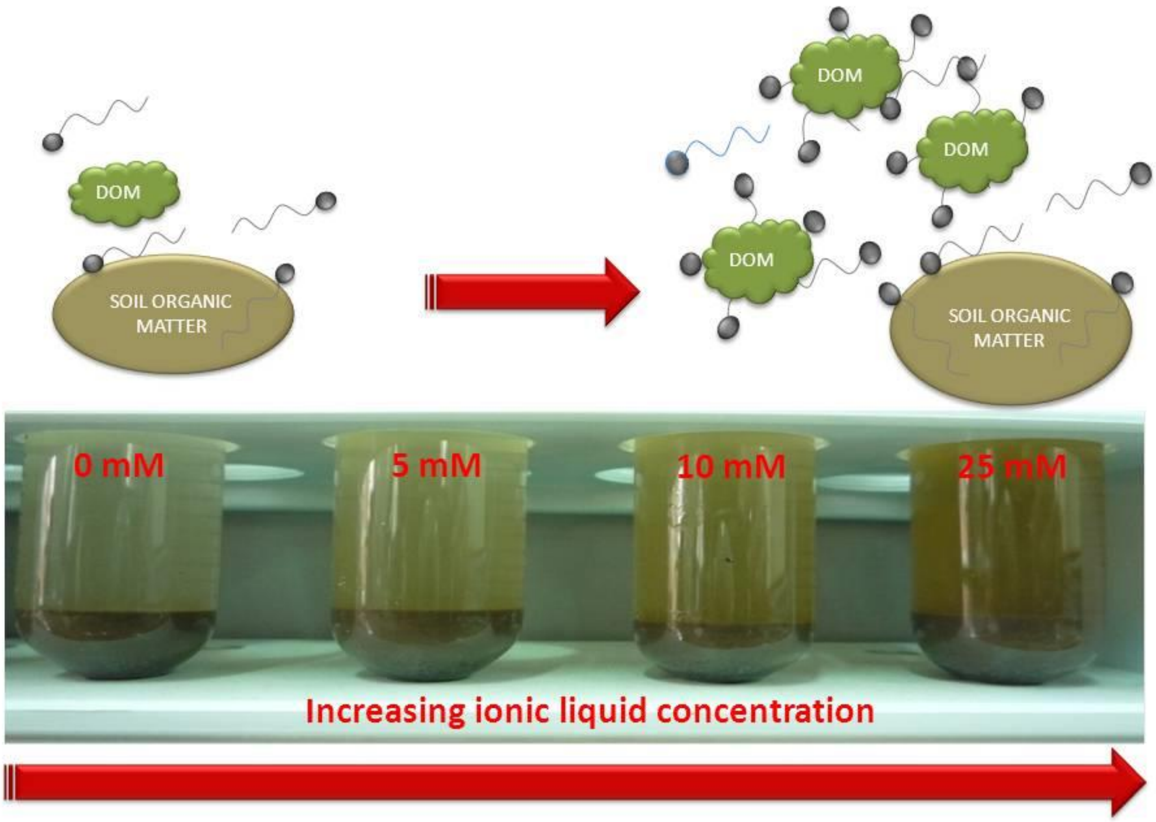

ABSTRACT

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

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

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

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

THEORETICAL BACKGROUND

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

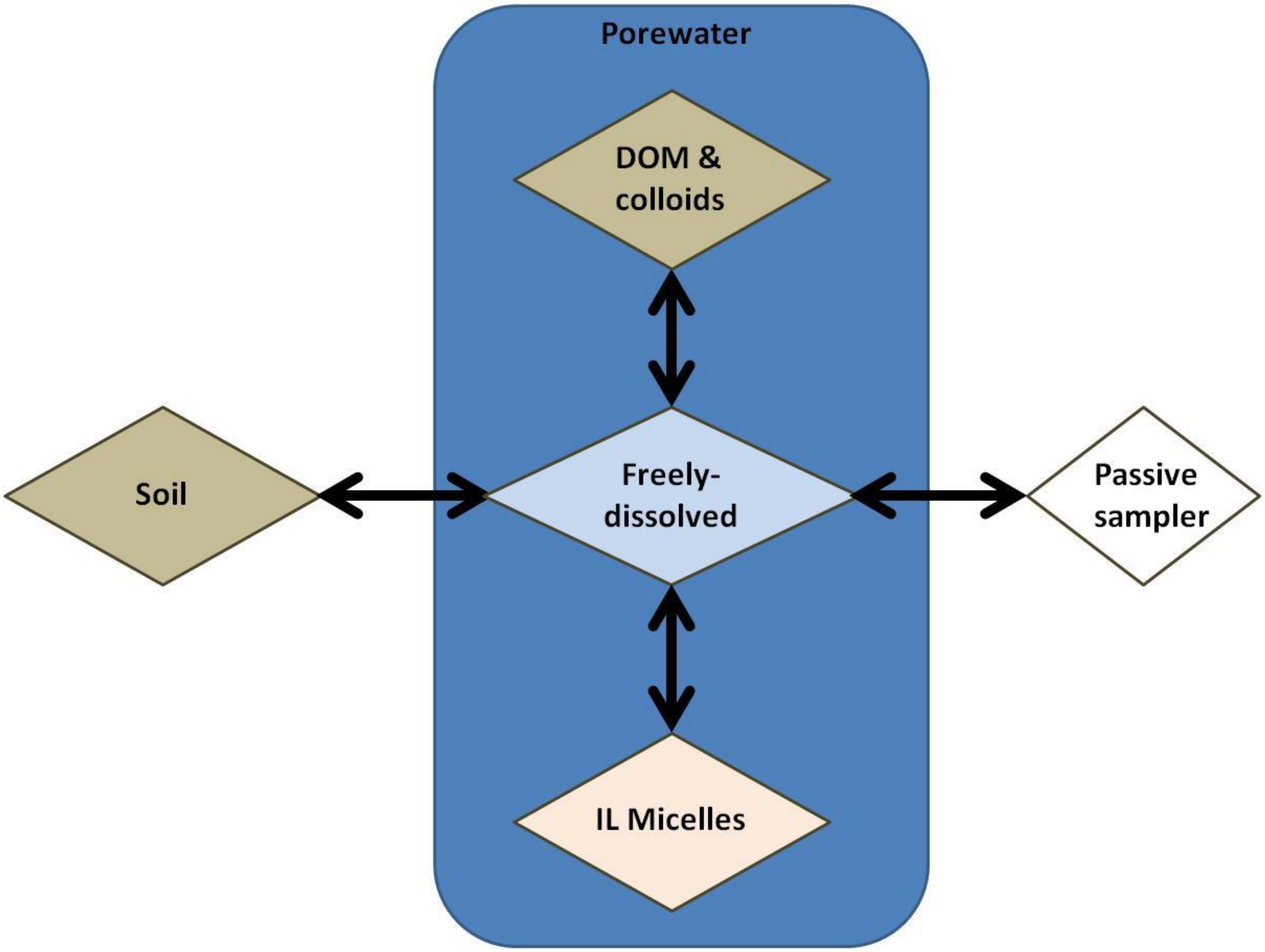

Figure 1. Partitioning processes for hydrophobic organic compounds (HOC) in a soil porewater system containing ionic liquid (IL) micelles. The potential phases for the HOC to exist are: soil sorbed, freely-dissolved (solvated by water), solubilized in an IL micelle, DOM-sorbed and colloid-sorbed. When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

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

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

DOM is considered anionic, like SOM. Negative charges present in both DOM and SOM cause mutual repulsion, resulting in a certain amount of suspended DOM in the porewater.[18-20] Any intervention into porewater H-bonding or surface charges can shift this fine balance and cause dissolution or precipitation of DOM. As explained above, increased dissolution of DOM can increase dissolution of HOCs. Conversely, adsorption of cationic surfactants can precipitate DOM and this in turn could cause simultaneous precipitation of HOCs.[9, 12, 18, 21]

MATERIALS AND METHODOLOGY

Chemicals. [OMIM][Cl] was obtained from Merck KGa (Darmstadt, Germany). $CaCl_2$ anhydride was obtained from POCh Gliwice, Poland. Acetone and hexane used for extraction and a mixture of deuterated PAH (including d8-naphthalene, d10-phenanthrene, d10-pyrene, d12-benz(a)anthracene, d12-benzo(a)pyrene, d12-benzo(ghi)perylene) used as an extraction efficiency standard were obtained from VWR International AS, Oslo, Norway. For preparation of the HPLC mobile phase, HPLC–grade acetonitrile from Lab-Scan (Dublin, Ireland) and spectrophotometric-grade trifluoroacetic acid (Sigma-Aldrich, Germany) were used.

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

Dissolution-Solubilization Experiment. 2 g (dry weight) of PAH contaminated soil were weighed into each test vial. Then, 20 mL of [OMIM][Cl] solution in concentrations of 0mM, 2.5 mM, 10 mM, 25 mM, 50 mM, 100 mM, 250 mM, 300 mM, or 400 mM were added, together with 200 mgL^{-1} NaN_3 (to prevent microbial degradation) and 0.01M $CaCl_2$. All solutions were prepared in duplicate, and the freely-dissolved total porewater concentrations (Figure 1) were determined separately as described below.

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

$$\textit{freely dissolved } C_{pw} = K_{POM} \cdot C_{POM}^{-1} \qquad (1)$$

The POM C_{pw} extraction method used was adapted from Hawthorne et al.,[25] though here a 55-µm POM strip was used instead of a 76-µm strip, also a different solvent extraction step and different quantities of soil and POM were used (see below). The detection limits for this method range from 1 ng/L for naphthalene to 1 pg / L for the 5,6-ring PAHs.[25] In brief, POM strips were precleaned by shaking end-over-end for one day with heptane, one day with methanol, and five days in Millipore water while changing the water periodically. To each vial, 0.1 g of pre-cleaned POM was added. Samples were sealed, placed in dark container to prevent photolysis, and shaken end-over-end at 8-10 rpm for 30 days, which is sufficient time for equilibration.[25] Then, POM was removed, the sample vials centrifuged and remaining aqueous phase isolated for the total C_{pw} extractions (see below). Visible particles on the POM surface were removed with a tissue and gentle rinsing with deionized water. The POM was then placed in a new vial, and a 20 mL mixture of 80:20 hexane:acetone spiked with deuterated PAHs was added, the later to serve as an extraction efficiency internal standard. The vials containing POM were then shaken end-over-end in the dark for another 5 days, the hexane:acetone was collected and was quantified using GC/MS[26] to determine C_{POM} (see the SI for the GC/MS method description). Freely-dissolved C_{pw} was obtained by use of equation 1 and available K_{POM} values.[25]

Total C_{pw}. The isolated aqueous phase obtained after POM removal was divided into two fractions: 1 mL was used to measure the IL concentration by HPLC/UV analysis, and the remainder was extracted to obtain the total C_{pw} of PAHs. For the latter, the aqueous phase was extracted with three portions of 20 mL of hexane. Surrogate standards of deuterated PAHs were added to the solvent. Solvent extracts were combined and then dried by adding sodium sulphate, and quantified using GC/MS[26] (see the SI).

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

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

Ionic Liquid Analysis. The amount of IL adsorbed by soil was calculated as the difference between the initial concentration and concentration measured in the aqueous phase at the end of experiment. The degradation of IL was assumed to be negligible since concentrations of [OMIM][Cl] used here were too high to be biodegraded (unless the local microbial community is adapted, which is unlikely), additionally a sterilizing agent was used (sodium azide).[5, 6] A Perkin Elmer Series 200 HPLC consisting of a chromatographic interface (Link 600) binary pump, UV/VIS detector, vacuum degasser and Rheodyne injection valve was used. For IL cation separation a C_6-Phenyl (Phenomenex) 150×4.6 mm column was used in conjunction with detection by UV adsorption at a wavelength of 218 nm. The sample injection volume was 10 µL and the mobile phase applied was 27% acetonitrile/water + 0.1% (v/v) trifluoroacetic acid at a flow rate of 0.8 mL min^{-1}.[27]

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

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

RESULTS AND DISCUSSIONS

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

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

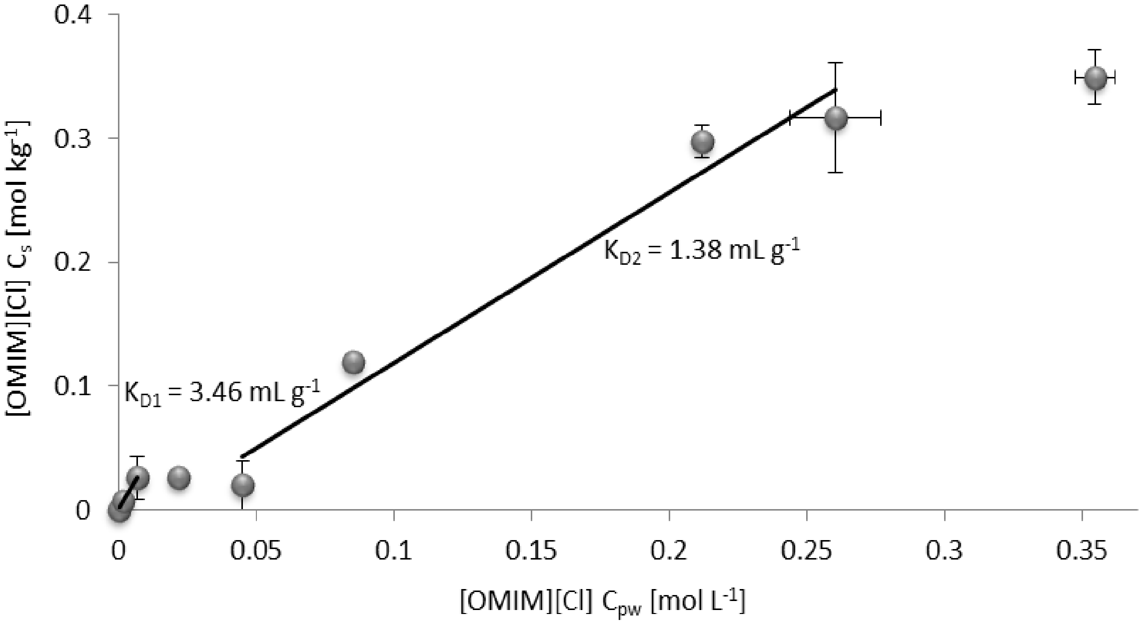

Figure 2. Sorption isotherm of [OMIM][Cl] to the sampled contaminated landfill soil (each point is an average of two replicates, standard errors of both C_s and C_{pw} values are marked with an error bar). The isotherm shows two plateau regions (between 0.01 - 0.05 M, and 0.25 - 0.04 M); K_{D1} and K_{D2}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

The isotherm shows two ascending regions and two plateau regions, which is characteristic for surface active agents that modify the properties of surface on which they adsorb.[28] From the ascending regions, two soil/porewater partition coefficients were calculated as slopes of linear, ascending parts of the isotherm. It should be noted beforehand that the delineation and accuracy of K_D values (ascending regions) and plateau regions are biased based on the concentrations interval at which the isotherms were measured. The first K_D, K_{D1}, was extrapolated as 3.46 mL g^{-1}, and corresponds to the partitioning of IL between soil and solution (up to ~0.01 mM), whereas the second, K_{D2}, extrapolated as 1.38 mL g^{-1}, and describes the sorption of the second layer of IL onto soil modified by the adsorption of the previous layer (between~ 0.04 mM and 0.25mM). The first K_D is slightly larger than the second. The general justification for this is that the first K_D accounts for both electrostatic and London dispersion interactions, and the second K_D only accounts for the London dispersion interactions between already adsorbed IL molecules and IL molecules forming the second layer.

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

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

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

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

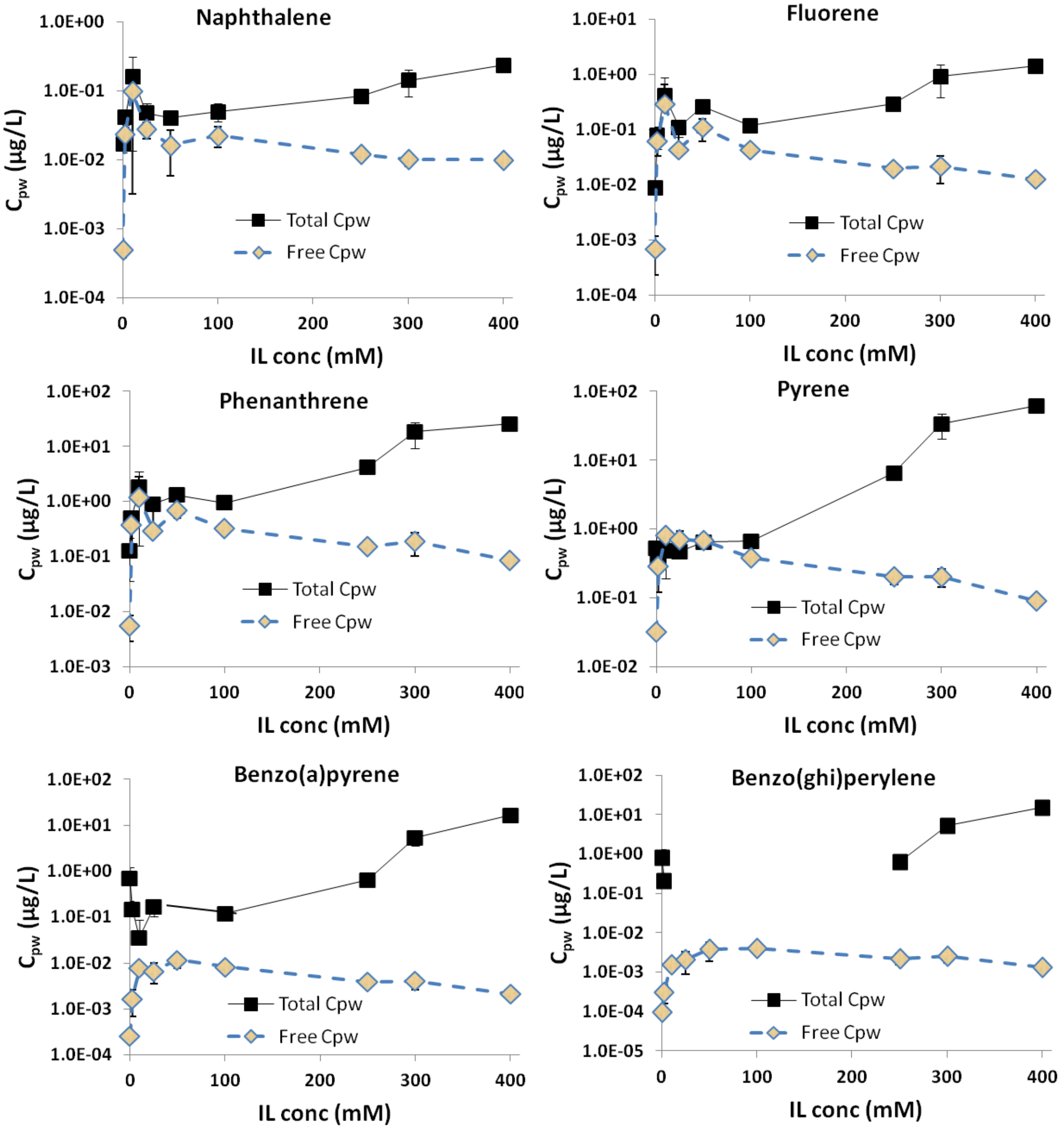

Figure 3. Amount of total and freely-dissolved C_{pw} of PAHs from a contaminated soil in the presence of various initial [OMIM][Cl] concentrations, showing results for two-ring (naphthalene, fluorene), three-ring (phenanthrene), four-ring (pyrene) and five-ring (benzo(a)pyrene) PAHs. Data are an average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

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

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

The average percentage of PAHs released into the porewater in the presence of 400 mM IL based on previously determined soil concentrations (Table S1) is presented in Figure 4. Note that naphthalene in soil was not measured (due to high solvent blanks) and these percentages assume that changes in total PAH concentration from analysis in 2007 to experiments here in 2010 were negligible, thus may be underestimating the amount removed. The efficiency of release above the CMC was substantially higher for the 4-6 ring PAHs. This is in agreement with previously discussed findings by Liu *et al.*[31]. We propose that because smaller PAHs are more prone to dissolution (e.g. as seen in Figure 3), they could have been preferentially depleted in the environment, compared to the larger PAHs, before the soil was collected for analysis. This would cause the relative proportion of smaller PAHs remaining to be less prone to solubilization than the larger PAHs. Such trends have also been observed for PAH contaminated sediments.[15] Of the larger PAHs, chrysene was depleted noticeably the least. The reasons for this are unclear and may be unique to the present system; studies looking at removal of PAHs by use of surfactants do not find such outlying behavior for chrysene.[32,33] How effective ILs (or surfactants) are at removing PAHs will likely depend on the history of pollution.

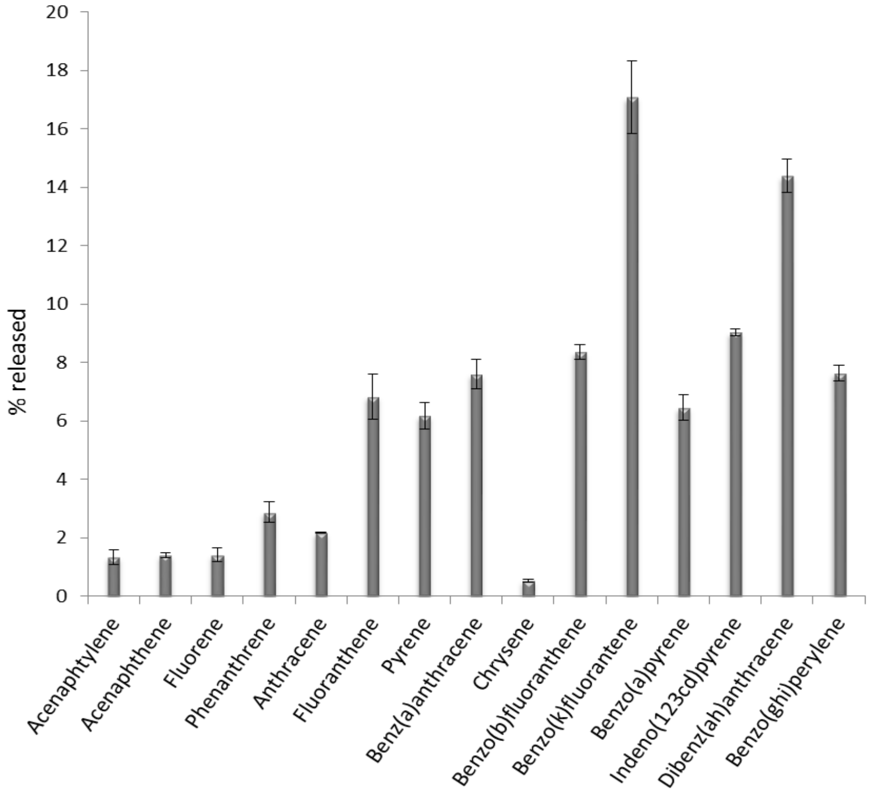

Figure 4. Percentage release of various PAHs from a contaminated landfill soil upon addition of 400 mM [OMIM][Cl]. Data are an average of two replicates, with error bars shown.

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).

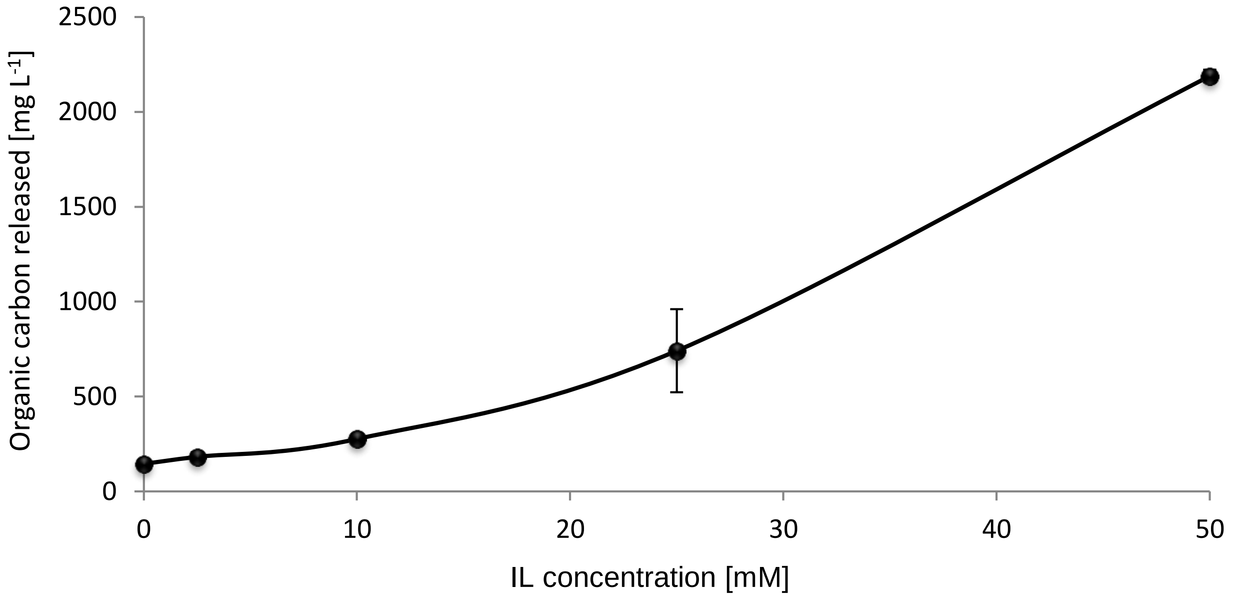

Figure 5. Exponential release of organic carbon from soils under the influence of [OMIM][Cl]. Initial IL concentrations are shown (average of two replicates, standard error is marked with bars but generally smaller than markers)

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

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

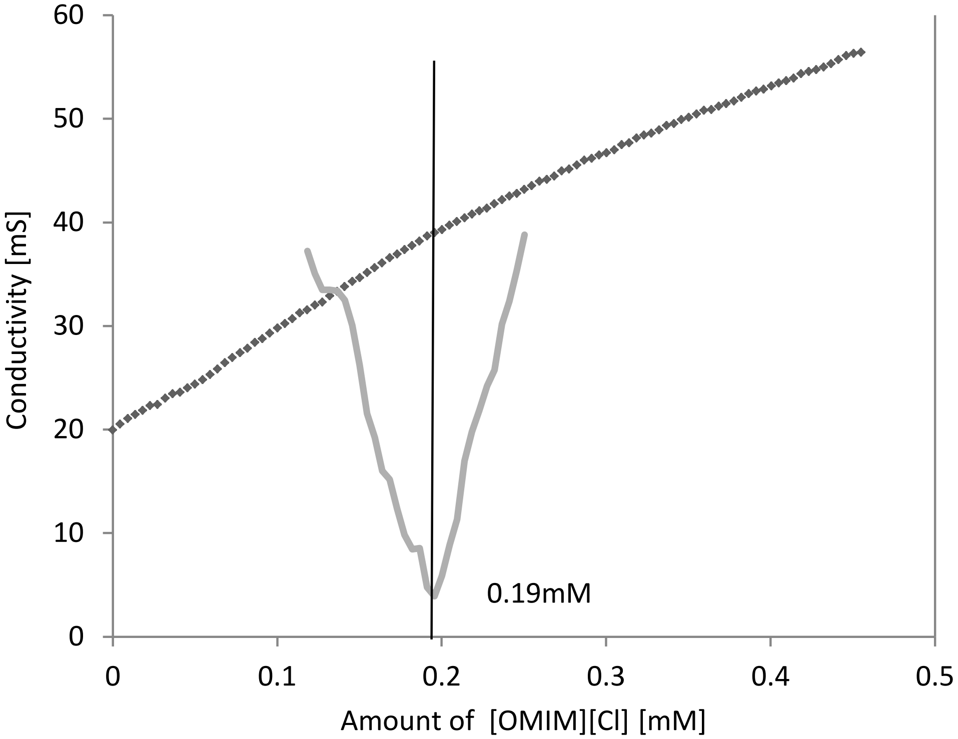

Figure 6. Conductivity titration curves of humic acid titrated with 1 mM [OMIM][Cl]. The dotted line represents the 2^nd^ derivative.

Proposed Mechanism. Based on the observations of both freely-dissolved PAHs and DOM increasing in the porewater with initial IL additions well below the CMC, there appears to be a dissolution-type mechanism at play. One possibility is the formation of soluble complexes of IL and soil components to form IL-DOM complexes, which can release PAHs by either changing/breaking-up the (surface) structure of the SOM in a way that lowers affinity to soil, or alternatively by decreasing H-bonding in the aqueous porewater mixture to facilitate dissolution (e.g. by cosolvency or salting in effects[14]). An illustration of the above interpretation is presented in Figure 7.

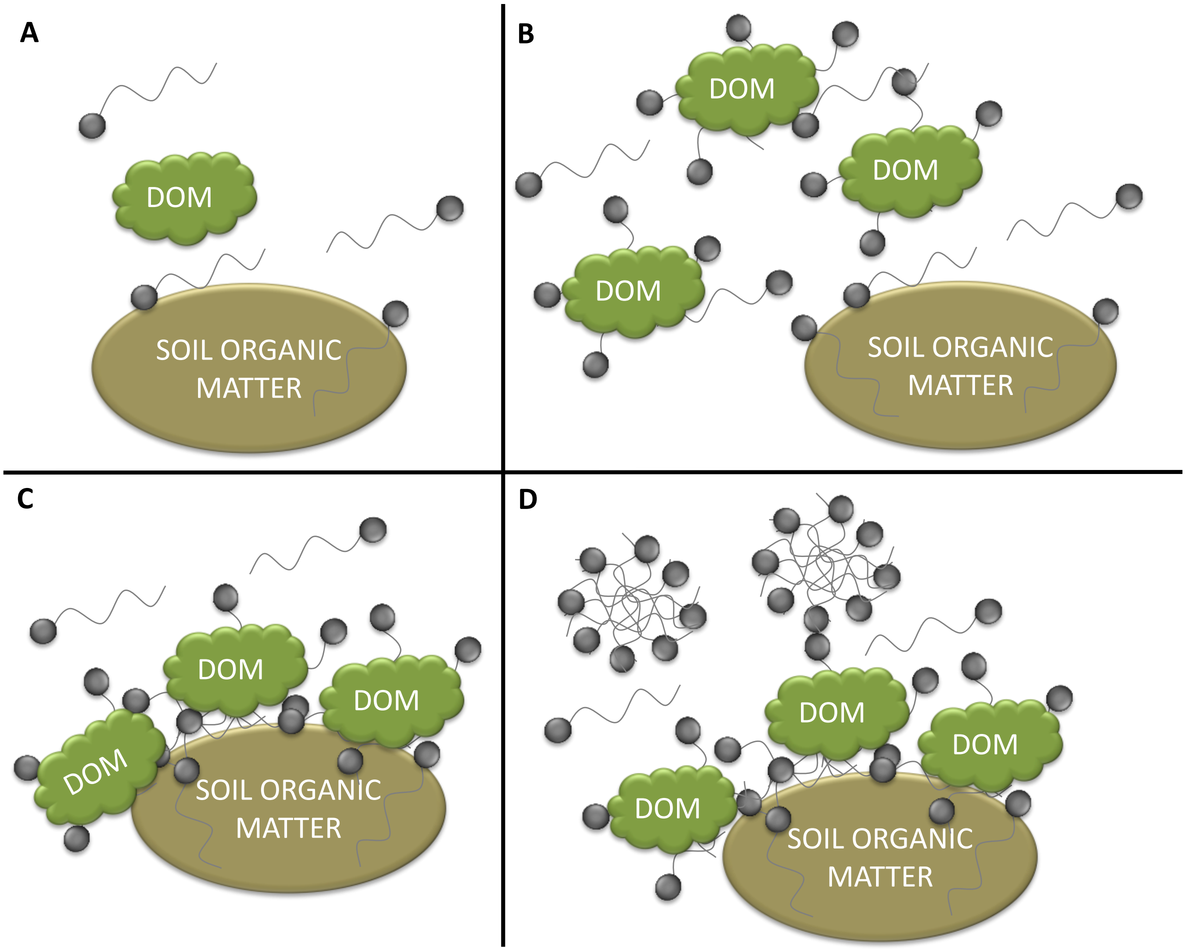

Figure 7. Schematic representation of ILs' interactions with soil particles and dissolved organic matter (DOM) in four stages: A) initial IL addition in which DOM and SOM repel each other and the IL cations sorbs to some negatively-charged surfaces; B) IL-DOM complex formation at slightly elevated IL 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).

The first stage of extra PAH and DOM dissolution occurs as presented in Figure 7B, in which the introduction of more IL causes additional DOM to be released into the solution, and the formation of IL-DOM complexes. The presence of increased amount of IL-DOM complexes leads to or coincides with increased freely-dissolved PAH dissolution, likely by lowering H-bonding in the water solution[14] or possibly by breaking up the soil and changing its properties to sorb less effectively. Recall that the presence of the IL at low concentrations does not account for this on its own (Figure S2). In Figure 7B, two to three ring PAHs are mainly present in the porewater in freely-dissolved state, whereas 5-6 ring PAHs are mainly associated with other porewater phases (colloids, DOM, IL-DOM complexes) (Figure 3). As the concentration of IL increases, different species peak in concentration (Figure 6): first the freely-dissolved 2-4 ring PAHs, then the 5-ring PAHs, followed by the 6-ring PAHs and the IL-DOM complexes. The decrease in IL-DOM and DOM concentration is due to charge reversal (Figure 7C). The presence of a peak in freely-dissolved PAH concentrations is likely due to a trade-off between increased solubility in the porewater followed by increased sorption to suspended colloids (though this sorption is weaker than to the native soil before adding IL). Meanwhile, the total porewater concentration of PAHs does not change during the phase depicted at Figure 7C. . Then at the CMC (Figure 7D), IL micelles substantially increase the solubilization of PAHs and therefore the total C_{pw} of all ring sizes increases with increasing IL concentration, though dissolution and therefore freely-dissolved C_{pw} decreases as more PAHs are present in micelles.

Because the increase in freely-dissolved concentrations is similar for all PAH ring sizes (Figures 3, S3-S5), it cannot be accounted for by molecular volume or related factors (e.g. K_{ow}), which is typically observed when adding completely miscible organic solvents to water (Figure 5.8 of Schwarzenbach et al. [14]), or if the soil were to become less “hydrophobic”. Changes in solubility not substantially related to the molecular volume could be indicative of a salting-in type phenomena (e.g. PAH independent salting constant in Table 5.7 of Schwarzenbach et al. [14]), a polar interaction between the IL-DOM porewater and PAHs that is only weakly dependant on PAH size (e.g. interactions of the pi electrons on the PAHs with electron accepting functionalities in the IL-DOM-porewater matrix), or proportional changes regarding volume-dependant interactions in the soil or water that are opposite to each other (e.g. a change in cavity formation energy in the porewater or soil being approximately proportional and opposite to a change in van der Waals interactions in the porewater or soil).

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

SUPPORTING INFORMATION

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

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