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Journal of Soils and Sediments

ISSN 1439-0108

Volume 13

Number 2

J Soils Sediments (2013) 13:450-459

DOI 10.1007/s11368-012-0631-9



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Application of ionic liquids for the extraction and passive sampling of endocrine-disrupting chemicals from sediments

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Received: 20 March 2012 / Accepted: 20 November 2012 / Published online: 5 December 2012
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Abstract

Purpose The aim of this study was to assess the applicability of ionic liquids (ILs) in the extraction of organic contaminants from sediments and in passive sampling as a receiving phase material.

Materials and methods Solutions of two water-soluble ionic liquids (WSILs)—1-butyl-3-methyl imidazolium tetrafluoroborate ([BMIm]BF₄) and *N*-butyl-3-methyl pyridinium tetrafluoroborate ([BMPy]BF₄)—were used for the extraction of endocrine-disrupting chemicals (EDCs), including bisphenol A (BPA), 17 β -estradiol (E2), and nonylphenol (NP), from different sediments. Furthermore, a hydrophobic IL (1-hexadecyl-3-methyl imidazolium hexafluorophosphate) was filled in a polyethylene (PE) membrane tubing to build an IL-PE passive sampler for sediment pore water. Uptake kinetics were studied by exposing samplers to sediments artificially contaminated by EDCs and identified by exposing samplers to field-contaminated sediments.

Results and discussion EDCs were efficiently extracted by WSIL solutions from the two artificially contaminated

sediments, with maximum extraction efficiencies of 84.2–104.6 % by the [BMIm]BF₄ solution and 74.9–103.7 % by the [BMPy]BF₄ solution. However, WSIL solutions are not suitable for EDC extraction from sediment with very low organic carbon contents. EDCs in sediment pore water can be efficiently taken up by the IL-PE sampler, with uptake rate constants of $2.08 \times 10^{-2} \text{ l g}^{-1} \text{ day}^{-1}$ (BPA), $5.74 \times 10^{-2} \text{ l g}^{-1} \text{ day}^{-1}$ (E2), and $2.10 \text{ l g}^{-1} \text{ day}^{-1}$ (NP).

Conclusion BPA, E2, and NP can be extracted efficiently by IL water solution from most of the artificially and field-contaminated sediments used in this study. The IL ([HDMIm]PF₆)-PE passive sampler can be used to monitor EDCs in the pore water of sediments. A good match between the calculated and measured concentrations of BPA and E2 in pore water of field-contaminated sediments was observed.

Keywords Endocrine-disrupting chemicals · Extraction · Ionic liquid · Passive sampling · Sediment pore water

Responsible editor: Jay Gan

Electronic supplementary material The online version of this article (doi:10.1007/s11368-012-0631-9) contains supplementary material, which is available to authorized users.

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1 Introduction

Endocrine-disrupting chemicals (EDCs) have already become a threat to the global ecosystem and human health (Diamanti-Kandarakis et al. 2009; Weiss 2011). To monitor EDCs in soil or sediment environments, different methods—such as liquid extraction (Temes et al. 2002), microwave-assisted extraction (Hibberd et al. 2009), and Soxhlet extraction (Peng et al. 2006)—have been applied in the past few decades. Volatile organic solvents were used as the extractants in several of these methods, and most of these solvents exhibit high toxicity and pose risks to ecosystems and human health. Ionic liquids (ILs) are a relatively new class of solvents that are generally considered less toxic and provide a potential alternative to traditional volatile solvents. ILs consist of organic cations and organic or inorganic anions and have a strong ability to dissolve a large variety of organic and inorganic substances

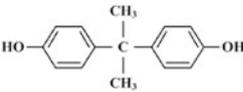
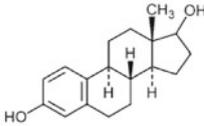
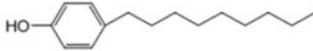
(Earle and Seddon 2000; Fan et al. 2008). By changing the anion/cation or adjusting their substituent group, ILs with different properties can be obtained to meet the different requirements of various applications, including extracting or separating organic contaminants (OCs) from different matrices (Khodadoust et al. 2006; Fan et al. 2008; Pino et al. 2008; Mallah et al. 2009; Deng et al. 2011). For example, hydrophobic 1-butyl-3-methyl imidazolium hexafluorophosphate ([BMIm]PF₆) and hydrophilic 1-butyl-3-methyl imidazolium-chloride ([BMIm]Cl) were reported to have similar capabilities in OC extraction from glacial till soil, but [BMIm]PF₆ was more suitable for the extraction of pesticides from montmorillonite (Khodadoust et al. 2006). Furthermore, ILs are also used as the media of liquid phase microextraction and solid phase microextraction (Liu et al. 2003, 2005; Cruz-Vera et al. 2008; Berton and Wuilloud 2010; Lopez-Darias et al. 2010).

In addition to traditional “active” sampling protocols, passive sampling techniques have been commonly used for in situ monitoring of contaminants in the atmosphere, water, sediment, and soil environments (Seethapathy et al. 2007; Tao et al. 2008; Vermeirssen et al. 2009; Bao and Zeng 2011; Walgraeve et al. 2011). For example, semi-permeable membrane devices (SPMDs), a representative technique developed by Huckins et al. (1993), have been widely used in the past two decades (Seethapathy et al. 2007). A standard SPMD was constructed from a low-density polyethylene (LDPE) tubing filled with a thin film of triolein. However, other solvents, e.g., isooctane (Leonard et al. 2002), 1-dodecanol (Hyne and Aistrop 2008), and dimethyl sulfoxide (Rogers et al. 2005), have also been used as the receiving phase materials of SPMD or SPMD-like passive samplers. Passive sampling of EDCs in aquatic environments has been reported extensively in the literature. For example, SPMD (Stuer-Lauridsen and Kjølholt 2000; Harman et al. 2008; Grabic et al. 2010), polar organic chemical integrative samplers (Arditsoglou and

Voutsas 2008; Harman et al. 2008; Zhang et al. 2008; Liscio et al. 2009; Grabic et al. 2010), and Chemcatcher (Tan et al. 2007; Vermeirssen et al. 2009; Kuster et al. 2010) were used to sample EDCs in a number of laboratory and field studies. Ionic liquids were also used as the receiving phase materials in passive sampling of organic or inorganic chemicals from aquatic environments (Zhao et al. 2006; Martínez et al. 2011). However, there were no obvious advantages of IL ([BMIm]PF₆) in sampling polyaromatic hydrocarbons (PAHs) from water environments when compared to triolein-SPMD (Zhao et al. 2006). This suggests that ILs might not be suitable for passive sampling of non-polar OCs.

Bisphenol A (BPA), 17 β -estradiol (E2), and nonyl-phenol (NP) are typical EDCs that are widely present in aquatic environments, including overlying water and sediments (Huang et al. 2007; Duong et al. 2010; Cao et al. 2010). Due to the difference in molecular structures, the chemical properties (e.g. K_{ow} , water solubility, pK_a) of the three analytes are significantly different, as shown in Table 1. In this study, BPA, E2, and NP were used as the target analytes. Two water-soluble ILs (WSILs)—1-butyl-3-methyl imidazolium tetrafluoroborate ([BMIm]BF₄) and *N*-butyl-3-methyl pyridinium tetrafluoroborate ([BMPy]BF₄)—were selected to represent imidazolium-based and pyridinium-based ILs. We evaluated the extraction efficiencies of BPA, E2, and NP from three different sediments by WSIL water solution at different IL concentrations. Furthermore, a long-alkyl-chain hydrophobic IL (1-hexadecyl-3-methyl imidazolium hexafluorophosphate, [HDMIm]PF₆) was used as the receiving phase material to build an IL-PE passive sampler. Then, the application of this passive sampler was assessed via sampling target EDCs from pore waters of artificially contaminated and field-contaminated sediments.

Table 1 Some properties of the target analytes

Analyte	MW	WS	pK_a	$\log K_{ow}$	MS	Structure
BPA	228.1	120	9.28	3.3	width X: 0.94 width Y: 0.53 width Z: 0.43	
E2	272.3	3.85	10.23	3.67	N/A	
NP	220.4	1.66	10.25	4.5	width X: 1.7 width Y: 0.7 width Z: 0.3	

Sources of pK_a , $\log K_{ow}$, and molecular size are shown in ESM Table S2

MW molecular weight, *WS* water solubility (in milligrams per liter), *MS* molecular size (in nanometers), *N/A* not available

2 Materials and methods

2.1 Materials and sediments

Three ionic liquids—[BMIm]BF₄, [BMPy]BF₄, and [HDMIm]PF₆—were used in experiments of extraction and passive sampling; their structures are shown in Fig. 1. [BMIm]BF₄ and [HDMIm]PF₆ were provided by the Center for Green Chemistry and Catalysis of the Lanzhou Institute of Chemical Physics, Chinese Academy of Science (CAS). [BMPy]BF₄ was purchased from Alfa Aesar, Inc. (Tianjin, China). Standards of BPA and E2 were purchased from J&K Scientific, Ltd. (Beijing, China), while NP (technical grade) was purchased from Tokyo Chemical Synthesis Ind. Co., Ltd (Tokyo, Japan).

For the extraction experiments, three sediments with different properties were selected as model matrices (Table 2). These sediments were collected from different areas of China, namely, the Yellow River (YR sediment), the Yuqiao Reservoir (YQR sediment), and the Liaohe River (LR sediment). In addition, two types of sediments were collected from Dagu Drainage Canal (DDC), one of the largest sewage canals in Tianjin, China, which were selected to represent the field-contaminated sediments.

In the laboratory exposure passive sampling experiments, YQR sediments spiked with BPA, E2, and NP at 10 ng g⁻¹ (dry weight) for each compound were used as the artificially contaminated sediments. In addition, four field-contaminated

sediments collected from different sites of DDC were also used to perform the passive sampling experiments.

2.2 Extraction experiments

Batch sorption experiments were conducted before the extraction experiments to obtain the sediment matrix which was artificially contaminated by different EDC analytes. For each analyte, 50 μl of analyte/acetonitrile solution and 9 ml of deionized water were mixed and added into a 10-ml glass centrifuge tube with 1.0 g of sediment. The tubes were sealed and oscillated by a shaker at 150 rpm and 25±1 °C for 48 h. Preliminary kinetic studies showed that this period was sufficient for EDCs to reach steady-state adsorption conditions. A 48-h blank control (without solids) showed that the loss of EDCs via adsorption to glassware was <2 % for BPA and E2 and <5 % for NP during this process. Then, the sediments were separated from aqueous solution by centrifugation at 4,800 rpm for 20 min, and the supernatants were measured for the target EDCs by high-performance liquid chromatography coupled with a fluorescence detector (HPLC-FL). Sorbed concentrations of target EDCs on the sediment were calculated by mass differences of EDCs in solution. By accounting for the amount of EDC applied, sediments contaminated by a single EDC (BPA, E2, or NP) at a concentration of ~1,000 ng g⁻¹ were obtained.

After the pre-sorption experiment, 5 ml of water solutions containing [BMIm]BF₄ or [BMPy]BF₄ at different concentrations (0, 0.53, 1.06, 1.81, and 2.66 mol l⁻¹) was added to the tube containing artificially contaminated sediments. The tubes were sealed and shaken at 150 rpm and 25±1 °C for 30 min. Centrifugation (4,800 rpm, 5 min) was conducted and the supernatant was collected and analyzed directly by HPLC. The extraction efficiencies of EDCs from the three artificially contaminated sediments by 1.06 mol l⁻¹ [BMIm]BF₄ solution at different initial pH conditions (pH 3, 5, 7, 8, 10) were also determined. The initial pH of [BMIm]BF₄ solution was adjusted using NaOH and HCl solutions.

The extraction of EDCs from two field-contaminated DDC sediments was also conducted by adding 5 ml of the selected IL solution to 2.0 g of the sediment sample. The results were compared to those of Soxhlet extraction by dichloromethane (described in detail in the [Electronic supplementary material \(ESM\)](#)). All extraction experiments were performed in duplicate.

2.3 Passive sampling experiments

2.3.1 Design of a passive sampler and pretreatment method for EDCs in IL phase of the passive sampler

Imidazolium-based IL was used as a receiving phase material to build a passive sampler in this study due to its higher

Fig. 1 Structures of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF₄; molecular formula, C₈H₁₅BF₄N₂, molecular weight, 226; CAS no. 174501-65-6) (a); *N*-butyl-3-methylpyridinium tetrafluoroborate ([BMPy]BF₄; molecular formula, C₁₀H₁₆BF₄N; molecular weight, 237; CAS no. 597581-48-1) (b); and 1-hexadecyl-3-methylimidazolium hexafluorophosphate ([HDMIm]PF₆; molecular formula, C₂₀H₃₉F₆N₂P; molecular weight, 453; CAS no. 219947-95-2) (c)

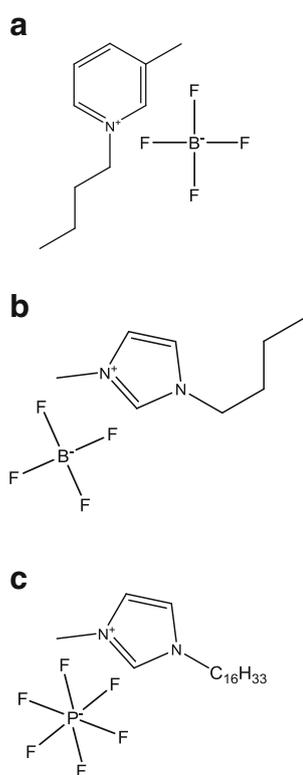


Table 2 Properties of sediments used in the extraction study

Sediments	f_{oc} (%) ^a	Sand (%)	Silt (%)	Clay (%)	CEC ^b (cmolkg ⁻¹)	pH
YR sediment	0.27	82.62	9.80	7.58	56.52	7.03
YQR sediment	2.56	38.32	50.38	11.30	267.30	7.13
LR sediment	5.89	36.65	55.92	7.43	320.14	6.75

YR Yellow River sediment, YQR Yuqiao Reservoir sediment, LR Liaohe River sediment

^b f_{oc} was determined using the Walkley–Black method (Walkley and Black 1934, in references of the ESM)

^cCEC was determined by the ammonium acetate method (ISS 1978, in references of the ESM)

affinity for EDC analytes than pyridinium-based IL, as observed in previous extraction experiments. However, a non-negligible loss of ILs (<30 %) during the sampling experiments was found when using a PE membrane milled with [BMIm]BF₄ or [BMIm]PF₆ as the receiving phase of the passive sampler. This might be due to the hydrophilicity and relatively small size of these two IL molecules. Therefore, [HDMIm]PF₆, a long-alkyl-chain hydrophobic IL, contained in LDPE tubing (Environmental Sampling Technologies Inc., Missouri, USA) was used as the receiving phase of the IL-PE passive sampler. PE tubing was filled with 100 mg of [HDMIm]PF₆; the tubing was heat-sealed and fixed into a polymethyl methacrylate frame with screws (ESM Fig. S1). The active sampling area was 12 cm² (60 × 20 mm) for each passive sampler.

After exposure, the passive samplers were taken out from the sediments and the membrane surface was cleaned with wet cotton wool. Then, the tubing was cut and [HDMIm]PF₆ was transferred to a glass tube with 2 ml of acetonitrile. The IL acetonitrile solution was then concentrated to 1 ml under a gentle N₂ flow before direct analysis by HPLC-FL. The loss of [HDMIm]PF₆ during the exposure period was determined to be <10 % by comparing the [HDMIm]PF₆ amount before and after the experiments, as determined by HPLC-UV.

2.3.2 Uptake kinetics experiment

To obtain the artificially contaminated sediments used in this experiment, acetonitrile solution containing three EDCs was added slowly to the YQR sediment at a ratio of 5 ml per 100 g sediment (dry weight) under constant stirring. The sediments were further stirred for another 30 min and then air-dried in a fume hood for 2 h. In the EDC uptake kinetics experiment, 600-ml glass beakers were used as the exposure systems, each containing 300 g of EDCs spiked YQR sediments (10 ngg⁻¹, dry weight) and 200 ml of deionized water. The beakers were sealed with PE film and wrapped with aluminium foil to minimize volatilization and photodegradation. Preliminary experiments indicated that equilibrium can be reached in 48 h for both spiked

and field-contaminated EDCs. Therefore, two passive samplers were inserted vertically into sediments of each beaker after the system was equilibrated in a shaker for 48 h (25 °C, 20 rpm). The beakers were placed on the shaker and shaken at 20 rpm under 25 °C. At different intervals (1, 2, 3, 5, and 7 days), one beaker with a pair of passive samplers was taken out and the samplers were treated using the method mentioned in Section 2.3.1.

Pore water concentrations of target EDCs (BPA, E2, NP) were also determined. Sediment pore water was collected by centrifugation at 6,000 rpm for 20 min and then an aliquot of 100 ml water sample was transferred and concentrated by solid phase extraction (SPE; see ESM).

Quantification of dissolved OC concentration (C_w) through the SPMD method can be modeled by considering a diffusion process between the contaminated water and the passive sampler (Huckins et al. 1993; Vrana et al. 2005).

$$C_s(t) = C_w \frac{k_u}{k_e} (1 - e^{-k_e t}) \quad (1)$$

where $C_s(t)$ is the analyte concentration in the sampler at exposure time t and k_u and k_e are the uptake and elimination rate constants, respectively.

In the linear uptake stage, it is assumed that the rate of desorption of the analyte from the receiving phase to water is negligible ($\lim(e^{-k_e t} + k_e t)(k_e t \rightarrow 0) = 1$). Accordingly, $1 - e^{-k_e t}$ in Eq. 1 can be approximated as $k_e t$, and the rate of change of C_s is given as follows (Vrana et al. 2005):

$$dC_s/dt \approx k_u C_w \quad (2)$$

2.3.3 Laboratory exposure experiment using field-contaminated sediments

The applicability of IL-PE passive samplers was assessed in a laboratory exposure experiment using field-contaminated sediments collected from different reaches of DDC. Sediments were freeze-dried and stored at -20 °C before use. Organic carbon contents (f_{oc}) and the EDC concentrations of sediments were measured and are listed in ESM

Table S1. The exposure experiment was conducted using the methods described in Section 2.3.2. Two passive samplers were placed in each beaker. After 7 days of exposure, the samplers were taken out and the EDC concentrations in the IL phase were analyzed. Furthermore, EDCs in pore water were detected by HPLC analysis after SPE.

2.4 Analysis

EDC analysis was conducted using a Waters 1525 HPLC combined with Waters 2475 FL detector and 2487 UV detector (Waters Company, USA). A Waters C₁₈ column (with μ Bondapak 3.9-mm i.d. \times 300 mm \times 10 μ m; Waters Company) was used for separation. An isocratic elution was carried out at a flow rate of 0.8 ml min⁻¹ with acetonitrile and water (70:30, v/v) used as mobile phases. BPA and NP were quantified by the FL detector at the excitation/emission wavelengths of 233/302 nm. For the analysis of E2, the excitation/emission wavelengths of 280/310 nm were used. [HDMIm]PF₆ was detected using a UV detector at 215 nm. The chromatograms of the EDC analytes and [HDMIm]PF₆ are shown in ESM Fig. S3.

2.5 Quality assurance and quality control

Potential contamination of sediment samples by target compounds during extraction was evaluated by running solvent blanks and procedure blanks without the matrix using 2.66 mol l⁻¹ WSIL water solution. No analytes were detected in either solvent blanks or procedure blanks. An aliquot of the same sediment sample, equilibrated in deionized water for 48 h without EDCs added, was also used to assess the backgrounds of YR, YQR, and LR sediments. The backgrounds of target EDCs in sediments extracted by 2.66 mol l⁻¹ WSIL solution were negligible compared with the spiked amounts of EDCs. Solvent blanks of [HDMIm]PF₆ (dissolved in acetonitrile) also indicated no EDC background. Recoveries of spiked EDCs in [HDMIm]PF₆ were 94 % (for BPA), 98 % (for E2), and 95 % (for NP).

The detection limits for BPA, E2, and NP in sediments were 0.50, 0.80, and 1.00 ng g⁻¹, which were calculated based on the lowest acceptable calibration standard, the extractant volume of 5 ml, and the sediment sample weight of 1.0 g. Duplicate analyses were conducted for each sample, and the average responses were calculated. A calibration check standard and a continuing acetonitrile blank were run after every five samples to check the drift of instrument sensitivity and the carryover of analysis between adjacent samples. Instrument calibration was carried out by injection of ten calibration standards, with the regression coefficients (*R*) of all calibration curves higher than 0.99.

3 Results and discussion

3.1 Extraction of EDCs by [BMIm]BF₄ or [BMPy]BF₄ solution

In the extraction experiments using deionized water as the extractant, 24–55 % of sorbed BPA and 22–50 % of sorbed E2 were desorbed into the aqueous phase (Fig. 2). Higher extraction efficiencies of BPA and E2 from the YR sediment (~50 %) indicated a low affinity of sediment surface to EDC analytes, which is due to the low *f*_{oc} (0.27 %) of this matrix (see Table 2). Dissolved NP was not detected in all deionized water–sediment systems, which was attributed to the high hydrophobicity (log*K*_{ow}=4.5) and low water solubility (1.66 mg l⁻¹) of this analyte (see Table 1).

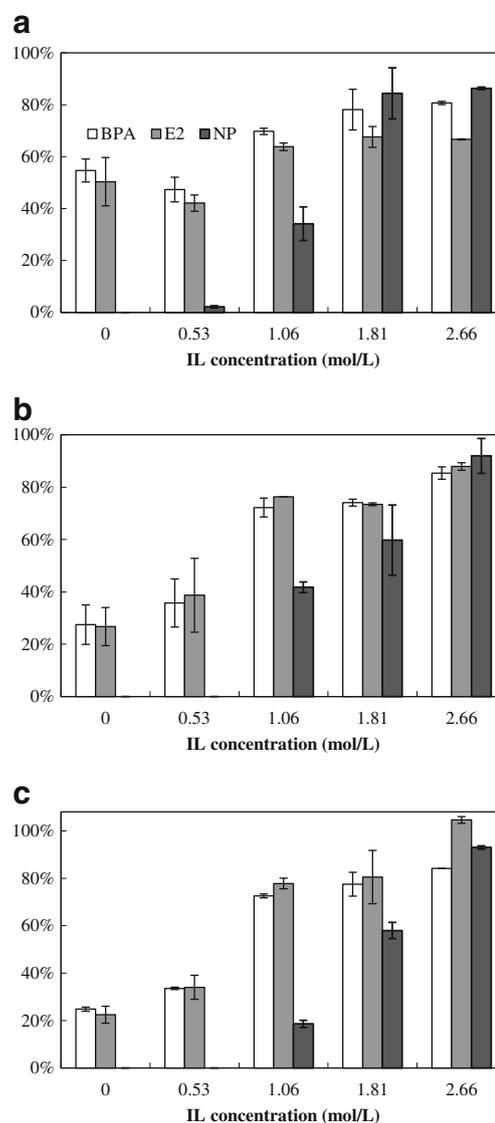


Fig. 2 Extraction efficiencies of EDCs by [BMIm]BF₄ water solution from the YR sediment (a), YQR sediment (b), and LR sediment (c)

In most cases, there was only a slight increase of extraction efficiency for BPA and E2 extraction when 0.53 mol l^{-1} [BMIm]BF₄ or [BMPy]BF₄ water solution was used as the extractant. For example, the extraction efficiencies of BPA from the YQR and LR sediments were only 25.5–35.8 % (Figs. 2 and 3b, c). A relatively high extraction efficiency (68.4 %) only occurred in the case of E2 extraction from the YQR sediment (by 0.53 mol l^{-1} [BMPy]BF₄ solution). For BPA and E2 in the YR sediment, the extraction efficiencies even slightly decreased when low-concentration WSIL solutions were used as the extractants. The limited increase or even inhibition of extraction by [BMIm]BF₄ at a low concentration might be due to the sorption of IL to mineral surfaces (Gorman-Lewis and Fein 2004; Stepnowski et al. 2007) and the organic matter (Zhang et al. 2011) of sediments.

The extraction efficiencies of EDCs from sediments increased significantly when higher concentrations of [BMIm]

BF₄ or [BMPy]BF₄ solutions, i.e., 1.06, 1.81, and 2.66 mol l^{-1} , were used as the extractants. For the YQR and LR sediments, the maximum extraction efficiencies by 2.66 mol l^{-1} [BMIm]BF₄ solutions were 84.2–85.4 % (BPA), 87.9–104.6 % (E2), and 92.0–93.0 % (NP; see Fig. 2), while those by 2.66 mol l^{-1} [BMPy]BF₄ solutions were 84.1–94.8 % (BPA), 84.3–103.7 % (E2), and 74.9–85.0 % (NP; see Fig. 3). It seems that both [BMIm]BF₄ and [BMPy]BF₄ solutions are suitable for EDC extraction from these sediments. Exceptions were observed for EDC extraction by [BMPy]BF₄ solutions from the YR sediment, which has a high sand content and very low f_{oc} . In these cases, the extraction efficiencies of BPA and E2 decreased when the [BMPy]BF₄ concentration increased from 1.81 to 2.66 mol l^{-1} (see Fig. 3a).

Different interactions can occur between the IL and the analyte molecule. Khodadoust et al. (2006) indicated that the H-bond interaction between sorbed OCs and IL anion (PF₆⁻ and Cl⁻) contributed to the extraction of hydrophobic OCs from soils. The C–H of the imidazolium unity can also interact with the benzene ring via CH– π hydrogen bonds when using imidazolium IL to extract aromatic compounds (Cassol et al. 2007). In addition, π – π interaction of imidazolium/pyridinium-based IL cation and aromatic group has also been discussed in previous studies (Stepnowski et al. 2006; Cheong et al. 2011). Furthermore, electrostatic forces could be another important interaction between [BMIm]BF₄ and EDCs because the ionizability of phenolic hydroxyl and alcoholic hydroxyl groups in EDCs enables their interaction between the cationic charge of imidazolium. Cation– π interaction (Holbrey et al. 2003) and micellar effects (Pino et al. 2008) may also explain the affinity between ILs and target extractants. However, cation– π interaction can be greatly reduced due to space steric hindrance when the alkyl group is bound to the “N” atom of the heterocyclic structure (Tsuzuki et al. 2007). Meanwhile, it is difficult for ILs with short alkyl chains ($C \leq 8$), such as the [BMIm]BF₄ used in this experiment, to form micelles in solution (Blesic et al. 2007).

Compared with [BMPy]BF₄, the extraction capability of the [BMIm]BF₄ solution was higher in most cases. This might be due to the higher affinity of imidazolium-based IL to EDCs because (1) the electron cloud density of the five-member imidazolium ring is higher than that of the six-member pyridinium ring, which is favorable for “ π – π ” interaction between the heterocyclic ring of IL and the aromatic ring of EDCs; (2) strong hydrogen bond interaction exists between the “–N=C(H)–N–” structure of imidazolium-based IL and the aromatic or hydroxyl group of target analytes; and (3) “cation– π ” interaction between the imidazolium cation and the aromatic ring of EDC occurs easier than that between the pyridinium cation and EDCs due to the two “N” cation centers of the imidazolium structure.

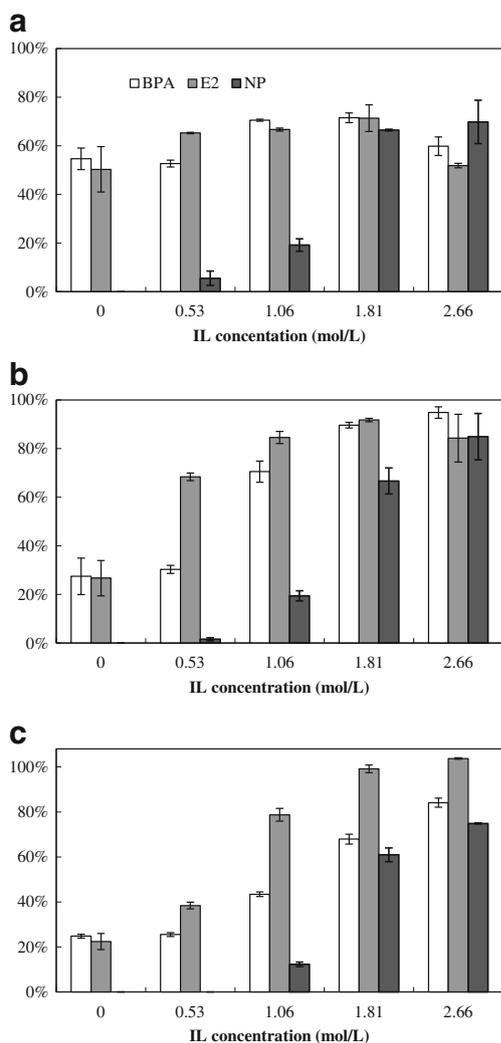


Fig. 3 Extraction efficiencies of EDCs by [BMPy]BF₄ water solution from the YR sediments (a), YQR sediments (b), and LR sediments (c)

3.2 Effects of sediment properties and pH of extractants on the extraction efficiency

The affinity of sediment surfaces for EDC or IL can also affect the extraction efficiency. When using low-concentration IL solution as the extractant, a slight increase of the extraction efficiencies of BPA and E2 can be observed for the YQR and LR sediments. However, for sediments with low f_{oc} , e.g., the YR sediment, the existence of [BMIm]BF₄ induced a decrease of the extraction efficiencies of BPA and E2 (see Fig. 2a), and the existence of [BMPy]BF₄ at a low concentration also reduced the BPA extraction efficiency. This inhibition can be explained by the adsorption of IL to sediment surfaces because the mineral surface of the YR sediment is more favorable for the sorption of the IL molecule compared to the surface covered by organic matter (Stepnowski et al. 2007). At higher IL concentrations ($>0.5 \text{ mol l}^{-1}$), it is favorable to extract EDCs from high- f_{oc} sediments than from low- f_{oc} YR sediments. This indicates that organic pollutants dissolved in the OC phase of sediments are easily extracted by IL water solutions. Lower extraction efficiencies of EDCs from YR sediment suggest that parts of the sorbed EDCs adsorb to sediment surfaces through a strong interaction and are difficult to be extracted by IL water solutions. The cation exchange capacity (CEC) of the sediments was in the order YR < YQR < LR, which is in accordance with the order of f_{oc} (see Table 2). Since the sorption of non-polar or weakly polar compounds mainly depends on their partition to soil/sediment organic matter, the effects of CEC on EDC sorption/desorption is hypothesized to be limited in this study. However, the interaction of ILs and sediment organic matter might affect the extraction of EDCs. Imidazolium-based ILs have been reported to associate strongly with dissolved organic matter (Zhang et al. 2011). At a low IL concentration, this interaction might inhibit or delay the extraction because of the increase of IL sorption to the sediment phase. With an increase of IL concentration, parts of sediment organic matter can transfer to the extractants and thus increase the extraction efficiencies (see Figs. 2 and 3).

The effects of pH on liquid–liquid extraction of phenols by IL have been reported before (e.g., Fan et al. 2008). In general,

the affinity of phenol analytes and IL decreases with an increase of pH. However, little is known about the effects of pH on the extraction efficiency of contaminants from soil or sediment by WSIL solution. The extraction efficiencies of EDCs from the YR, YQR, and LR sediments by 1.06 mol l^{-1} [BMIm]BF₄ solution at different pH ranges from 3–10 are shown in ESM Fig. S2. Generally, the extraction efficiencies decreased with an increase of pH for BPA and E2. For example, the extraction efficiency of E2 from the LR sediment decreased significantly from 82 % (pH 3) to 43 % (pH 10). However, the lowest extraction efficiency of NP was found at neutral pH. This might be due to the dissolution of sediment organic matter under alkaline conditions. The effects of pH on the extraction efficiency in this study was not as significant as that on the distribution of phenol compounds between water and the IL phase (Fan et al. 2008) and could be due to the pH buffering capacity of the sediments.

3.3 Extraction of EDCs from field-contaminated sediments

Two field-contaminated DDC sediments were selected and extracted by 2.66 mol l^{-1} [BMIm]BF₄ water solution. The results were compared with those using Soxhlet extraction (Table 3). In the DDC2 sediment collected at the upper reach of the channel, the calculated EDC concentrations were 0.39 ng g^{-1} (for BPA) and 1.10 ng g^{-1} (for E2) based on [BMIm]BF₄ water solution extraction, which were very close to those by Soxhlet extraction, i.e., 0.35 ng g^{-1} (for BPA) and 1.19 ng g^{-1} (for E2). For the DDC4 sediment, with greater pollution collected from the lower reach, all of BPA, E2, and NP were detected by both the IL ([BMIm]BF₄) water solution extraction and the Soxhlet extraction, with concentrations of 57.23 ng g^{-1} (BPA), 2.85 ng g^{-1} (E2), and 0.63 ng g^{-1} (NP) by IL water solution extraction and 59.59 ng g^{-1} (BPA), 3.15 ng g^{-1} (E2), and 0.88 ng g^{-1} (NP) by Soxhlet extraction.

3.4 Uptake kinetics of EDCs in IL-PE passive samplers from pore water of artificially contaminated sediments

ILs were regarded as a potential alternative to triolein for SPMD-like passive samplers because (1) ionized chemicals

Table 3 EDC concentrations in two field-contaminated sediments from the DDC extracted by Soxhlet or [BMIm]BF₄ water solution at a concentration of 2.66 mol l^{-1} (in nanograms per gram)

DDC sediment	Soxhlet			[BMIm]BF ₄		
	BPA	E2	NP	BPA	E2	NP
DDC2	0.35 ± 0.04	1.19 ± 0.31	ND	0.39 ± 0.04	1.10 ± 0.15	ND
DDC4	59.59 ± 8.25	3.15 ± 0.56	0.88 ± 0.19	57.23 ± 1.37	2.85 ± 0.08	0.63 ± 0.08

Concentrations without recovery correction were shown in this table

ND not detected

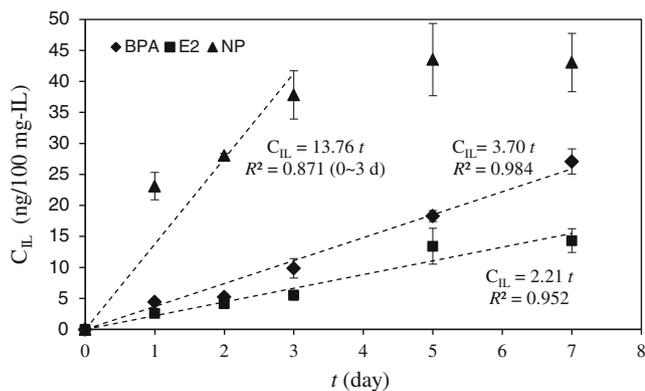


Fig. 4 Uptake kinetics of EDCs in IL-PE passive samplers from pore water of artificially polluted sediments. Each sampler contains 100 mg of [HDMI]PF₆

cannot diffuse through the PE membrane due to the high electrical resistance of the PE membrane, which can decrease the loss of IL; (2) some interactions between ILs and organic contaminants are stronger than the partition mechanism of organic contaminants to triolein, which can reduce the elimination rate of target HOC and increase, in theory, the accuracy of the linear uptake model; and (3) compared to the dialysis pretreatment required by triolein-SPMD, pretreatment of the IL-PE sampler can be simplified by dissolving IL in organic solvents and directly analyzing by HPLC. The uptake kinetics of EDCs in [HDMI]PF₆-PE passive samplers from pore water of artificially contaminated sediments was studied through a 7-day laboratory exposure experiment (Fig. 4). For BPA and E2, the uptake kinetic curves were linear, with R^2 values of 0.98 (BPA) and 0.95 (E2). The uptake kinetic curve of NP seems to be composed of linear, curvilinear, and equilibrium stages, and the linear slope of the curve in the first 3 days was fitted. Based on the equilibrium concentrations of NP in IL (43 ng per 100 mg IL) and in pore water phase (65 ng g⁻¹), the logarithm of the distribution coefficient ($\log K_d$) for NP is calculated to be 3.82, which is lower than its $\log K_{ow}$ (4.5; see Table 1). This K_d value is comparable to the result of a SPMD study (Xu et al. 2006) which reported a $\log K_d$ of ~ 3.2 . In addition, a much lower enrichment factor of 163

was observed when using [C₆MIm]PF₆ as the receiving phase of microextraction (Liu et al. 2004), which suggests that a longer alkyl chain was significantly conducive to the enrichment of NP in the IL phase.

The concentrations of BPA, E2, and NP in pore water of EDC-spiked YQR sediments were also measured, which were 1,780 ng l⁻¹ (BPA), 385 ng l⁻¹ (E2), and 65 ng l⁻¹ (NP). Furthermore, based on the slopes of the uptake kinetic curves of EDCs (see Fig. 4) and their pore water concentrations, the k_u of the different analytes can be calculated as follows: $k_{u,BPA} = 2.08 \times 10^{-2} \text{ l g}^{-1} \text{ d}^{-1}$, $k_{u,E2} = 5.74 \times 10^{-2} \text{ l g}^{-1} \text{ day}^{-1}$, $k_{u,NP} = 2.10 \text{ l g}^{-1} \text{ day}^{-1}$, according to Eq. 2. The order of k_u of the three analytes in this study was the same as their k_{ow} order, which is in accordance with the results of SPMD studies for the sampling of PAHs (Huckins et al. 1999).

3.5 Application of IL-PE passive samplers to field-contaminated sediments

To identify the applicability of IL-PE passive samplers, exposure experiments were conducted using field-contaminated sediments (i.e., DDC sediments) under the same conditions as the kinetics experiments described above. Target EDC concentrations and f_{oc} of DDC sediments are provided in ESM Table S1. BPA and E2 can be detected in all four DDC sediments at relatively high concentrations. The concentrations of these two analytes increased significantly from the upper reach (DDC1) to the lower reach (DDC2) due to the continuous input of wastewater along the canal and the increase of sediment f_{oc} . However, NP was only detected in sediment from DDC4, with a relatively low concentration of 8.7 ng kg⁻¹.

BPA and E2 were also measured (Table 4). The C_{pw_det} of BPA ranged from 64.4 to 14,000 ng l⁻¹, while that of E2 ranged from 13.2 to 175 ng l⁻¹. Furthermore, the calculated pore water concentrations (C_{pw_cal}) of these two analytes were obtained using Eq. 2 based on the analyte concentrations in the IL phase of passive samplers and the k_u values obtained in the kinetics experiments. As shown in Table 4, all C_{pw_cal} of

Table 4 Comparison of the calculated and measured concentrations of BPA and E2 in pore water of sediments in laboratory exposure experiments

Sediment no.	BPA			E2		
	C_{IL_7d} (ng/100 mg-IL)	C_{pw_cal} (ng l ⁻¹)	C_{pw_det} (ng l ⁻¹)	C_{IL_7d} (ng/100 mg IL)	C_{pw_cal} (ng l ⁻¹)	C_{pw_det} (ng l ⁻¹)
DDC1	$9.37 \times 10^{-1} \pm 2.67 \times 10^{-1}$	6.43×10	6.44×10	$9.35 \times 10^{-1} \pm 1.77 \times 10^{-1}$	2.33×10	2.32×10
DDC2	$1.05 \pm 2.55 \times 10^{-1}$	7.20×10	6.57×10	$1.22 \pm 3.13 \times 10^{-1}$	3.04×10	3.22×10
DDC3	$2.27 \pm 5.36 \times 10^{-1}$	1.56×10^2	1.95×10^2	$3.55 \pm 3.16 \times 10^{-1}$	8.86×10	9.85×10
DDC4	$1.49 \times 10^2 \pm 5.51 \times 10$	1.02×10^4	1.40×10^4	6.55 ± 1.21	1.64×10^2	1.75×10^2

C_{PS_7d} = analyte concentration in the IL phase of the passive sampler exposed for 7 days

C_{pw_cal} = calculated concentration of analyte in pore water according to C_{PS_7d} and k_u ($k_{u,BPA} = 2.08 \times 10^{-2} \text{ l g}^{-1} \text{ day}^{-1}$, $k_{u,E2} = 5.74 \times 10^{-2} \text{ l g}^{-1} \text{ day}^{-1}$)

C_{pw_det} = detected concentration of analyte in pore water

BPA and E2 were in the same order of magnitude with their corresponding C_{pw_det} . For DDC1 and DDC2 sediments, the calculated concentrations of BPA and E2 were highly consistent with the detected concentrations. For example, the C_{pw_det} of BPA and E2 in pore water of DDC1 were 64.4 and 23.2 ng l⁻¹, while the calculated concentrations based on the passive sampling results were 64.3 and 23.3 ng l⁻¹, respectively. For DDC3 and DDC4 sediments, the C_{pw_cal} of BPA and E2 were somewhat lower than C_{pw_det} . This difference might be attributed to the relatively high f_{oc} of DDC3 and DDC4 sediments, which were 5.09 and 5.46 %, respectively. A higher f_{oc} might induce a more dissolved organic matter in the pore water, which might affect the analyte uptake by samplers (Gourlay et al. 2005). In contrast, the f_{oc} of DDC1 and DDC2 sediments (2.23 and 3.27 %, respectively) were close to that of the artificially contaminated YQR sediment (2.56 %). Therefore, the effects of dissolved organic matter (DOM) on k_u were hypothesized to be similar in these cases. However, further studies on the role of DOM in the uptake of different compounds to the ionic liquid phase are needed.

4 Conclusions

Solutions of water-soluble ILs—[BMIm]BF₄ and [BMPy]BF₄—were found to be potential extractants for the extraction of EDCs (BPA, E2, and NP) from sediments. BPA, E2, and NP can be extracted efficiently from all sediments by IL solutions at relatively high concentrations, with maximum single extraction efficiencies of 70–100 %. Compared to pyridinium-based [BMPy]BF₄, the extraction efficiencies by imidazolium-based [BMIm]BF₄ solution were much higher.

In addition, a passive sampler using [HDMIm]PF₆ as the receiving phase material was developed. Linear uptake of BPA and E2 from pore water of artificially contaminated sediments was observed during the 7-day experimental period. This IL-PE passive sampler was demonstrated to be effective in sampling BPA and E2 from pore water of four field-contaminated sediments.

Acknowledgments This study was supported by the National Science Foundation for Natural Science, China (nos. 21177065, 20807024, 41225014) and the Research Fund for the Doctoral Program of Higher Education of China (nos. 200800551051, 20090460092).

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