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RESEARCH ARTICLE

Simulation of aromatic polycyclic hydrocarbons remobilization from a river sediment using laboratory experiments supported by passive sampling techniques

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Abstract Resuspension of bedded sediments was simulated under laboratory-controlled conditions in order to assess the amount of polycyclic aromatic hydrocarbons (PAH) remobilized in the dissolved fraction during one short and vigorous mixing. The desorbed amount of PAH was compared to the exchangeable fraction, the total amount of PAH sorbed on the sediment particles, and the dissolved PAH amount contained in the interstitial pore waters in order to evaluate the contribution of each fraction to the total amount of PAH released. To monitor the desorption of PAH and measure low trace level concentrations, passive samplers were used in an experimental open flow through exposure simulator. Results show that for the selected sediment, a substantial fraction of sorbed PAH (69 % of the total amount) is not available for remobilization in a depleted medium. Obtained data pinpoint that over 9 days, only 0.007 % of PAH are desorbed by passive diffusion through a water-sediment interface area of 415 cm^2 and that an intense resuspension event of 15 min induces desorption of 0.015 % of PAH during the following 9 days. Results also highlight that during resuspension simulation, modifications of the sediment and the water body occurred since partitioning constants of some pollutants between sediment and water have significantly decreased.

Keywords PAH · Sediment · Water · Passive sampling · Remobilization simulation · Accessible fraction

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Highlights - The accessible fraction of PAH sorbed on sediment particles was evaluated from passive samplers.
- The passive diffusion of PAH from bedded sediments and their remobilization induced by artificial resuspension were simulated through a laboratory experiment.
- Results show significant effects of suspension of sediment on the water column PAH concentration and on the affinity of sediments with some of the studied PAH.

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Introduction

Passive samplers (PS) have been widely studied and promoted to sample the dissolved fraction of the water column notably through the water framework directive (Allan et al. 2006; Vrana et al. 2014). However, passive samplers may be also used in larger systems including sediment beds. Sediments can trap a significant amount of hydrophobic pollutants in comparison with the water compartment where hydrophobic chemicals show only a limited solubility (Karacık et al. 2013). Sediments play a significant role in the fate of pollutants in the aquatic system as events such as bioturbation, bio-irrigation, tidal currents, trawling, and dredging operations can stimulate the transfer of chemicals between the sediment beds and the water column compartments (Adams 2003; Friedman et al. 2009; Roberts 2012; Bradshaw et al. 2012). In this context, it appears crucial to apply PS in the water column while considering sediment beds. In addition, in the sediment beds, the properties of the PS to sample exclusively the accessible fraction of the pollutants are of great interest because in this compartment, the total and the accessible amount of chemicals are most of the time very different (Cornelissen et al. 1997; Yates

et al. 2013; Smedes et al. 2013; Li et al. 2015). The accessible fraction being the one considered in risk assessment procedures defines its magnitude is highly valuable. In this context, using PS simultaneously in both compartments (water column and sediment) greatly enhances the elucidation of the fate of pollutants in the aquatic system.

In the present study, the remobilization of polycyclic aromatic hydrocarbons (PAH) from river sediment was investigated under controlled laboratory conditions using simultaneously passive samplers in sediment slurries and in the water column above sediment beds as an integrated solution providing a global view of the simulated hydrosystem.

The accessible fraction of PAH sorbed to the sediment is determined through a laboratory experiment using PS devices (Smedes et al. 2013; Yates et al. 2013). This approach is based on a finite medium (a small bottle) that encloses various amounts of samplers and sediments until equilibrium is reached. The larger the amount of PS, the larger the quantity of PAH accumulated by the samplers. Extrapolation of the PAH amount accumulated by an infinite sampler (full depleted medium) provides the maximal PAH amount which can be desorbed from the sediment particles and can potentially interact with the biota. Only the readily available sediment-bound PAH are removed and trapped by the samplers. On the other hand, extrapolation of PAH accumulated by a negligible amount of samplers provides PAH concentration available in the dissolved fraction (using partitioning constants) without interfering with their distribution between sediment and water (an example of graphical extrapolation is provided in Fig. 1). The deduced water concentration can be assimilated to the pore water concentration assuming the equilibrium between the interstitial water and the sediment particles is reached.

In order to study the transfer to the water column, a second experiment was conducted to evaluate the amount of sorbed PAH which can desorb from the sediment beds by passive diffusion in a static exposure and during the resuspension of sediments. The aim of this experiment is to evaluate the actual fraction of PAH which can be remobilized in "real" conditions (dredging event for example) in comparison to the accessible (labile) fraction and the total amount of sorbed PAH.

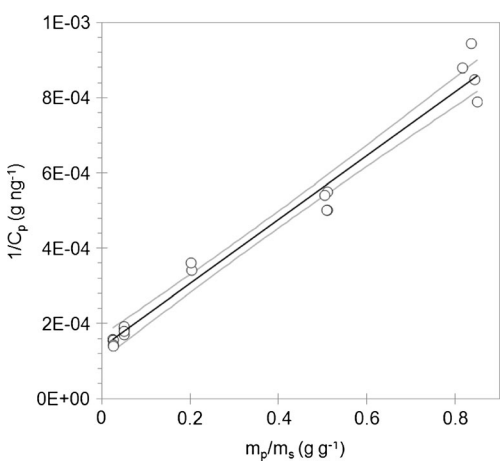

Fig. 1 Pyr sorption plot of $1/C_p$ vs m_p/m_s to determine pore water concentration and mobile fraction of sorbed PAH. *Dashed line* is the 95 % confidence interval of the linear regression

Several previous studies (Latimer et al. 1999; Feng et al. 2007; Yang et al. 2008) aimed to quantify the remobilization of chemical components under laboratory-controlled experiments without elucidating the dissolved PAH concentration because a low release to the water makes the study of PAH transfer arduous. Consequently, the literature data is most of the time scarce concerning the PAH transfer. In the present study, support of passive samplers to evaluate low trace level contamination is a major advantage by allowing accurate determination of remobilization processes and focusing on the dissolved fraction concentration. In addition, simulating suspension and measuring the accessible concentration on the same sediment provide useful information about the fate of PAH and the real PAH fraction which can be deleterious for the environment.

Materials and methods

Materials

Organic solvents: dichloromethane, n-hexane, 2,2,4-trimethylpentane were purchased from Fisher Scientific (France). Native and perdeuterated PAH were supplied by Cluzeau Info Labo (Sainte-Foy-la-Grande, France): Nap (Naphthalene), Acy (Acenaphthylene), Ace (Acenaphthene), Flu (Fluorene), Phe (Phenanthrene), Ant (Anthracene), Fla (Fluoranthene), Pyr (Pyrene), BaA (Benzo[a]anthracene), Chr (Chrysene), Bb+kF (Benzo[b]fluoranthene+ Benzo[k]fluoranthene), BaP (Benzo[a]pyrene), IP (Indeno[1, 2,3-cd]pyrene), BP (Benzo[g,h,i]perylene), DBA (Dibenzo[a, h]anthracene). GF/F glass fiber filters (47 mm diameter), and sodium azide biocide were purchased from VWR (Fontenay-sous-bois, France). Polyethylene (PE) (100 μm thickness) was purchased from Fisher Scientific (France), and silicone rubber (SR) (1 mm thickness, peroxide-based catalyst, SEF8CC46) from Solutions Elastomères (France). All passive samplers were pre-extracted by soaking twice in dichloromethane during 24 h.

Sediment preparation and characterization

Twenty kilograms of sediments were collected in the Escaut River (France). The selected sediments were chosen to present contaminant concentrations and organic carbon content close

to the other river sediments studied in the same area in order to be the most representative of the contaminated sediments of northern France (Sanctorum et al. 2011; Charrasse et al. 2014). After collection, sediments were freeze-dried, homogenized by ball mills and sieved to 250 μm diameter. Dried sediments were then stored at room temperature in darkness before use. Organic carbon content of sediments was evaluated to 4.5 % with a TOC analyzer in compliance with the European Standardisation (EN 13137). Total PAH concentrations in sediments (C_{sed}) were determined in triplicate by accelerated solvent extraction (ASE Dionex 200) as described in the supporting information S1 and results are reported in Table 1.

Estimation of accessible and pore water concentrations of PAH

The experiment consisted in determining (i) the accessible PAH concentrations (C_{as}; ng g^{-1}) which are reversibly bound to the sediment particles and releasable in a water medium depleted from PAH and (ii) water PAH concentrations when the equilibrium is established between water and sediment which assuming equilibrium state corresponds to the pore water concentration (C_{pw}; ng L^{-1}). For this purpose, several experiments were conducted by introducing in enclosed bottles various mass ratios of PE passive samplers and sediment to induce a gradual depletion of PAH in the medium by the PS. Following Eq. 1, the concentration of PAH in the PS at equilibrium (C_p; ng g^{-1}) is function of the mass ratio between the PS and the sediment (m_p/m_s; g g^{-1}) where K_{PE} is the PE-water partitioning coefficient of PAH (Smedes et al. 2013).

$$\frac{1}{C_p} = \frac{1}{C_{pw}K_{PE}} + \frac{m_p}{m_s C_{as}} \quad (1)$$

C_p reflects the concentration at the equilibrium with pore water if m_p/m_s is negligible (non-depleted condition). Conversely, PS contain all accessible PAH of the sediment and the interstitial water when m_p/m_s is infinite because the samplers are then an infinite sink of pollutants. The procedure consists of mixing with an orbital stirrer 2.5 g of PE with 3, 5, 12, 50, and 100 g of dried sediment and 9 mL of deionized water per gram of dried sediment. In addition, 2 g of sodium azide per liter of water was added in all batches to inhibit bacterial activity. Bottle sizes from 60 to 2500 mL were used in order to achieve effective filling between 20–50 %, ensuring a satisfactory mixing. All experiments with a given sampler-sediment mass ratio were duplicated to evaluate the variability of results. After 3 months of equilibration period at 20 °C, PS were retrieved, cleaned, and analyzed for PAH concentration. Substantial equilibrium establishment was confirmed by a second batch of the same experiments conducted over a 4-month period. Since the amount of desorbed PAH between the third and fourth months of equilibration is not significant, it was assumed that the fraction unreleased after 100 days can be neglected and assigned to the unavailable fraction. The duration of the experiment was chosen in order

Table 1 Total sediment concentration (C_{sed}; ng g^{-1} dw), pore water concentration (C_{pw}; ng L^{-1}), accessible sorbed concentration (C_{as}; ng g^{-1} dw), sediment-water partitioning coefficient normalized by the organic carbon content K_{oc}, PAH flux from the bedded sediment (Flux; ng d^{-1} m^{-2}), and average half equilibration time of passive samplers (*d*)

	Abbr.	C_{sed} (ng g^{-1})	C_{pw} (ng L^{-1})	C_{as} (ng g^{-1})	log K_{oc} (g g^{-1})	Flux (ng d^{-1} m^{-2})	Half eq. time (*d*)
Naphtalene	Nap	394±28	28.8±3.2	50±12	4.59±0.13	1675±69	<1
Acenaphthylene	Acy	14±1	4.5±0.3	7±0.4	4.51±0.05	0±0	2
Acenaphthene	Ace	226±16	171.6±33.5	108±5	4.15±0.09	1099±362	3
Fluorene	Flu	335±24	110.8±20.6	130±7	4.42±0.09	1621±350	3
Phenanthrene	Phe	1400±98	166.6±19.9	544±24	4.86±0.07	2388±607	9
Anthracene	Ant	631±44	55.0±10.4	200±12	4.91±0.1	228±110	7
Fluoranthene	Fla	2308±162	120.9±7.3	1737±54	5.50±0.04	1769±546	28
Pyrene	Pyr	1672±117	101.9±11.3	1177±45	5.41±0.06	1146±798	25
Benzo[a]anthracene	BaA	1416±99	11.6±2.9	618±43	6.07±0.12	283±121	112
Chrysene	Chr	5104±358	27.0±6.8	843±53	5.84±0.12	463±158	138
Benzo[b]fluoranthene + Benzo[k]fluoranthene	Bb+kF	7212±507	6.0±1.4	576±68	6.33±0.13	114±51	362
Benzo[a]pyrene	BaP	1144±80	4.5±1.9	429±61	6.33±0.19	72±46	322
Indeno[1,2,3-c,d]pyrene	IP	238±17	0.8±0.4	268±53	6.88±0.25	93±44	1198
Benzo[g,h,i]perylene	BP	764±54	0.9±0.4	302±48	6.89±0.22	118±46	720
Dibenz[a,h]anthracene	DBA	112±8	0.2±0.1	116±23	7.08±0.18	72±31	789
∑HAP	∑HAP	22970±1613	811±121	7106±509	–	11143±3032	–

to ensure significant equilibrium reaching considering that Lohmann et al. (2005) reported 182 days of equilibration and that Smedes et al. (2009) recommended 46 days of equilibrium period. Since statistically equivalent results were obtained for both temporal batches, dataset from both batches were indifferently used to compute accessible and pore water concentrations (difference between both series was generally similar or lower than the dispersion within the duplicates of a same series, about 16 %). In this experiment, thin samplers (100 μm) were intentionally used to speed up the equilibrium establishment needed for the determination of the accessible fraction of PAH (Cornelissen et al. 2008a, b). Polyethylene was used as sampler material because K_{PE} is well reported in the literature with a good reproducibility between laboratories and studies. The relationship K_{PE}-K_{ow} reviewed by Lohmann (2012) based on the values reported by seven studies (variability about 50 %) was used to perform our calculation (selected values of partitioning coefficients are given in supporting information S2).

Laboratory suspending sediment experiment

Experimental setup

The influence of sediment resuspension on the mobility of PAH sorbed on sediment particles was investigated by exposing the sediment sample to clean tap water under controlled laboratory conditions. For this purpose, a 27 L Biolafitte fermentor was customized with hermetic and plastic-free enclosure to avoid volatilization and sorption of PAH. Five kilograms of previously prepared sediment (dw) (above-mentioned) were disposed in the fermentor, and about 20 L of tap water were added in order to remove air bubbles of the apparatus. To ensure significant desorption of PAH sorbed on sediment particles, water concentration was maintained close to zero using a peristaltic pump which continuously supplied clean water in the sediment enclosure (20 L d^{-1}). During the first 21 days of the experiment, the sediment was left to consolidate without mixing the water column. Between days 21 and 29, the overlaying water was gently mixed for homogenization purposes. At day 29, the sediment was subjected to 15 min of artificial resuspension by a vigorous mixing to obtain a homogeneous sludge. After that, the sediment was left to consolidate over the next 17 days. Exceeding water from the sediment exposure tank flowed into a second and third enclosure disposed in series (sampling tanks) where water was sampled by two SR devices in each of them (Fig. 2). Dissolved PAH concentrations were monitored over the whole course of the experiment by passive sampling to assess the average water concentration and by solid-phase microextraction (SPME) of collected water samples in order to follow the instantaneous water concentration with a high time resolution.

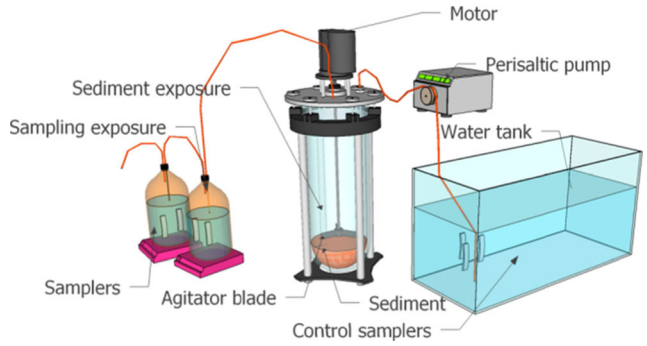

Fig. 2 Experimental setup

SR passive samplers (2.5×10×0.1 cm; 3 g) with low surface to volume ratio were selected to ensure that the accumulation of PAH by PS remained in the initial linear part of the uptake curve. In this way, a strict mean water concentration was available for a larger set of PAH. A 0.5-L sampling tank was chosen to reflect accurately the water concentration thanks to its high renewal rate (40 times per day). Nevertheless, the water volume renewed per day remained limited and thus precluded the exposure of several samplers as they would have induced a significant depletion of PAH concentrations in the water. Consequently, data were restricted to a limited number of samplers to ensure they all kept their integrative properties. For this purpose, the number of passive samplers (2 SR samplers per sampling tank) was chosen to ensure that the water volume cleared from their PAH remained insignificant in comparison to the total water renewed per day in the sampled enclosure. To monitor that samplers do not reduce significantly PAH water concentrations, the second sampling exposure tank containing two other PS was fed by the overflow water of the first one. Statistically, similar amounts of PAH were trapped in the samplers of the first and second sampling tanks, confirming that PS exposure did not reduce PAH concentrations and that the water concentration deduced from PS was the actual mean PAH water concentration. Three PS disposed in the tap water tank during all the experiments revealed no trace of PAH above the acceptability threshold which was set at ten times the blank level (see the Quality control section). One passive sampler from each sampling tank was retrieved and substituted by a new device after 10, 21, 29, 38, 46 days while the second passive sampler was replaced by a new device after a longer accumulation period to promote detection of PAH by accumulation of larger amounts of these contaminants (after 21 and 38 days). In addition, spot samples were frequently collected to perform SPME extraction (at least every 2 days and up to 10 times per day during resuspension simulation). Furthermore, pH, oxydoreduction potential (Eh), conductivity and dissolved oxygen probes were continuously immersed in the sediment enclosure (combination electrode with Ag/AgCl reference electrode).

Water concentration determination by passive samplers approach

Mean water concentrations in the sample enclosure were deduced from the PAH accumulated in the SR passive samplers and the sampling rates of the target analytes calculated through the performance reference compound (PRC) approach, based on the non-linear least square (NLS) method proposed by Booij and Smedes (2010) and successfully applied by Monteyne et al. (2013) and Vrana et al. (2014). Briefly, this approach is based on the first order dissipation rate of several PRC (Ace-d10, Ant-d10, BaA-d12, BaP-d12, DBA-d12) spiked into the devices (cca. 2 μg g^{-1}) prior to exposure (Booij et al. 2002). Dissipation is then assumed following Eq. 2 where the residual fraction of PRC (N_t/N_0) is a function of the partitioning coefficient of PAH between water and SR (K_{SR}) and sampling rates (R_s; L d^{-1}) (partitioning coefficients are adopted from Smedes et al. (2013) and reported in supporting information S2). V_s is the volume of the sampler (2.60±0.05 mL).

$$\frac{N_t}{N_0} = e^{-\frac{R_s.t}{V_s.K_{SR}}} \quad (2)$$

R_s is equivalent to the volume of water cleared by the samplers from their PAH content per unit of time. When the water boundary layer (WBL) controls the uptake process of PAH, Rusina et al. (2010) assumed that R_s can be modeled by the Eq. 3 where M (g mol^{-1}) is the PAH molecular weight, A the sampler area (cm^2), and F an exposure adjustment factor which reflects the effect of exposure conditions on R_s.

$$R_s = F.A.M^{-0.47} \quad (3)$$

The WBL control assumption has been recognized realistic in many studies for PAH with log K_{ow}>4.5 and for SR samplers in usual exposure conditions. The model is then applied in our study to deduce dissolved water concentrations. In the case of PAH with log K_{ow}< 4.5, the determination of accurate sampling rates is not required as equilibrium state can be pragmatically assumed, limiting the influence of the sampling rate value on the deduced water concentrations (Lohmann et al. 2012). Consequently, Eq. 3 is applied indifferently for all PAH. By combining Eqs. 2 and 3, the adjustable parameter F can be estimated to model the observed PRC dissipation. F is then used to calculate the sampling rates of all target PAH (Eq. 3). Knowing the specific R_s of the sampling tank, the mean water concentration (C_w) is computed from Eq. 4 where m_{PAH} (ng) is the sorbed amount of PAH.

$$C_w = \frac{m_{PAH}}{V_s.K_{SR}.\left(1-e^{\frac{R_s}{V_s.K_{SR}}.t}\right)} \quad (4)$$

Extraction procedure and chromatographic determination

The water samples collected during the laboratory simulation were taken in 1 L glass bottle rinsed three times with the water of the sediment enclosure to minimize the effect of PAH sorption on the glassware. After that, the water samples were immediately filtered through GF/F filters (previously combusted during at least 10 h at 400 °C) and a 9-mL aliquot was transferred in SPME extraction vials, spiked with internal standards and extracted by SPME using a CTC PAL Combi-*xt* autosampler (refer to supporting information S3 for the detailed procedure). PAH extraction from the whole sediment was performed using an accelerated solvent extractor (ASE 200, Dionex) according to EPA method SW-846 3545A. The detailed extraction protocol is reported in supporting information S1. Extraction of the samplers was performed by applying the procedure used by Fernandez et al. (2014) by soaking samplers three times in 40 mL of dichloromethane during 24 h with the internal standard mixture. The extracts were then purified through a column of 4 g of aluminum oxide and eluted with 30 mL of hexane. Finally, extracts were concentrated under nitrogen flux at 55 °C and reconstituted with 300 μL of 2,2,4-trimethylpentane. PAH extracts were then quantified using gas chromatography coupled to a mass spectrometer detector (Agilent 7890B series-5977 MSD in SIM mode) as described in supporting information S4. Internal standards used for each extraction and analysis procedure are listed in supporting information S4.

Quality control

The SPME extraction method was adapted from the optimized method developed by de Perre et al. (2014). Detection limits of the method were extrapolated from the linear regression of five artificial samples spiked at 100, 50, 10, 5, and 1 ng L^{-1} to a signal to noise ratio of three. The limits of detection are in all cases lower than 0.2 ng L^{-1}. SPME blanks were performed by analyzing an empty vial to ensure that an exhaustive extraction of the PAH was achieved during the previous analysis (carry over effects). Usual PAH contamination of the blank was less than 1 % of the area observed in the previous sample. Recovery rates of the filtration and extraction procedures were evaluated from artificial samples composed of deionized water spiked with a standard solution to reach a nominal target concentration of 50 ng L^{-1} (overall procedure was tested as the filtration step was included). Recovery ranged between 82 and 100 % with lower recovery rates for the heaviest PAH, likely due to loss during collection and filtration procedures.

The entire analytical procedure of the sediment extraction (S2) was applied to the certified marine sediment, SRM 1944 (NIST, USA). The recoveries on this SRM were between 85

and 105 % with reproducibilities ranging between 5 and 15 % depending on the compounds.

Validation of the passive sampler extraction encountered specific issues as the uncertainties in the K_{SR} and R_s models used can impact the final estimates of water concentrations and detection limits. In the present study, K_{SR} were adapted from Smedes et al. (2009) who observed variability over 0.5 log units on five different silicone rubbers. This bias could result in a deviation of factor 3 in the deduced water concentration of the pollutants at equilibrium state between the water and the samplers. R_s model is in counterpart linked to the reliability of the deduced water concentration of the chemicals remaining in the linear uptake regime. Currently, the reliability of the R_s model is insufficiently assessed. However, the model developed by Rusina et al. (2010) on SR passive samplers was selected in this study because it was established on theoretical basis and confirmed by several field trials (Monteyne et al. 2013; Vrana et al. 2014). Detection limits were evaluated from the sampling rates of the exposed passive samplers, the sampling period, and the analytical detection limit of the chromatographic determination method. Using Eq. 4, the limits of detection were estimated between 0.3 and 21.3 pg L^{-1} for the PS of the sampling enclosure as well as the PS of the water tank. The recovery assessment ranged between 91 and 101 % was performed using pre-cleaned passive samplers which were spiked with an analytical standard mixture in the extraction vial.

All results were corrected for recovery of the extraction procedure. Reproducibility is evaluated through replicate analysis (at least n=2). In addition, blanks and enriched samples were analyzed along the analysis sequence. A blank threshold based on the analysis of field control samples was systematically applied as a rejection criterion: results lower than ten times the blank average level was discarded. Blank values were finally subtracted from the accepted results. Detection limits, recovery rates, and rejection criterion (blank threshold) are given in supporting information S5.

Results and discussion

Water exchangeable fraction

According to the model of sampler-sediment exchange developed by Smedes et al. (2013), a linear regression treatment applied to the plot of ($\frac{1}{C_p}$) vs ($\frac{m_p}{m_s}$) provides simultaneously $\frac{1}{C_{as}}$ (slope) and $\frac{1}{C_w K_{sw}}$ (y -intercept) (Eq. 1; Fig. 1). The water exchangeable fraction of sorbed PAH was in the range 11 to 100 % of the total PAH sediment concentration depending of the considered chemicals. By comparison, Smedes et al. (2013) calculated an exchangeable concentration between 10 and 50 % of the total concentration of PAH while Yates et al. (2013) reported values between 3 and 100 %. No direct relationship was observed between the accessible fraction and the total concentration or hydrophobicity of PAH, underlining complex interaction between chemicals and sediment (Fig. 3) (Gao et al. 1998; Aminot et al. 2015). The estimated water exchangeable fraction of PAH sorbed to the sediment reflects the fraction potentially mobilized into the pore water and the water column where compounds can interact with biota. The water exchangeable concentration of PAH is an essential parameter to define actual PAH partitioning coefficients as it does not consider the PAH irreversibly bound to sediment particles, uninvolved in the partitioning process of chemicals between the sorbed and the dissolved states. Organic matter is known to play a significant part in the sorption of PAH on particle sediments (Yang et al. 2011). Extrapolated water concentrations when equilibrium is reached with the exchangeable fraction range between 172 ng L^{-1} for Ace and 0.2 ng L^{-1} for DBA. Although sediment contamination is not uniform for all PAH, the expected concentration of pore water follows an overall decreasing trend with hydrophobicity/solubility of PAH.

Remobilization simulation

The analysis of residual amounts of PRC used to calibrate the PS revealed that PAH lighter than Phe exceed the half equilibration period in most samplers (half equilibration periods are reported in Table 1). Consequently, for these compounds, the concentration deduced from the PS is close to the value at the time of the device retrieval and not necessarily the value of the actual mean water concentration. As a result, some observations based on the mean water concentration provided by the PS underestimate the actual magnitude of the remobilization

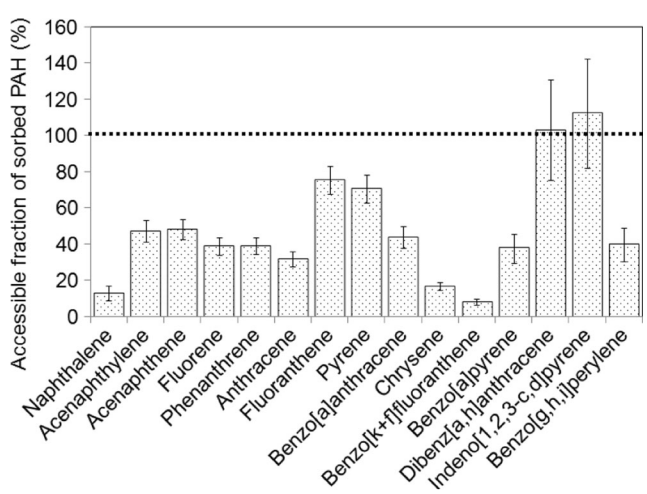

Fig. 3 Water exchangeable fraction for each PAH. Data are presented as mean value±standard deviation

effect. This assumption is confirmed by the SPME analysis which shows a rapid decrease of peak water PAH concentrations immediately after agitation is stopped (Fig. 4). For example, the PS do not translate the Nap contamination peak observed with SPME analysis (S6-8) because of the too short integrative capability of the PS regarding this compound (half equilibration period is about 1 day for Nap). Despite these limitations, the water concentrations provided by SR and SPME during the steady period of water concentration (T0-T30 and T38-T46) are not significantly different for the most detected PAH (Ace, Flu, Phe, Ant, Fla, Pyr; S8-S10). The concentration monitored by the PS methodology showed no significant increase of heavier PAH concentrations (5–6 rings) during the mixing period while the less hydrophobic PAH (2–4 rings) were released 5 times faster during the 9 days following the resuspension simulation (Fig. 5). This observation is clearly explained by the higher solubility in water of the 2–4 ring PAH combined with the high accessible concentration of the 4 ring PAH. By contrast, the high mobile fraction of 6 ring PAH (>40 %) does not seem to be translated by higher water concentrations during resuspension because of the low amounts of these chemicals contained in the accessible fraction (C_{as}<302 ng g^{-1}). In addition, it is recognized that hydrophobic organic contaminants tend to desorb more slowly with a desorption time that reaches 1 year (Eggleton and Thomas 2004). All individual PAH concentrations derived from PS are available in supporting information S6. On the contrary, discrete sampling performed by SPME allows the instantaneous water concentration determination during resuspension events and allows tracking with a high time resolution PAH water concentration variations (Fig. 4). However, most of the highly diluted PAH are not detected by the SPME method because of its lower sensitivity, underlining the interest of the integrative passive sampling methodology. Nap, Ace, Flu, Ant, Phe, and Pyr which are easily observed by SPME showed rapid release during suspension simulation with concentrations between 6 and 70 times higher after only 1 h of mixing. These results are in line with the observation of Allan et al. (2012) which reported in the field a concentration increase of one order of magnitude of PCDD/F within minutes of the sediment resuspension. In the same way, Schneider et al. (2007) observed 22 % desorption of PCB after only 2 h of remobilization. After suspension simulation, a return to baseline condition was observed after a couple of days for both water physicochemical properties (Fig. 6) and dissolved PAH concentrations. Measurements in the sampling enclosure showed that water concentration was at least 10 times higher than in the tap water tank, demonstrating that the PAH were significantly released from the sediment (in the tap water tank, the contamination signal was below the previously discussed quality control threshold). The PAH amount released over each time period of the experiment was evaluated using the averaged PAH concentration deduced from PS and the rate of water renewal. During the first 21 days (before resuspension), the release rate of PAH from the bedded sediment is evaluated at 445± 101 ng d^{-1} with a lower value during T0-T21 period where no homogenisation of the overlaying water was done. Normalized to the surface area of the sediment interface, the average flux in the present study (≈10.7±2.4 μg d^{-1} m^{-2}) was of the same order of magnitude as the one reported by Eek et al. (2010) from an in situ measurement of harbor sediments. Estimation of the mass transfer coefficient between the water column and the sediment bed (calculated according to Flux/(C_w-C_{pw}); (Liu et al. 2014)) was about 1264 m s^{-1} similarly to Lick (2006) which reported values ranging between 800 and 8000 m s^{-1}. During resuspension and the 9 following days, the amounts of desorbed PAH increased by a factor of four ($\sum_{PAH}$=1899±191 ng d^{-1}).

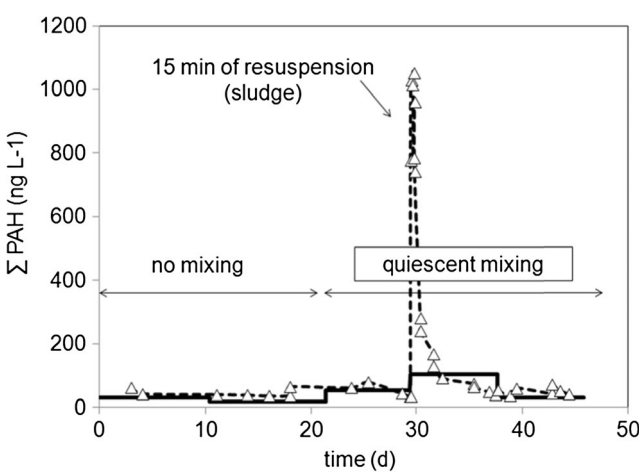

Fig. 4 PAH concentration in the dissolved fraction during remobilization experiment: (*triangle*) concentration obtained from SPME sampling; (*dashed line*) concentration derived from passive samplers

Mechanistic interpretation

According to the equilibrium partitioning theory (Rico-Rico et al. 2009), the most evident reason of PAH water concentration increasing during mixing simulation is induced by the enhanced equilibration rate of PAH between the sediment particles and the dissolved fraction, in disequilibrium before mixing because of the continuous refilling of the tank by fresh tap water. In this case, the turbulent conditions reduce the diffusion path of sorbed PAH to join the dissolved fraction and allow for a faster transfer of chemicals between sorbed and dissolved states (Higashino et al. 2004). This fact results in the increasing of the observed water concentration during T21-T29 period, when the mixing motor was turned on to generate weak mixing of the overlaying water. In the same way, the observed concentration is greatly increased again when mixing is accelerated to generate a homogeneous slurry (T29-T38 period). In addition, assuming that pore water was in equilibrium with sediment particles and that overlaying

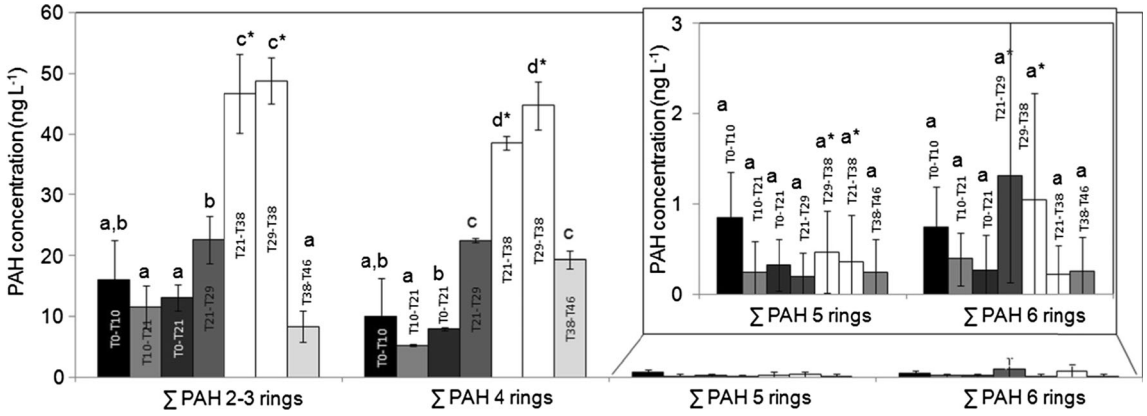

Fig. 5 PAH water concentration monitored by passive samplers during resuspension experiment. Treatments with the same *letter* were not significantly different ($p>0.05$). Data are presented as mean value±standard deviation. *Asterisk* represents period including resuspension *simulation*

water was not equilibrated with the sediment before mixing, dilution (advection) of pore waters in water column when resuspension is simulated could increase water concentration of PAH in the dissolved fraction. Using pore water concentration determined above and the water content of bedded sediments (cca. 0.92 mL g^{-1}), we evaluated that 20 % of the amount of PAH released during the resuspension simulation resulting from dissolution of pore water in the water column. Although significant, the advection of pore water is too small to explain alone the increase of PAH transferred into the dissolved fraction during resuspension. Desorbed amounts of PAH from bedded sediments during a 9-day period represent 51 % of the observed desorption of PAH on the 9 days following resuspension simulation. Considering both results, we concluded that 29 % of the PAH released from sediments during the 9 days following the 15 min of resuspension simulation may be assigned exclusively to the remobilization effect (refer to the suspension state of the particles). Our results, although partial, show that a significant release can be induced by the suspension of sediment but that desorbed amounts of PAH are far below the total amount of accessible PAH sequestrated by the sediment (Fig. 7).

Assuming that the diffusion out of the sediment is performed from the superficial layer, the thickness of the sediment depleted from its PAH during the period of 9 days before resuspension simulation can be estimated. The first observation is that pore water does not contain enough PAH to explain the released amount in the water column (the released PAH amount is between 2 and 90 times higher than the PAH dissolved in pore water). Consequently, the accessible fraction of sorbed PAH seems to be remobilized in the dissolved fraction of pore water. Considering that only the accessible fraction of PAH can diffuse and is released in the water column, we can estimate that the virtual thickness of superficial sediment depleted from its accessible fraction of PAH ranges between 7 and 700 μm according to the chemical.

Using the water concentration when equilibrium is reached (evaluated simultaneously with the water exchangeable fraction determination and referred as C_{pw} in Table 1), it can be estimated that the maximal concentration in the water column which could be achieved if resuspension was enough to establish thermodynamic equilibrium. However, spot samples showed for Nap, Ace, Acy, and Flu that the maximal concentration was higher than expected (i.e., 12, 2, 2, 2, times higher, respectively). This observation, which in regard of the error propagation method could not be explained by the uncertainty associated to the defined partitioning constant, suggests a decrease of K_{oc} and indicates a modification of sediment sorption capacity when mixed (uncertainties of K_{oc} are reported in Table 1). Therefore, PAH distribution between water and sediment is not driven by a simple equilibrium between two known media (sediment and water) but also several other parameters affecting the properties of both compartments appear to play a significant role in the distribution process. The sorption of accessible fraction of PAH is probably not driven by linear isotherm because it results from sorption on various geosorbent materials (Cornelissen et al. 1997; Lohmann et al. 2005). Other processes could explain the observed apparent K_{oc} shift such as the contribution of sorption of PAH on dissolved organic matter (de Perre et al. 2014) which is probably more concentrated during the resuspension experiment (sediment to water ratio is higher in resuspension experiment). Additional processes can be taken into account as the modification of the water body and organic matter properties when resuspension is simulated. Physicochemical parameters evaluated by a multiparameter probe immersed in the sediment exposure tank showed that resuspension of the sediment affected many properties of the water body as conductivity, pH, oxydoreduction potential and dissolved oxygen (Fig. 6). The observed pH decrease in water column from 7.2 to 6.7 during resuspension simulation implied a pH

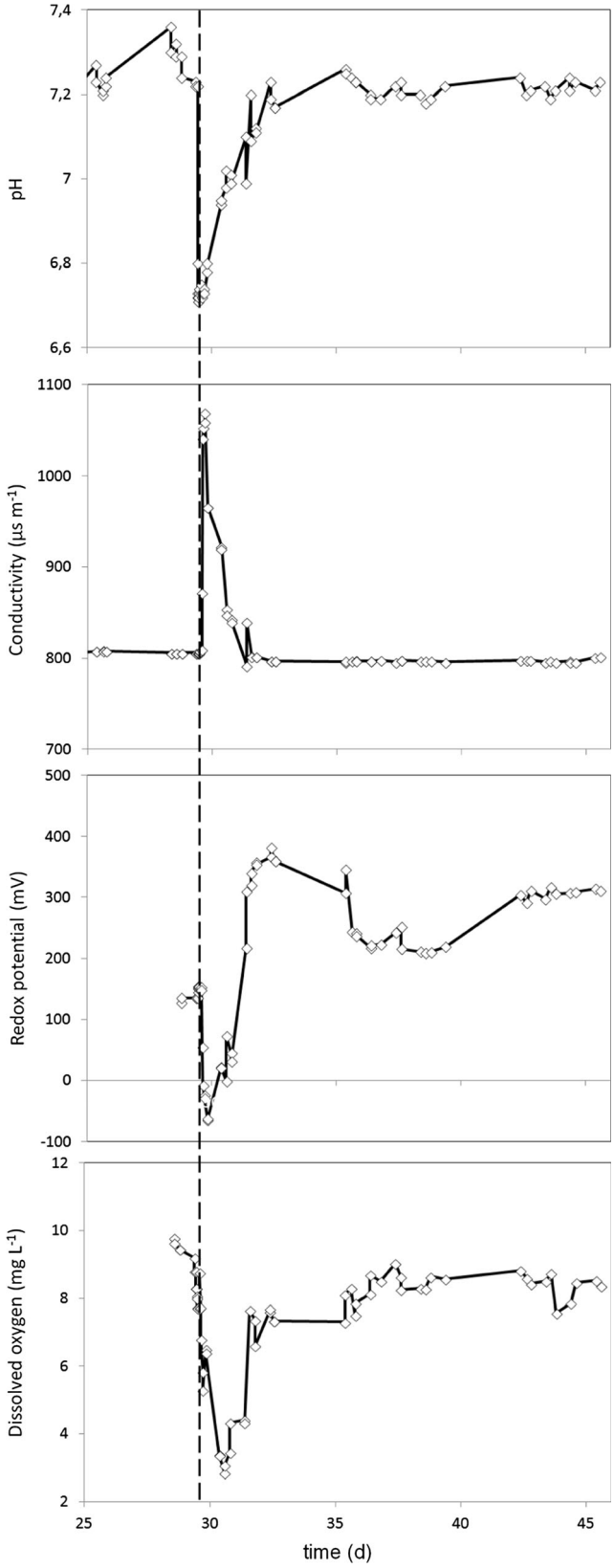

Fig. 6 Physical-chemical conditions measured in the sediment enclosure during the laboratory simulation of resuspension. The *dashed line* marks the resuspension event

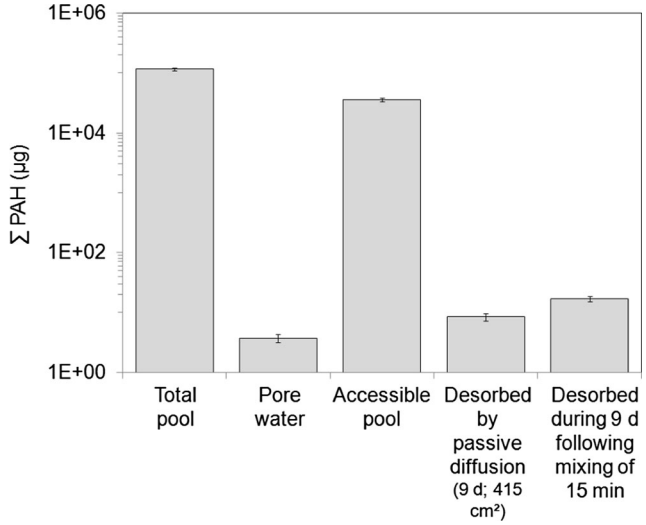

Fig. 7 Comparison between amounts of PAH, in whole sediment, in accessible fraction, in pore water and transferred to the dissolved fraction by passive diffusion and during artificial resuspension for a 9-day period (value given for 5 kg of sediment). Data are presented as mean value±standard deviation

increase for sediment particles, sorbed organic matter, and sorbed PAH which in turn could influence PAH sorption on sediment particles. Gao et al. (1998) reported similar observations while indicating significant effects of pH on sorption capability of sediments for pesticides. Increasing pH may enhance the release of organic matter from the sediment in the dissolved fraction and therefore results in increased PAH release. On the other hand, several other processes could impact PAH concentration in the dissolved fraction during suspension simulation as enhanced bacterial activity (Quantin et al. 2005; LeBlanc et al. 2006) and salting-out effect which could promote sorption of PAH. Because sediment to water ratio is different in both experiments (remobilization simulation and the water exchangeable fraction determination), all of these parameters may have evolved in specific ways in both experiments leading to different observed K_{oc}. It is difficult to distinguish the main processes as these entire phenomena occur concomitantly and further investigation targeting the effects of one specific parameter are needed to understand more precisely the dynamics of the system.

We underlined that the observed peak concentration and the rate of dynamic equilibrium recovery are dependent on the water renewing rate and are consequently specific of the present experimental setup. As such, experimental setup does not represent field situation where many uncontrolled parameters could differ from the laboratory (Handlin et al. 2014). However, the comparison of water PAH concentration under mixed and static conditions, keeping constant all other parameters, provides useful data on PAH behavior during suspended

events, on the amount of PAH which could be released and on the kinetic of the remobilization.

Conclusions

The present study underlines the suitability of PS methodology to investigate the fate of PAH in the hydrosystem, in one hand, to evaluate the mobile fraction of PAH sorbed to the sediments and, on the other hand, to track low water concentration levels of these contaminants in the water column. The results show that the studied sediment can release significant amounts of PAH in the dissolved fraction in the simulated open flow through exposure system, and they also highlight that a quick remobilization could induce significant increase of the released PAH. Sediment is in our work, a significant source of PAH for the dissolved fraction even if only a small fraction of the releasable PAH is effectively desorbed when sediment is resuspended. The difference between partitioning constant in the two experiments conducted (accessible fraction determination and resuspension simulation) can be attributed to non-linear sorption isotherm of the releasable fraction, the dissolved organic matter contribution or the impact of some physicochemical parameters which may probably not occur in the same way in both experiments. On the other hand, no evidence shows that the fraction irreversibly sorbed to the sediment is dependent to the environmental conditions. It would be highly valuable to demonstrate that the unavailable fraction of PAH remains desorption resistant in all usual conditions to ensure that laboratory measurements of accessible fraction are sufficient for the risk assessment of contaminants.

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