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Behaviour of polycyclic aromatic hydrocarbons in dissolved, colloidal, and particulate phases in sedimentary cores

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Solid-phase microextraction (SPME) has been successfully used for extracting polycyclic aromatic hydrocarbons (PAHs) from porewater samples from the Mersey Estuary, UK. The majority of the PAHs in porewater samples are associated with colloids due to the high DOC concentrations. The truly dissolved PAH concentrations varied from 66 to 1050 ng L⁻¹ in core 2 and from 95 to 740 ng L⁻¹ in core 3, and were dominated by naphthalene, fluoranthene, and pyrene. Although absent in the dissolved phase, the high-molecular-mass compounds were found in the colloid-associated fraction of porewater. PAHs in sediments arose from a range of compounds with 4- and 5-ring PAHs dominating. The partitioning of PAHs between sediment and porewater shows that PAHs are enriched in the sediment phase. When the soot carbon content was considered, predictions of the partition behaviour were found to agree more closely with the observed distribution. The results reiterate the importance of evaluating the speciation of organic pollutants in both porewater and sediments in order to accurately predict their environmental fate and potential toxicity.

Keywords: PAHs; Porewater; Sediment; Soot carbon; Solid-phase microextraction

1. Introduction

PAHs are an important class of organic contaminants, arising primarily from pyrolytic and petrogenic sources and shown to have potential deleterious effects on a range of aquatic organisms [1, 2]. PAHs can accumulate in sediment interstitial water to concentrations above those observed in overlying water [3, 4]. It has been shown that sediment porewater can provide an important exposure route of PAHs to organisms including fish [5], filter-feeding bivalves, and burrowing organisms [6]. The fate of such persistent compounds in the marine environment is largely controlled by their physicochemical speciation in terms of phase distributions [7, 8]. This phase distribution is typically described using an equilibrium partitioning approach that allows the prediction of a compound behaviour from its physicochemical properties such as water

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solubility and octanol/water partition coefficient (K_{ow}). However, PAH concentrations measured in the aqueous phase can vary widely from those predicted by equilibrium partitioning models. For example, in interstitial waters, PAH levels both above and below predicted values have been obtained [9, 10], raising questions about our understanding of PAH behaviour in aquatic systems.

Through the formation of stable complexes, aqueous PAHs may associate with dissolved organic carbon (DOC) and show enhanced solubility and resistance to degradation as well as reduced bioavailability. It has been suggested that it is the dissolved fraction that is largely responsible for potential biological effects [7, 11]. This is particularly important for interstitial water where DOC concentrations can be up to 10-fold higher than in overlying water [12]. DOC is a generic term applied to all filter passing organic material in the aqueous phase, including known molecules such as amino acids, sugars as well as the so-called humic substances [13]. It has been widely reported that organic contaminants such as PAHs can interact strongly with colloidal organic carbon (COC) which is part of DOC. Recent research suggest that it is the 1 kDa–0.2 μm fraction that is responsible for pyrene sorption [14].

Due to the importance of identifying the speciation of organic contaminants, it is highly desirable to distinguish between colloid-bound and truly dissolved fractions during the analysis of aqueous samples, which is most challenging and not achieved with many analytical techniques. Consequently, reported aqueous concentrations of organic contaminants are frequently 'total' loading including both dissolved and colloid-bound fractions, despite the limited availability of bound compounds for causing biological effects and partitioning to sediments. As a result, contamination levels in water may have been overestimated. Recent research shows that SPME provides a good means to solve this problem, as it appears to extract primarily PAHs in the dissolved phase [11, 15–18]. The objectives of the work were therefore to determine the depth profiles of PAHs in sediment cores and associated porewater from the Mersey Estuary, UK; to assess the distribution of PAHs between colloids and dissolved phase through the application of the SPME technique; and to model the distribution of PAHs between sediment and porewater.

2. Experimental

2.1 Chemicals

Reference PAHs (16 compounds, each at $2000\ \mu\text{g mL}^{-1}$) and deuterated internal standards (IS) containing acenaphthene- d_{10} , phenanthrene- d_{10} , and chrysene- d_{12} each at $500\ \mu\text{g mL}^{-1}$ were obtained from Supelco. All glassware was cleaned thoroughly by soaking overnight in Decon-90 and rinsing with ultra-pure water (Maxima water purification system, USF Elga) followed by dichloromethane (DCM). All solvents used were of glass-distilled grade from Rathburns (Scotland).

2.2 Sampling and sample processing

Sediments were collected in Perspex tubes (7 cm i.d.) in 2001, from the southern bank of the Inner Mersey Estuary, UK (figure 1). Cores were extruded from the tubes and

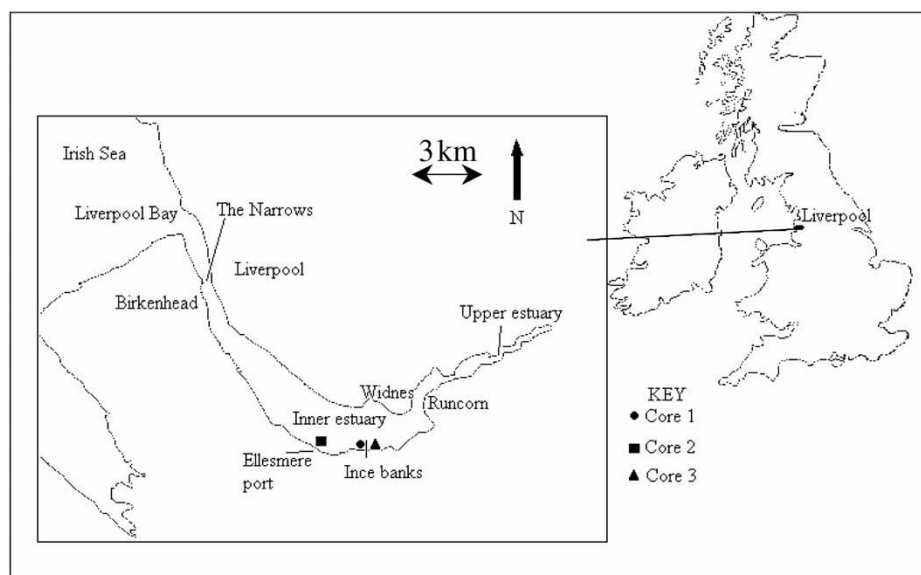


Figure 1. Map showing the Mersey Estuary and sampling locations.

sliced at 2.5 cm intervals using a solvent-rinsed stainless steel hacksaw. Each slice was well mixed to ensure homogeneity and divided into two portions, A and B. Sub-samples from portion A were characterized for water content, sediment dry bulk density, particle density, and organic and soot carbon measurements using a Flash EA1112 series CHN–O analyser [19]. Results are shown in table 1. PAH concentrations were determined from samples from portion B.

2.3 PAH extraction from porewater

Porewater was separated from sediment by centrifugation at 4000 rpm for 15 min and transferred to glass vials. Of these fractions, one portion was spiked with IS at a concentration of $1 \mu\text{g L}^{-1}$ and PAH concentration determined using the SPME method developed by King *et al.* [17]. Briefly, the SPME device with polydimethylsiloxane fibres (100 μm film thickness, Supelco) was left in the samples for 45 min with agitation by ultrasonication, to absorb PAHs. The SPME fibre was then directly inserted a gas chromatography–mass spectrometry (GC–MS) for desorbing PAHs from fibre and analysis. Another portion was spiked with $5 \mu\text{L}$ of 50% H_3PO_4 in order to arrest biological activity [20] and was stored at -15°C until DOC analysis using a TOC-5000A total organic carbon analyser (Shimadzu). A selection of sub-samples from core 3 were also collected, spiked with IS ($1 \mu\text{g L}^{-1}$) and extracted by liquid–liquid extraction (LLE) using DCM in order that results could be compared with those obtained using SPME. Sample extracts were dried with pre-combusted Na_2SO_4 and concentrated under a gentle stream of N_2 to approximately $250 \mu\text{L}$ before analysis by GC–MS.

Table 1. Summary of sediment properties in cores 1–3 from the Mersey Estuary (results are mean values with standard deviation in parentheses).

	Core 1	Core 2	Core 3
Water content (%)	18.61 (2.04)	38.61 (7.56)	37.63 (6.31)
Organic carbon content (%)	^a	2.99 (0.80)	2.69 (0.62)
Soot carbon content (%)	^a	0.63 (0.18)	0.62 (0.15)
Sediment dry bulk density (g mL ⁻¹)	^a	1.05 (0.04)	1.04 (0.10)
Particle density (g mL ⁻¹)	^a	2.15 (0.25)	2.20 (0.19)
Porosity (%)	^a	51.05 (4.53)	52.65 (3.35)

^aNot determined.

2.4 PAH extraction from sediments

Sediments were extracted following a method developed by King *et al.* [21]. Briefly, dry sediment samples (10 g) were mixed with surrogate standards (2 µg), copper granules (3.5 g), sodium sulphate (6 g), and DCM (50 mL), then extracted for 30 min in an ultrasonic bath. The extracts were transferred to 250 mL round-bottomed flasks, another 50 mL DCM was added, and samples were subjected to a further 30 min ultrasonication. The extracts were then combined and concentrated using rotary evaporation to approximately 1 mL. Sample clean-up was achieved by passing extracts through columns containing 50 : 50 silica : deactivated alumina and elution with 25 : 75 DCM : hexane. The eluent was then concentrated under a gentle stream of nitrogen to approximately 250 µL before analysis by GC–MS.

2.5 Analyses

Analyses were performed using a PolarisQ (Thermoquest) GC–MS fitted with an RTX5 MS (5% phenyl:95% dimethylpolysiloxane, 30 m × 0.25 mm i.d., 0.25 µm film thickness) fused-silica capillary column. The carrier gas (helium) was maintained at a constant pressure of 14.5 psi. The injector port temperature was set to 220°C. For SPME analysis, fibre desorption took place in splitless mode with the splitter activated after 7 min to purge the fibres of any residual compounds so as to eliminate the risk of carryover of compounds between extractions. Desorption of analytes from the SPME fibre at a depth of 3 cm was found to provide maximum desorption. The GC temperature was programmed as follows: from 40 to 120°C at a rate of 10°C min⁻¹ and then to 325°C at a rate of 3°C min⁻¹ where it was held for 5 min. For non-SPME analyses, aliquots of 1 µL from sample extracts were analysed under the same condition as with SPME analysis, except with a slightly different temperature programme: 60°C for 2 min increasing at 10°C min⁻¹ to 120°C then increasing at 3°C min⁻¹ to 325°C where it was held for 5 min. The MS was operated in electron ionization (EI) mode with an ion source temperature of 250°C. The target compounds were analysed in the selected ion mode for quantitative analysis and in full-scan acquisition mode for compound confirmation. Quantification was performed by comparing the analyte response with that from standard solutions, using the so-called relative response factors.

The extraction and analytical procedures were subject to quality-control procedures, including the analyses of blanks with each batch of water and sediment samples [17, 21]. The sediment method was verified through the extraction of a certified reference

material (CRM) (Analytical reference material EC-4, Environment Canada, National Water Research Institute). The mean recovery ($n = 5$) was 70–110%, with RSD between 8 and 25%. The limit of detection (LOD) for each compound was calculated as three times the standard deviation of the baseline noise from 10 injections of procedural blanks prepared alongside sample extracts. LOD values of approximately 1 ng g^{-1} dry weight were obtained for each compound, with the exception of naphthalene and benzo[*g, h, i*]perylene (2 ng g^{-1}), benzo[*a*]anthracene (3 ng g^{-1}) and chrysene (4 ng g^{-1}). The LOD for SPME analysis was between 1 and 29 ng L^{-1} for individual PAHs [17].

3. Results and discussion

Core 1 comprised largely coarse-grained sand, while cores 2 and 3 consisted principally of clay with increasing sand content towards the base of the core. The sandy nature of core 1 meant that it retained very little water, and it was therefore impossible to collect sufficient porewater from this core for analysis. Hence, only the PAH concentrations in the sediments of core 1 are reported here.

3.1 Dissolved PAH concentrations in porewater

The dissolved Σ PAH concentrations were in the range $66\text{--}1050 \text{ ng L}^{-1}$ in core 2, and $95\text{--}740 \text{ ng L}^{-1}$ in core 3, which are significantly lower than those found in porewater from a gas plant [18]. As shown in the depth profiles (figure 2), the PAH compounds with the highest concentrations are naphthalene, fluoranthene, and pyrene. The 5- and 6-ring compounds are generally absent from sediment porewater.

Of the 2- and 3-ring compounds, naphthalene was the dominant compound throughout both cores. As shown in figure 2(a), naphthalene was measured in the highest concentration (500 ng L^{-1}) in core 2 in the 15–17.5 cm section. In contrast, in core 3 the maximum naphthalene concentrations were observed near the surface at 2.5–5 cm (600 ng L^{-1}), and towards the base of the core below 40 cm ($130\text{--}740 \text{ ng L}^{-1}$).

Concentrations of 3-ring PAHs were generally found in higher concentrations in core 3 than in core 2 with several concentration peaks observed in both cores. Maximum concentrations of acenaphthene in core 2 were observed in the surface layer (49 ng L^{-1}) while in core 3, relatively high concentrations ($66\text{--}78 \text{ ng L}^{-1}$) were found in the 7.5–10 cm, 27.5–30 cm, and 50–52.5 cm sections as well as in the surface sediment (figure 2b). The highest concentrations of fluorene (91 ng L^{-1}) were observed in the 15–17.5 cm section in core 2 (figure 2c). In contrast, in core 3, there were several peaks throughout the core with the maximum concentration of 105 ng L^{-1} observed at 7.5–10 cm. Phenanthrene was observed to peak at several depths throughout both cores with concentrations generally higher in core 3 (figure 2d). The maximum phenanthrene concentration (49 ng L^{-1}) in core 2 was measured in the 0–2.5 cm section, with similar concentrations being observed at other depths. In core 3, the maximum concentration of phenanthrene occurred at 7.5–10 cm (105 ng L^{-1}), with again high concentrations observed throughout the core. Anthracene concentrations were generally below LOD, with the exception of a few high concentrations in both cores (figure 2e).

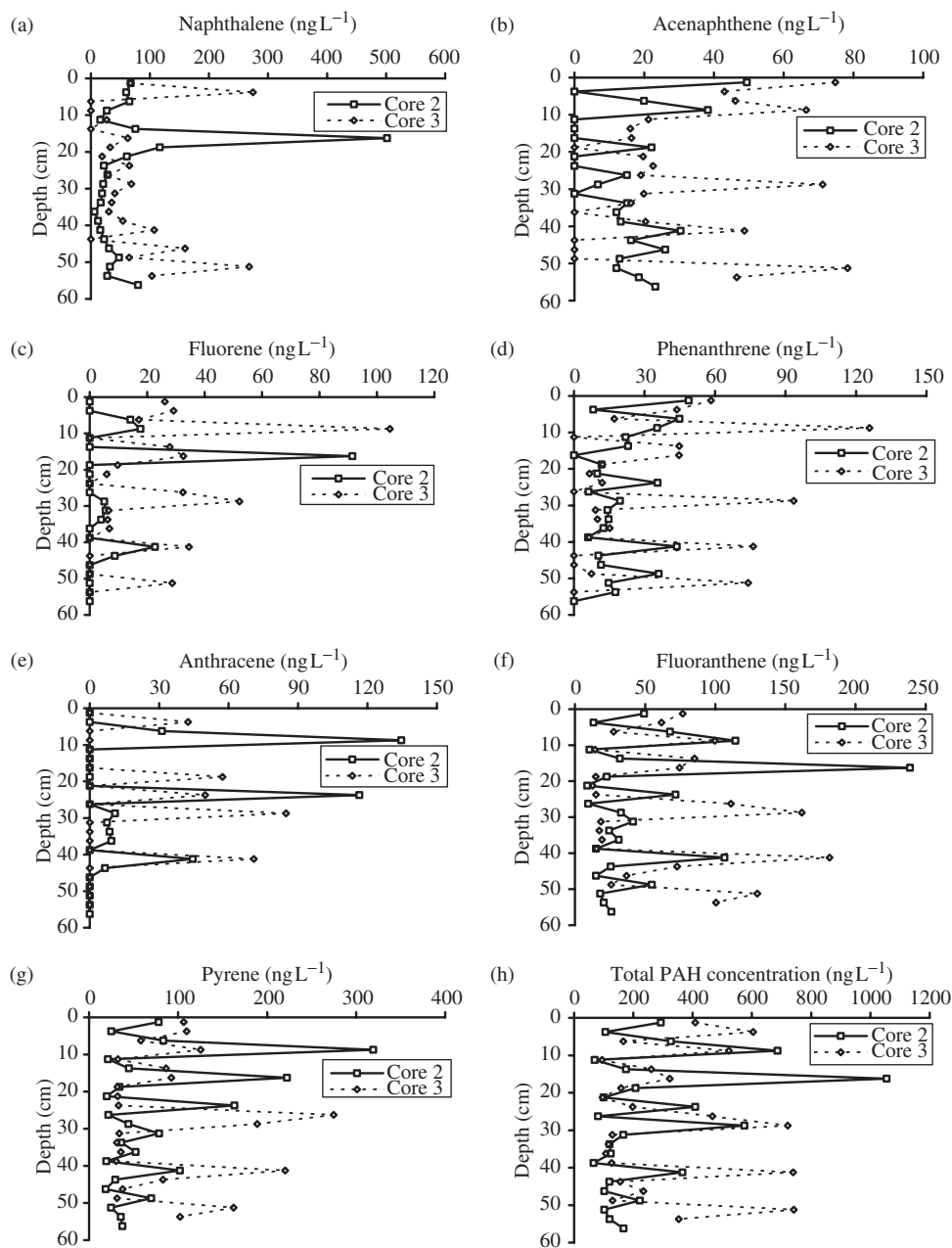


Figure 2. Depth profiles showing the dissolved concentrations of (a) naphthalene, (b) acenaphthene, (c) fluorene, (d) phenanthrene, (e) anthracene, (f) fluoranthene, (g) pyrene, and (h) sums of all 16 PAHs from cores 2 and 3 from the Mersey Estuary, UK.

Concentrations of fluoranthene and pyrene were found to co-vary in both cores 2 and 3 (figure 2f and g) with similar distribution patterns for both compounds. In core 2, the highest concentrations of pyrene and fluoranthene were observed at 7.5–10 cm (319 and 114 ng L^{-1} , respectively) and 15–17.5 cm (222 and 239 ng L^{-1} , respectively).

An additional pyrene peak was observed at 22.5–25 cm (163 ng L^{-1}) corresponding to a reasonably high fluoranthene concentration at this depth (72 ng L^{-1}). Greater similarities can be seen in the distribution of fluoranthene and pyrene in the porewaters of core 3 with maximum concentrations of both observed at 27.5–30 cm (189 ng L^{-1} pyrene, 162 ng L^{-1} fluoranthene) and 40–42.5 cm (220 ng L^{-1} pyrene, 181 ng L^{-1} fluoranthene). Furthermore, the total PAH concentration followed similar patterns between the two cores (figure 2h).

3.2 Combined (dissolved plus colloidal) PAH concentrations in porewater

Results from LLE of core 3 show higher PAH concentrations (dissolved plus colloidal) than those from SPME analyses (dissolved only). For example, the total concentrations of 16 PAH ranged from 6800 to $25,560 \text{ ng L}^{-1}$ from LLE measurements, in comparison with only 95 – 740 ng L^{-1} from SPME. In addition, 5- and 6-ring compounds, which were not detected in any of the SPME analysis, were found to be present in some of the samples when analysed by LLE. These significantly hydrophobic compounds associate preferentially with colloidal material present in samples, and low dissolved concentrations are to be expected. In figure 3, a comparison between total dissolved

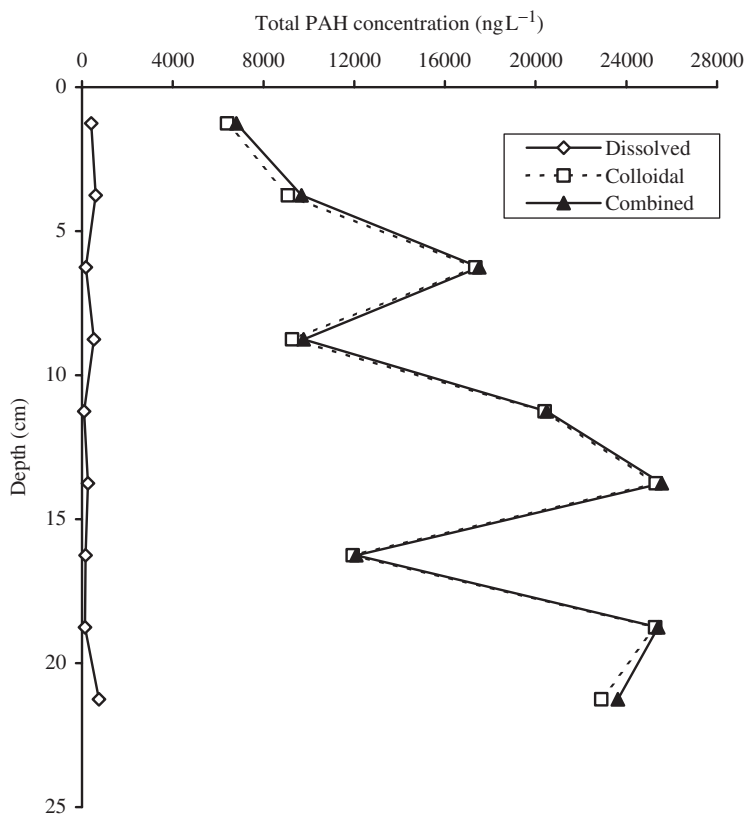


Figure 3. Concentrations of the sum of 16 PAHs in porewater from core 3.

concentrations measured using SPME, combined (dissolved plus colloidal) concentrations measured using LLE, and the difference between the two (i.e. colloid-bound PAH) is shown. The results show that on average, over 90% of PAHs in porewater were complexed by colloids, suggesting the abundance of colloids with strong binding capacity for PAHs. The finding is consistent with the high DOC values being measured in the core, ranging from 145 to 627 mg L⁻¹. As sediment porewater frequently contains high concentrations of colloidal material with concentrations of DOC in porewater up to 10-fold greater than in overlying water [12], it is likely that the dissolved PAH portion would be reduced due to the strong affinity of the compounds for colloidal material. Hawthorne *et al.* [18] also found that 5–80% of the total dissolved 4–6-ring PAHs were associated with DOC rather than being freely dissolved. The total combined PAH concentrations in porewater are slightly higher than those observed in Xiamen Harbour, but lower than those in Jiulong River Estuary and Minjiang Estuary, China [3, 4, 22].

3.3 PAH partitioning between colloidal and dissolved phases

The partition coefficient for individual compounds between the colloidal and dissolved phases may be described as follows:

$$\text{PAH}_{\text{free}} + \text{Colloids} \leftrightarrow \text{PAH}_{\text{Colloids}}, \quad (1)$$

where PAH_{free} is the truly dissolved PAHs determined using SPME, while $\text{PAH}_{\text{Colloids}}$ is the PAHs bound to colloids which is equal to the difference between the concentration determined by LLE and the concentration measured using SPME.

At equilibrium, the partition coefficient (K_p) of PAHs between colloids and dissolved phase can be calculated thus:

$$K_p = \frac{\text{PAH}_{\text{Colloids}} \text{ (ng L}^{-1}\text{)}}{\text{PAH}_{\text{free}} \text{ (ng L}^{-1}\text{)}}. \quad (2)$$

Here, DOC was used to represent colloids; K_p was then normalized to the measured DOC concentration thus:

$$K_{\text{DOC}} \text{ (L kg}^{-1}\text{)} = \frac{K_p}{\text{DOC concentration (mg L}^{-1}\text{)}} \times 10^6. \quad (3)$$

As shown in figure 4, the field-derived $\log K_{\text{DOC}}$ values are smaller than laboratory-derived $\log K_{\text{DOC}}$ values, due to the high concentrations and different nature of DOC in core samples in comparison with commercial humic acids [17]. Results by Ohlenbusch *et al.* suggested a linear relationship in the analysis of phenols by SPME [23]. However, other investigations have reported that $\log K_{\text{DOC}}$ for a range of organic compounds was not strongly dependent on $\log K_{\text{ow}}$ and that values of $\log K_{\text{DOC}}$ showed a greater variability for more hydrophobic compounds [15, 24]. It has been suggested that K_{DOC} may be influenced by the magnitude of steric hindrance associated with the sorbent [25]. A lower affinity of larger PAH molecules for dissolved material may be a result of this steric hindrance. Recent research also suggests that only a proportion of the DOC concentration, the so-called COC, is responsible for PAH interactions [14, 26].

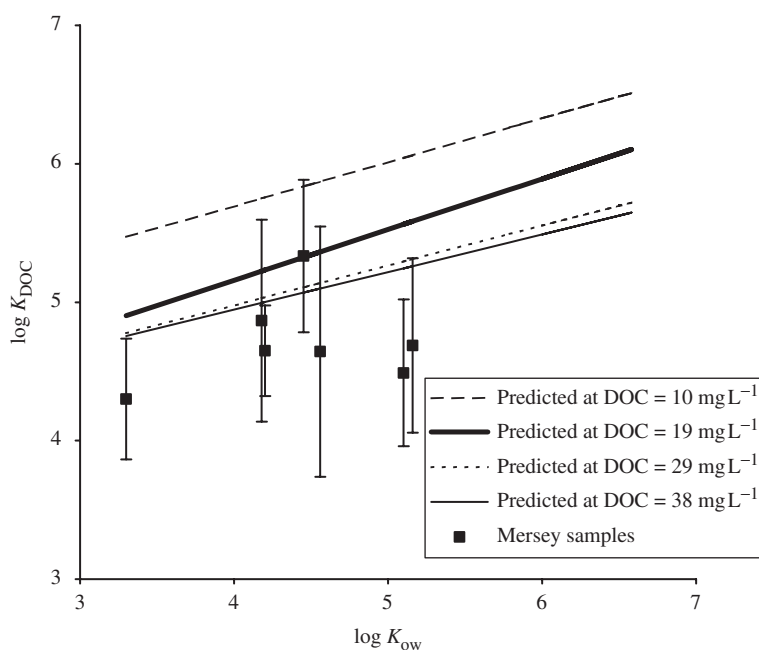


Figure 4. Relationship between $\log K_{\text{DOC}}$ and $\log K_{\text{ow}}$ with changing aqueous DOC concentrations. The four lines represent predicted values of PAH complexation with humic acid of different concentrations derived from laboratory experiments [17].

3.4 PAH concentrations in sediments

All 16 compounds were detected in sediment samples from the Mersey Estuary, in contrast to the dissolved phase. Total PAH concentrations were the highest in core 2 (mean = 5050 ng g^{-1}), followed by core 3 (mean = 3510 ng g^{-1}) and core 1 (mean = 607 ng g^{-1}). This agrees with the previous observation of the sandy nature of core 1 and the fact that sediments containing a high proportion of sand typically retain lower concentrations of PAHs than sediments with high proportions of clay and organic material, with which PAH compounds can interact strongly [27].

The PAH profile in all three cores was dominated by high-molecular-mass compounds (figure 5). In core 1, 4-ring compounds contributed 41% on average to total PAH burden in the sediments. Core 2 was dominated by 4- and 5-ring PAHs, contributing 42 and 31%, respectively, to total PAH loading. Similarly, core 3 was dominated by 4- and 5-ring compounds, accounting for 39 and 31% of total PAHs, respectively. The importance of high-molecular-mass PAHs has been commonly observed in sediments from marine or lacustrine environment as well as in atmospheric aerosols [28, 29]. Pereira *et al.* also showed that 4-ring PAHs dominated PAH distributions in sediments from San Francisco Bay [30]. Pyrolysis/combustion of fossil materials yields such PAH assemblages, which are subsequently introduced into the marine environment by coastal and river runoff and by direct dry or wet deposition from the atmosphere [31, 32]. Industrial and/or domestic wastes are often another

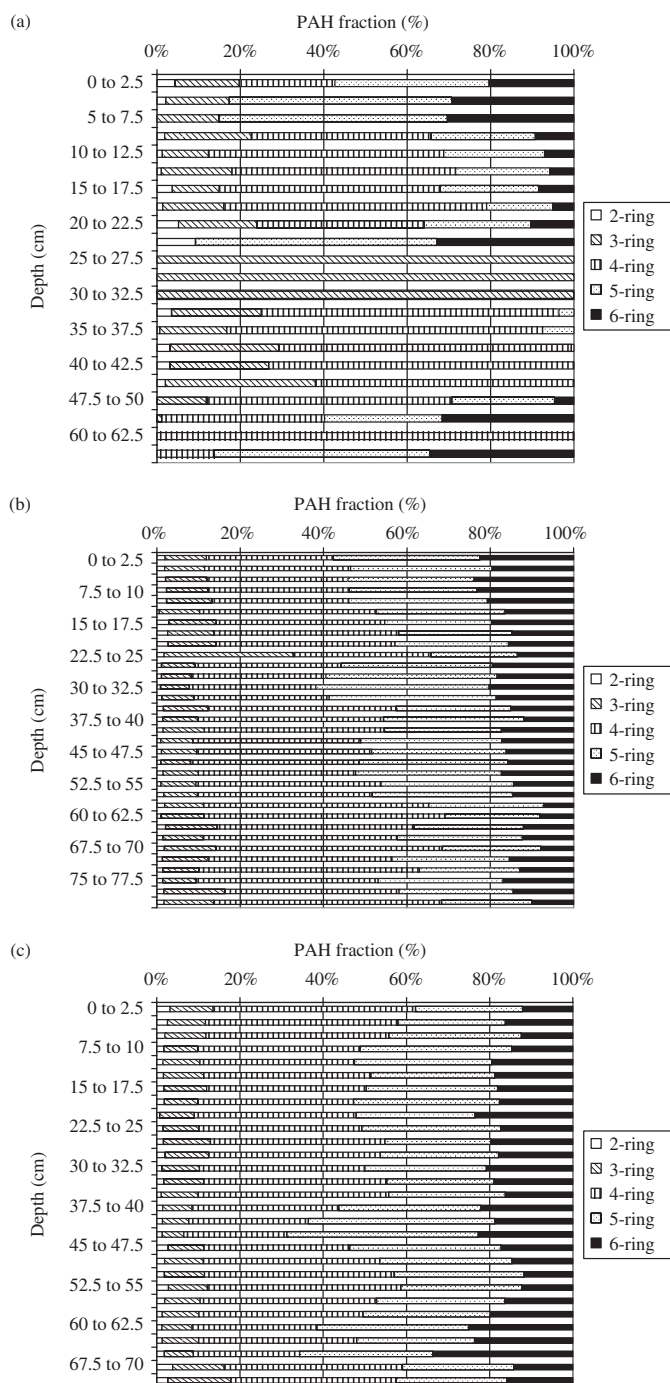


Figure 5. Composition of parent PAH in (a) core 1, (b) core 2, and (c) core 3 of the Mersey Estuary. Two-ring PAHs include naphthalene; 3-ring PAHs include acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene; 4-ring PAHs include fluoranthene, pyrene, benzo[*a*]anthracene and chrysene; 5-ring PAHs include benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene and dibenzo[*a,h*]anthracene; and 6-ring PAHs include indeno[1, 2, 3-*cd*]pyrene and benzo[*g,h,i*]perylene.

important local source. The predominance of 5-ring compounds of catacondensed structures (e.g. benzofluoranthenes) suggests a main origin from high-temperature pyrolytic processes [33]. The changes in the compositional pattern of PAHs between some sampling locations may occur due to variations in additional input sources (e.g. high- or medium-temperature combustion processes, different nature of fossil materials).

3.5 PAH partitioning between sediment and porewater

The partition behaviour of the PAHs between sediment and dissolved phase in porewater, and between the sediment and total aqueous (dissolved + colloid-associated) phase was investigated. Values of $\log K_p$ varied over a wide range, although results are broadly comparable between the two sediment cores. As expected, results obtained for the partitioning between sediment and the total porewater phase (K_p^*) were lower than those measured for partitioning between sediment and the truly dissolved phases (K_p). Since strong relationships are frequently found between K_p and sediment organic carbon content, the normalized partition coefficient (K_{oc}) was calculated. As shown in figure 6, the majority of organic carbon normalized sediment/dissolved PAH partition coefficients exceeded the predicted values of $\log K_{oc}$, suggesting compound enrichment in the sediment above that expected by equilibrium partitioning. In contrast, values of $\log K_{oc}^*$ calculated for sediment/total porewater PAH in core 3 were, with the exception of naphthalene and two values of phenanthrene, lower than predicted. This suggests strong association of the compounds with colloids in porewater, resulting in decreased partition coefficients. The results agree with those obtained by DiToro *et al.*, who observed that, in the presence of significant levels of DOC, the free dissolved concentration of hydrophobic compounds will typically be lower than the total dissolved concentration in porewater [7]. As a result, PAH partition coefficients between sediment and freely dissolved phase are generally higher than apparent partition coefficients calculated with the total dissolved porewater concentration. Results presented here show that high DOC concentrations can lead to enrichment of PAHs in the aqueous phase. However, the contrasting enrichment of the compounds in the sediment phase observed is not fully explained by normalization to the sediment organic carbon content.

To shed further light on the partition process of PAHs between sediment and porewater, field-derived K_p was compared with two sets of predicted values, one by Means *et al.* [34] and the other as a function of organic and soot carbon content calculated using the extended partition relationship described by Gustafsson *et al.* [8]. As shown in figure 7, normalizing to both sediment soot and organic carbon content leads to values of $\log K_{psc(pred)}$ of around 2 log units higher than $\log K_{p(pred)}$ as a function of organic carbon content alone, consistent with earlier studies of soot carbon control of PAH distributions [8, 26]. In addition, field-derived values of $\log K_p$ were mostly within the two sets of predicted values, suggesting that the extended partition model can simulate PAH distributions between sediment and porewater more accurately than the simple equilibrium partitioning.

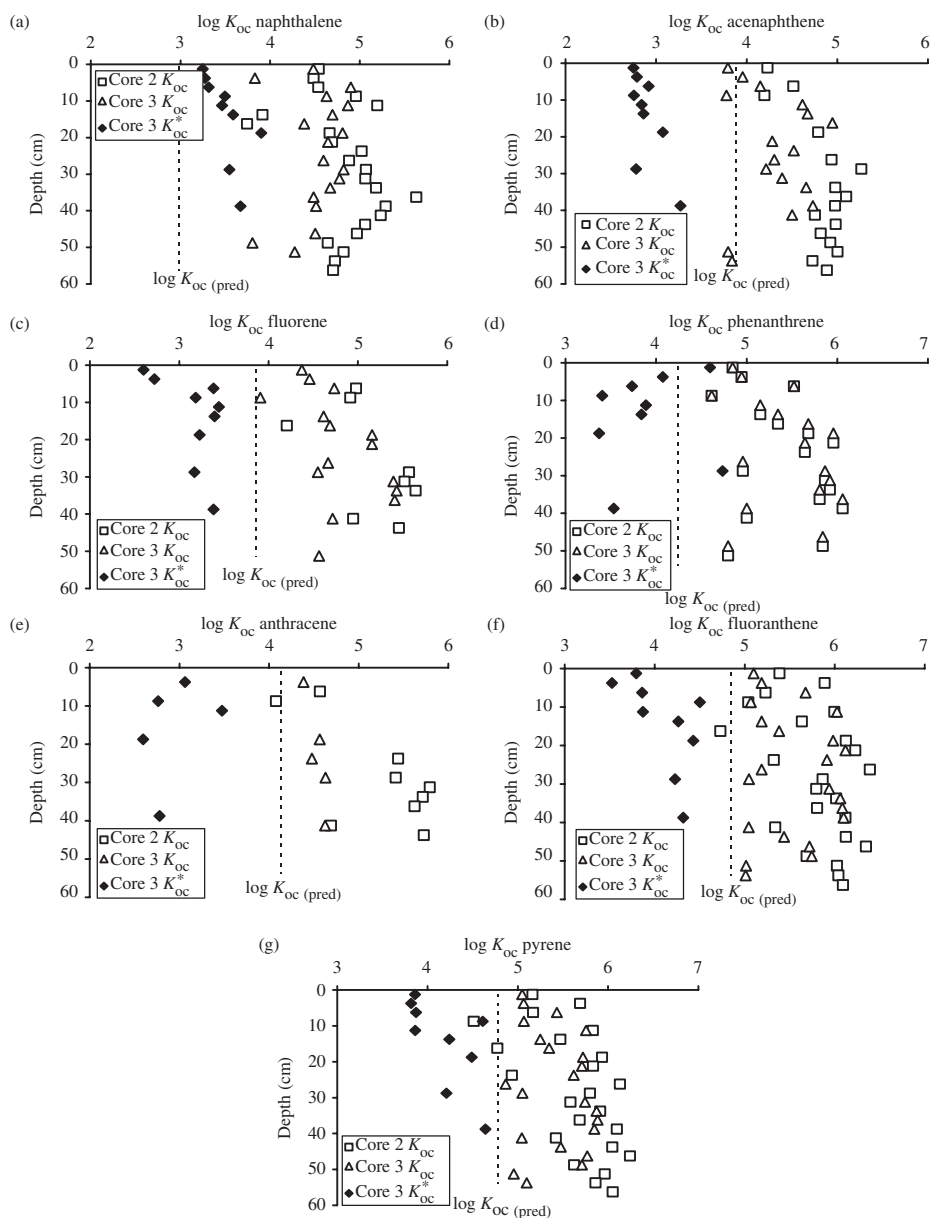


Figure 6. Variations in the organic carbon normalized partition coefficient between sediment/dissolved (K_{oc}) and between sediment/(dissolved + colloidal) (K_{oc}^*) in sediment cores from the Mersey Estuary. Predicted values of $\log K_{oc}$ were derived from the relationship $\log K_{oc} = \log K_{ow} - 0.317$ [34].

4. Conclusions

Results presented here illustrate the importance of phase differentiation in the evaluation of PAH fate and potential toxicity. If the combined (dissolved + colloid-associated) porewater PAH concentrations are considered, the observed levels of 6800–25,560 ng L⁻¹ have exceeded the range (2200–9200 ng L⁻¹) suggested by

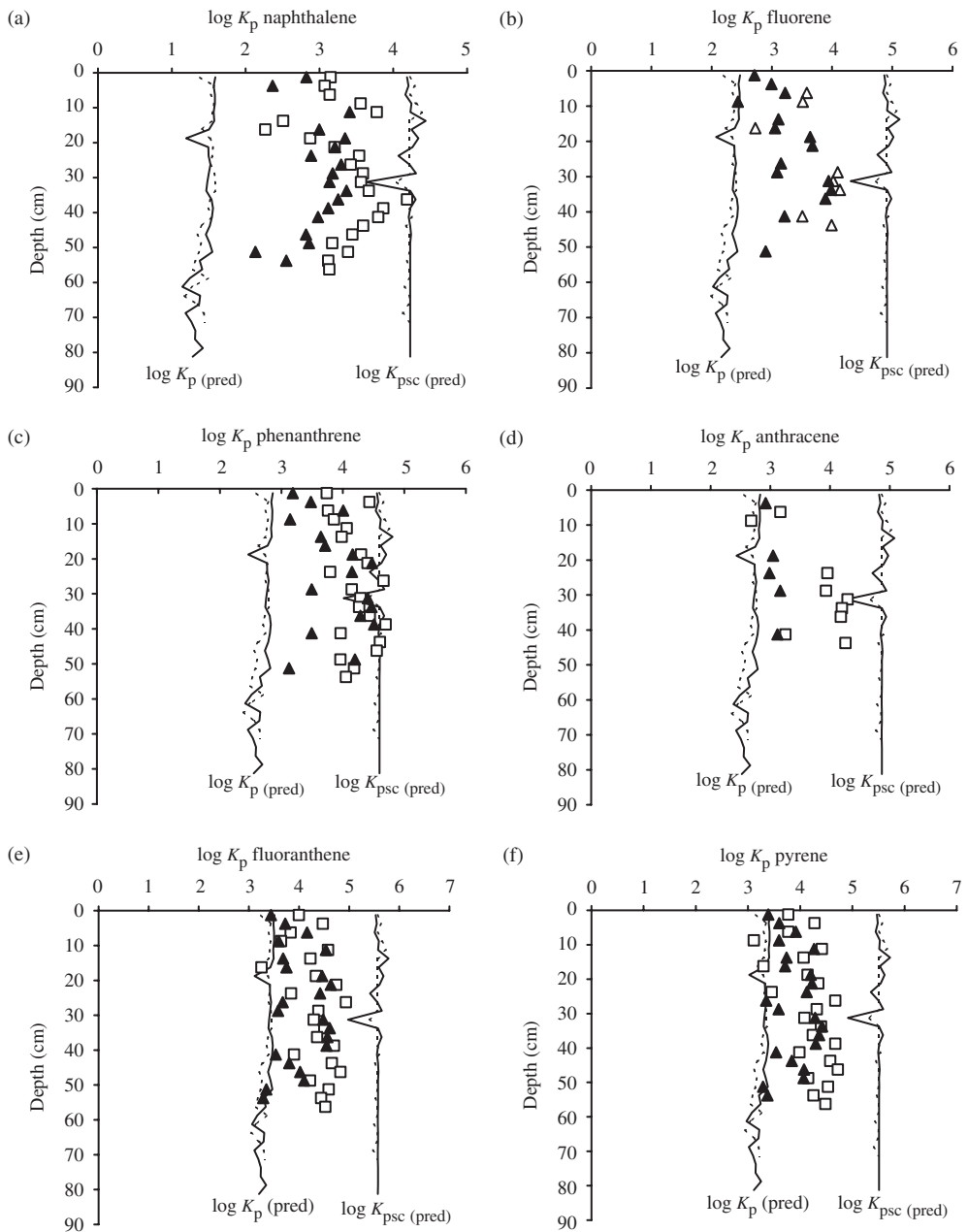


Figure 7. Comparison of partition coefficients measured from field data and those predicted based on partition models. Observed $\log K_p$ values for core 2 (\square) and core 3 (\blacktriangle), predicted $\log K_p$ ($\log K_{p(\text{pred})}$) values for core 2 (—) and core 3 (---) and predicted $\log K_p$ ($\log K_{psc(\text{pred})}$) values for core 2 (—) and core 3 (---). The $\log K_{p(\text{pred})}$ was calculated from the relationship: $\log K_{oc} = \log K_{ow} - 0.317$ [34]. The $\log K_{psc(\text{pred})}$ was calculated from the relationship: $K_p = K_{oc}f_{oc} + K_{sc}f_{sc}$ [8].

Barron *et al.* as causing deleterious effects on shrimps [35]. However, if, as suggested by DiToro *et al.*, it is the dissolved fraction that is responsible for biological effects, then the observed levels of 66–1050 ng L⁻¹ should not pose such a threat [7]. It is likely that the levels of contamination measured in the Mersey should not pose a short-term threat to organisms in the area. However, a prolonged exposure to moderate PAH concentrations and the potential for release of such compounds from contaminated sediments and porewater into the water column mean that potential toxicity to estuarine organisms nearby cannot be discounted.

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References

- [1] S. Kayal, D.W. Connell. *Estuar. Coast. Shelf Sci.*, **40**, 475 (1995).
- [2] J. Knutzen. *Sci. Total Environ.*, **163**, 107 (1995).
- [3] J.L. Zhou, H. Hong, Z. Zhang, K. Maskaoui, W. Chen. *Water Res.*, **34**, 2132 (2000).
- [4] K. Maskaoui, J.L. Zhou, H.S. Hong, Z.L. Zhang. *Environ. Pollut.*, **118**, 109 (2002).
- [5] R.J. Woodhead, R.J. Law, P. Matthiessen. *Mar. Pollut. Bull.*, **38**, 773 (1999).
- [6] P.M. Chapman, F. Wang, J.D. Germano, G. Batley. *Mar. Pollut. Bull.*, **44**, 359 (2002).
- [7] D.M. DiToro, C.S. Zarba, D.J. Hansen, W.J. Berry, R.C. Swartz, C.E. Cowan, S.P. Pavlou, H.E. Allen, N.A. Thomas, P.R. Paquin. *Environ. Toxicol. Chem.*, **10**, 1541 (1991).
- [8] Ö. Gustafsson, F. Haghseta, C. Chan, J. MacFarlane, P. Gschwend. *Environ. Sci. Technol.*, **31**, 203 (1997).
- [9] J.P. Gao, J. Maguhn, P. Spitzauer, A. Kettrup. *Int. J. Environ. Anal. Chem.*, **69**, 227 (1998).
- [10] S.E. McGroddy, J.W. Farrington, P.M. Gschwend. *Environ. Sci. Technol.*, **30**, 172 (1996).
- [11] J. Pörschmann, F.D. Kopinke, J. Pawliszyn. *J. Chromatogr. A*, **816**, 159 (1998).
- [12] M.J. Alperin, C.S. Martens, D.B. Albert, I.B. Suayah, L.K. Benninger, N.E. Blair, R.A. Jahnke. *Geochim. Cosmochim. Acta*, **63**, 427 (1999).
- [13] K. Næs, J. Axelman, C. Näf, D. Broman. *Environ. Sci. Technol.*, **32**, 1786 (1998).
- [14] Ö. Gustafsson, N. Nilsson, T.D. Bucheli. *Environ. Sci. Technol.*, **35**, 4001 (2001).
- [15] E.U. Ramos, S.N. Meijer, W.H. Vaes, H.J.M. Verhaar, J.L.M. Hermens. *Environ. Sci. Technol.*, **32**, 3430 (1998).
- [16] J. Poerschmann, F.-D. Kopinke. *Environ. Sci. Technol.*, **35**, 1142 (2001).
- [17] A.J. King, J.W. Readman, J.L. Zhou. *Anal. Chim. Acta*, **523**, 259 (2004).
- [18] S.B. Hawthorne, C.B. Grabanski, D.J. Miller, J.P. Kreitinger. *Environ. Sci. Technol.*, **39**, 2795 (2005).
- [19] J. King. The speciation of geochemical reactivity of polycyclic aromatic hydrocarbons in marine water and sediments. PhD thesis, University of Sussex (2003).
- [20] L.M. Tupas, B.N. Popp, D.M. Karl. *Mar. Chem.*, **45**, 207 (1994).
- [21] A.J. King, J.W. Readman, J.L. Zhou. *Mar. Pollut. Bull.*, **48**, 229 (2004).
- [22] Z.L. Zhang, H.S. Hong, J.L. Zhou, G. Yu. *Sci. Total Environ.*, **323**, 71 (2004).
- [23] G. Ohlenbusch, M.U. Kumke, F.H. Frimmel. *Sci. Total Environ.*, **253**, 63 (2000).
- [24] L.P. Burkhard. *Environ. Sci. Technol.*, **34**, 4663 (2000).
- [25] Y.P. Chin, G.R. Aiken, K.M. Danielsen. *Environ. Sci. Technol.*, **31**, 1630 (1997).
- [26] J.L. Zhou, T.W. Fileman, S. Evans, P. Donkin, J.W. Readman, R.F.C. Mantoura, S. Rowland. *Sci. Total Environ.*, **243/244**, 305 (1999).
- [27] D.P. Siantar, B.A. Feinberg, J.J. Fripiat. *Clays Clay Miner.*, **42**, 187 (1994).

- [28] T.S. Bates, P.P. Murphy, H.C. Curl, R.A. Feely. *Environ. Sci. Technol.*, **21**, 193 (1987).
- [29] J.R. Cretney, H.K. Lee, G.J. Wright, W.H. Swallow, M.C. Taylor. *Environ. Sci. Technol.*, **19**, 397 (1985).
- [30] W.E. Pereira, F.D. Hostettler, J.B. Rapp. *Mar. Environ. Res.*, **41**, 299 (1996).
- [31] E.J. Hoffman, G.L. Mills, J.S. Latimer, J.G. Quinn. *Environ. Sci. Technol.*, **18**, 580 (1984).
- [32] R.M. Dickhut, K.E. Gustafson. *Mar. Pollut. Bull.*, **30**, 385 (1995).
- [33] R.T. Simoneit. *Int. J. Environ. Anal. Chem.*, **22**, 203 (1985).
- [34] J.C. Means, S.G. Wood, J.J. Hassett, W.L. Banwart. *Environ. Sci. Technol.*, **14**, 1524 (1980).
- [35] M.G. Barron, T. Podrabsky, S. Ogle, R.W. Ricker. *Aquat. Toxicol.*, **46**, 253 (1999).