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Determination of polycyclic aromatic hydrocarbons in water by solid-phase microextraction–gas chromatography–mass spectrometry

A.J. King[a], J.W. Readman[b], J.L. Zhou[a,*]

[a] *Departments of Biology and Environmental Science, School of Life Sciences, University of Sussex, Falmer, Brighton BN19QJ, UK*
[b] *Plymouth Marine Laboratory, Prospect Place, The Hoe, Plymouth PL13DH, UK*

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Abstract

A solid-phase microextraction (SPME)–gas chromatography (GC)–mass spectrometry (MS) analytical method for the simultaneous separation and determination of 16 polycyclic aromatic hydrocarbons (PAHs) from aqueous samples has been developed, based on the sorption of target analytes on a selectively sorptive fibre and subsequent desorption of analytes directly into GC–MS. The influence of various parameters on PAH extraction efficiency by SPME was thoroughly studied. Results show that the fibre exposure time and the use of agitation during exposure are critical in enhancing SPME performance. The presence of colloidal organic matter (as simulated by humic acid) in water samples is shown to significantly reduce the extraction efficiency, suggesting that SPME primarily extracts the truly dissolved compounds. This offers the significant advantage of allowing the differentiation between freely available dissolved compounds and those associated with humic material and potentially biologically unavailable. The method showed good linearity up to 10 μg/l. The reproducibility of the measurements expressed as relative standard deviation (R.S.D.) was generally <20%. The method developed was then applied to extract PAHs from sediment porewater samples collected from the Mersey Estuary, UK. Total PAH concentrations in porewater were found to vary between 95 and 742 ng/l with two to four ring PAHs predominating. Results suggest that SPME has the potential to accurately determine the dissolved concentrations of PAHs in sediment porewater.

Keywords: SPME; PAHs; Porewater; Speciation; Mersey Estuary

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants arising from a variety of sources including fossil fuel combustion, oil spills and some industrial processes [1]. They are an important class of marine contaminants, since di- and tri-aromatic compounds are known to be narcotic to marine organisms such as the mussel, *Mytilus edulis* [2] while many high molecular mass PAHs are suggested to be either probable or possible human carcinogens [3]. Furthermore, PAHs have been identified as priority hazardous substances by the EC, and are part of a group of so-called persistent organic pollutants (POPs).

Upon entering the marine environment, PAHs distribute between various phases including water, particles and colloidal matter, and our understanding of such phase distributions of PAHs is still limited due to the difficulty of differentiating and quantifying the concentrations of PAHs in truly dissolved and colloid-bound phases. Even more difficult is the determination of the phase distributions of PAHs in sediment and associated porewater. Sediment porewater has been shown to play an important role in PAH speciation, PAHs can be found enriched in porewater in comparison to the levels found in overlying water [4,5]. It has been shown previously that PAHs associate strongly with dissolved organic carbon (DOC) in porewater, enhancing their apparent solubility but making them potentially unavailable to partition with water and sediment. It has been further suggested that it is only the dissolved fraction of PAHs that

* Corresponding author. Tel.: +44 1273 877318; fax: +44 1273 677196.
E-mail address: j.zhou@sussex.ac.uk (J.L. Zhou).

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is responsible for biological effects [6]. The differentiation between compounds truly dissolved in porewater and those associated with dissolved colloidal material is therefore particularly important. Furthermore, sediment perturbation or dredging may lead to the release of these compounds into the overlying water with subsequent implications for uptake by organisms. Hence, a detailed understanding of the distribution patterns of PAHs between sediment and porewater is vital to the establishment of sediment quality criteria.

In order to study the environmental fate and impacts of PAHs it is necessary to extract them from these matrices. One technique that is being used increasingly in the isolation and extraction of environmental contaminants is solid-phase microextraction (SPME). SPME is a solvent-free extraction technique that has been used by various researchers for a variety of environmental applications including the analysis of pesticides [7], PAHs [8], substituted benzene compounds [9] and trihalomethanes [10] in aqueous samples. SPME has a number of advantages over other water extraction techniques such as solid-phase extraction or liquid–liquid extraction. It uses little or no organic solvent, which is clearly of environmental benefit. Many of the more traditional extraction techniques involve multi-step procedures that always present the risk of analyte loss, while SPME achieves contaminant extraction and concentration in a single step thus reducing this risk. The technique is also relatively inexpensive with a single fibre being capable of performing between 50 and 100 extractions. Aqueous samples can be studied directly by immersing the fibres in the solution, while particulate as well as aqueous samples can be extracted by exposing fibres to the headspace above the samples. Finally, the technique can be used for in situ extraction of environmental samples, hence minimising the disturbance of sample matrices.

The aim of this research was to develop a robust SPME method that can be used for the analysis of PAHs in sediment porewater samples. The objectives were therefore to investigate the effects of the various sample parameters on the efficiency of extraction, and to apply the SPME method developed to the extraction of a range of PAHs from porewater samples. It is also hoped that SPME will predominantly extract the truly dissolved fraction of the analytes of interest, a hypothesis to be tested. If it proves positive, then SPME will provide an excellent means of determining the magnitude of PAH distributions between colloids and truly dissolved phase, information vitally important in speciation and fate studies.

2. Experimental

2.1. Standards

Reference PAHs (16 compounds, each at 2000 μg/ml) and deuterated internal standards (IS) containing acenaphthalene-d_{10}, phenanthrene-d_{10} and chrysene-d_{12} each at 500 μg/ml 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). Humic acid was purchased from Sigma-Aldrich (Dorset, England).

2.2. SPME device

The SPME device and polydimethylsiloxane fibres (100 μm film thickness) were purchased from Supelco. Fibres were conditioned in the injection port of a gas chromatography (GC) for 1 h according to the manufacturer's instructions before use. Blank desorptions of the fibre were carried out to ensure no contamination was present both before and during use.

2.3. Gas chromatography–mass spectroscopy (GC–MS)

Analysis was performed by exposing fibres to 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, 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 should take place in the hottest part of the GC injection port, this was determined through repeated sample extractions as described elsewhere [11]. A depth of 3 cm was found to provide maximum desorption and so has been used for all subsequent analysis. The GC temperature was programmed as follows: from 40 to 120 °C at a rate of 10 °C/min and then to 325 °C at a rate of 3 °C/min where it was held for 5 min. The MS was operated in electron impact (EI) mode with an ion source temperature of 250 °C. The target compounds were quantified in the selected ion monitoring (SIM) mode, using the molecular ion and one qualifier ions for each compound (Table 1). Selected samples were also analysed in full-scan acquisition for compound confirmation. Representative chromatographs obtained using both SPME and direct injection of a standard containing 19 PAHs are shown in Fig. 1. It can be seen that although the SPME technique shows a different response pattern to that obtained by direct injection, analyte resolution is comparable across the suite of compounds studied. For the more volatile compounds, in particular naphthalene and acenaphthylene, the relative response after sample introduction by SPME is slightly less than with direct injection. Such a decrease in response is due to the volatility of such low molecular mass molecules, resulting in a reduction in the sorption to the SPME fibre from solution. For the other compounds, the relative response after SPME is enhanced in comparison to results obtained by direct injection indicating strong sorption of these higher molecular mass compounds to the

Table 1
Quantitation and confirmation ions used in the analysis of PAHs by GC–MS

Compound	Quantitation ion	Confirmation ion
Naphthalene	128	127
Acenaphthylene	152	151
Acenaphthene-d_{10}	164	162
Acenaphthene	154	153
Fluorene	166	165
Phenanthrene-d_{10}	188	187
Phenanthrene	178	176
Anthracene	178	176
Fluoranthene	202	101
Pyrene	202	101
Benz[*a*]anthracene	228	114
Chrysene-d_{12}	240	239
Chrysene	228	114
Benzo[*b*]fluoranthene	252	126
Benzo[*k*]fluoranthene	252	126
Benzo[*a*]pyrene	252	126
Indeno[1,2,3-*cd*]pyrene	276	138
Dibenz[*a*,*h*]anthracene	278	139
Benzo[*ghi*]perylene	276	138

SPME fibre and therefore the concentrating effect of this technique.

2.4. SPME extraction

There are a number of factors that may influence the efficiency of the SPME technique including sample temperature, pH and salinity, the length of time fibres are exposed to samples and whether or not samples are agitated during extraction. In order to develop an SPME method for the extraction of PAHs from porewater, method development was undertaken in two stages. Preliminary experiments were carried out to determine which of these parameters were crucial in the extraction of PAHs from water samples [12]. Results suggested that changing sample pH, salinity and temperature had little effect on the extraction of PAHs so these were not investigated further. Fibre exposure time clearly had an effect on extraction of naphthalene and benzo[*a*]pyrene so the effect of changing extraction time on all 16 PAHs was studied in detail. In these method development experiments, samples of ultra-pure water (30 ml) were spiked with PAH standard (16 compounds) and three internal standards for compound quantification each at a concentration of 10 μg/l and the fibre was immersed in solutions for between 5 and 60 min without sample agitation. These experiments were repeated with sample agitation by ultrasonication. In all cases, the SPME device was transferred immediately to the GC, where analysis was carried out using the method described previously. Each analysis was carried out in triplicate. The spiking concentration of 10 μg/l is relatively high but can be found in highly contaminated sites [5] and afforded ease of detection. The effect of the DOC concentration on extraction efficiency was then extensively studied as this aspect is not well understood. In these experiments, humic acid, with an organic carbon content of 38.28% was chosen as a representative

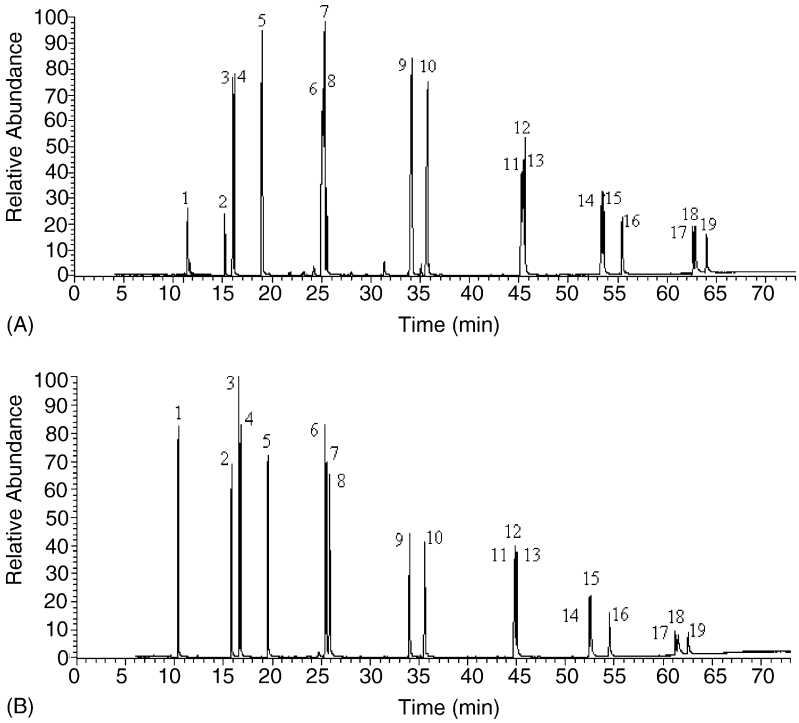

Fig. 1. Chromatogram obtained from (A) an SPME extraction from a 1 ml solution of 19 PAHs (10 μg/l) in water and from (B) a 1 μl injection of 19 PAH standard (10 ng/μl) in hexane. Peak numbers correspond to (1) naphthalene, (2) acenaphthylene, (3) acenaphthene-d_{10}, (4) acenaphthene, (5) fluorene, (6) phenanthrene-d_{10}, (7) phenanthrene, (8) anthracene, (9) fluoranthene, (10) pyrene, (11) benz[*a*]anthracene, (12) chrysene-d_{12}, (13) chrysene, (14) benzo[*b*]fluoranthene, (15) benzo[*k*]fluoranthene, (16) benzo[*a*]pyrene, (17) indeno[1,2,3-*cd*]pyrene, (18) dibenz[*a*,*h*]anthracene and (19) benzo[*ghi*]perylene.

colloidal material. Portions of humic acid were dissolved in ultra-pure water to prepare solutions with a range of DOC concentrations between 0 and 38 mg/l. Sub-samples (30 ml) were again spiked with PAH standard (16 compounds) at a concentration of 10 μg/l. Samples were left for an hour to allow compound–DOC interactions and then, as suggested by previous results, fibres were exposed to the solutions for 45 min each and agitated by ultrasonication during extraction.

2.5. Analysis of environmental samples

Sediment cores were collected from the Mersey Estuary, UK in June 2001 and frozen. They were then sliced at 2.5-cm intervals. Each slice was well mixed and then centrifuged to separate sediment and porewater. Porewater samples were collected in glass vials with Teflon-lined septa, to which IS at a concentration of 1 μg/l was then added. PAHs were extracted using SPME with a fibre exposure time of 45 min and agitation by ultrasonication. Quantification was carried out by comparing the sample response for each compound and the IS with the response obtained from a desorption of a standard solution containing 10 μg/l of the 16 PAHs of interest and the three deuterated internal standards. Extractions from the standard solution were carried out using exactly the same parameters used to analyse samples and analyte concentrations calculated using relative response factors.

3. Results and discussion

3.1. Effect of sample agitation and fibre exposure time on PAH extraction

Agitation of the sample during fibre exposure has been shown to enhance analyte extraction and reduce extraction time [13]. Results (Fig. 2) clearly show that agitation dramatically enhances extraction of a range of PAHs. It can also be seen that extraction times can be reduced through the use of ultrasonication. Without sample agitation, periods in excess of 1 h are necessary before equilibrium can be reached, when agitation is applied it can be seen that a fibre exposure time of 45 min provides optimum extraction. The decrease in extraction efficiency after 45 min has been observed for other compounds including certain pesticides [14] and attributed to a lack of stability of compounds in water, it may also be due to movement of analytes into the headspace above the sample over time that would in turn lead to reduced sample concentrations.

3.2. Effect of DOC concentration on extraction

Sediments represent an important sink for POPs due partly to the high levels of dissolved organic matter in porewater. Previous work showed that the levels of DOC in porewater

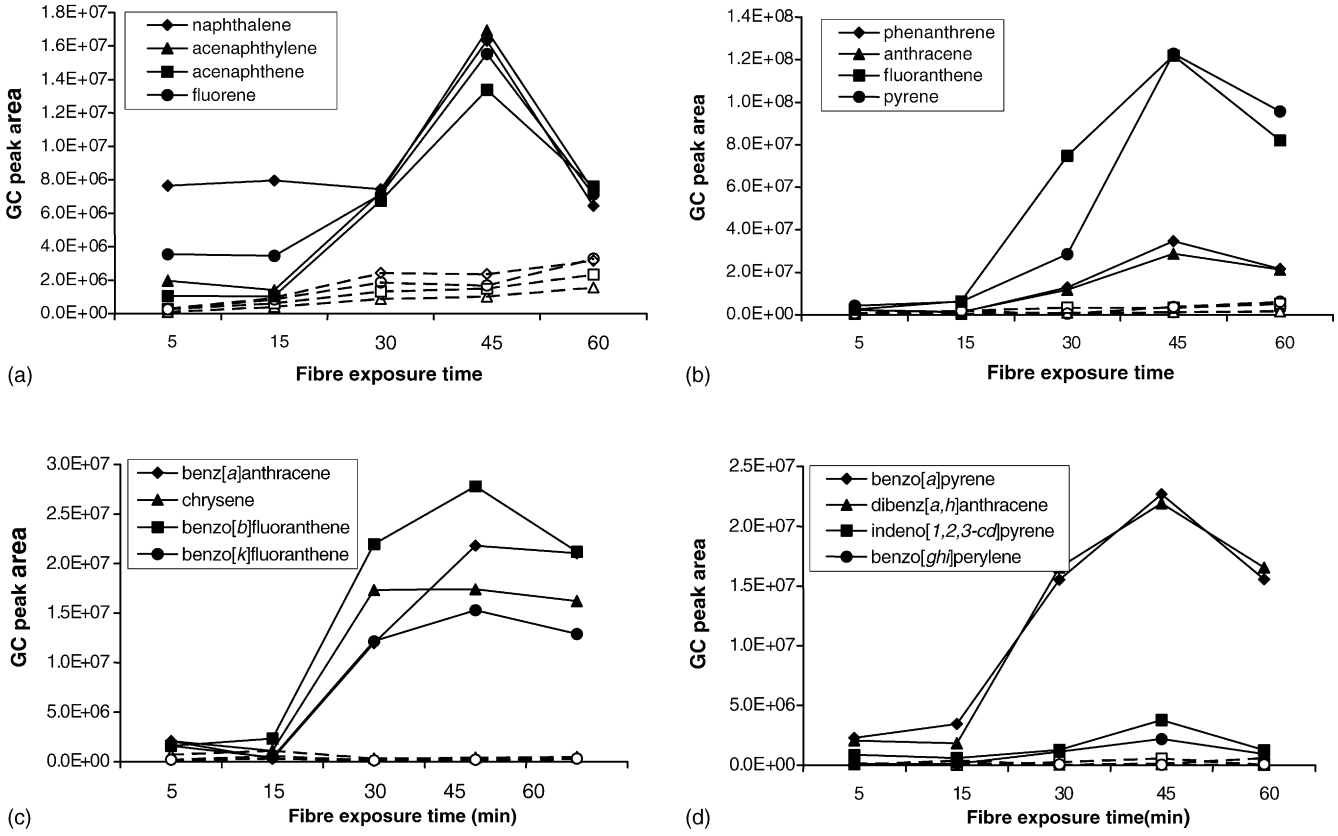

Fig. 2. The effect of sample agitation and fibre exposure time on the extraction of 16 PAHs (10 μg/l) by SPME (mean of three determinations, S.D. omitted for clarity). Filled symbols show results for extraction with agitation, open symbols show results for extraction without agitation.

were between 10 and 50 mg/l in cores from the lower Hudson river [14], and between 40 and 60 mg/l in cores from Germany [15]. Even DOC levels as high as 200 mg/l were measured in the deepest sediment layers in cores from Los Angeles, USA [16].

As shown in Fig. 3, it is clear that extraction of all compounds decreases substantially with increasing humic acid concentration, particularly between 0 and 10 mg/l, indicating that in the presence of humic acid PAHs become less available for extraction by SPME. This shows that SPME extracts primarily the truly dissolved fraction of analytes in porewater, leaving behind the fraction bound to colloidal particles. The results are consistent with those obtained by Pörschmann et al. [17] and Ramos et al. [18] who observed a similar decrease in the concentration of a range of organic compounds extracted by SPME in the presence of dissolved organic material. Results suggest that the effect of DOC on analyte extraction is greatest at low concentrations i.e. between 0 and 10 mg/l DOC and that with further increases in DOC concentration the effect on extraction by SPME is less significant. This may indicate that in the short time-scale between compound spiking and extraction, interaction between compounds and DOC reaches a maximum rapidly so little further association between the two occurs with further increasing DOC concentration. Periods of up to 5 days have been observed to be necessary to reach equilibrium between PAHs and humic acid in previous spiking experiments [19]. Similarly, association of PAHs with both sediment and dissolved organic material is believed to occur via a biphasic mechanism [20] with initial rapid compound association followed by a slower, retarded sorption process. It is likely therefore that, in the experiments described here only the initial, rapid, association of PAHs with DOC had occurred and that extended periods between sample spiking and extraction would have led to an increase in the partitioning of compounds to DOC, resulting in an increased reduction in extracted concentrations with increasing DOC concentration. In the application of the technique to environmental samples where equilibrium between the dissolved and DOC associated phases has been reached, SPME should allow for the determination of dissolved PAH concentrations.

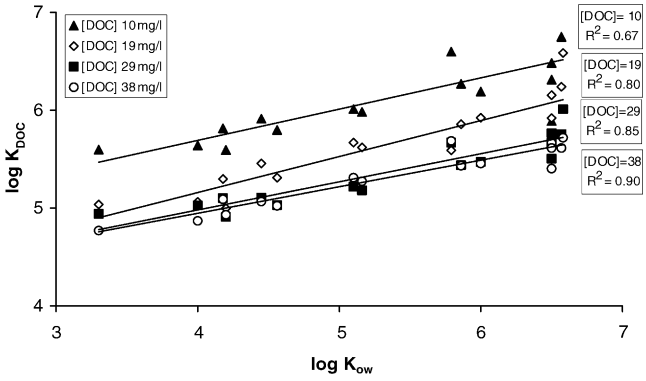

Fig. 4. The relationship between log K_{DOC} and log K_{ow} with changing aqueous DOC concentrations.

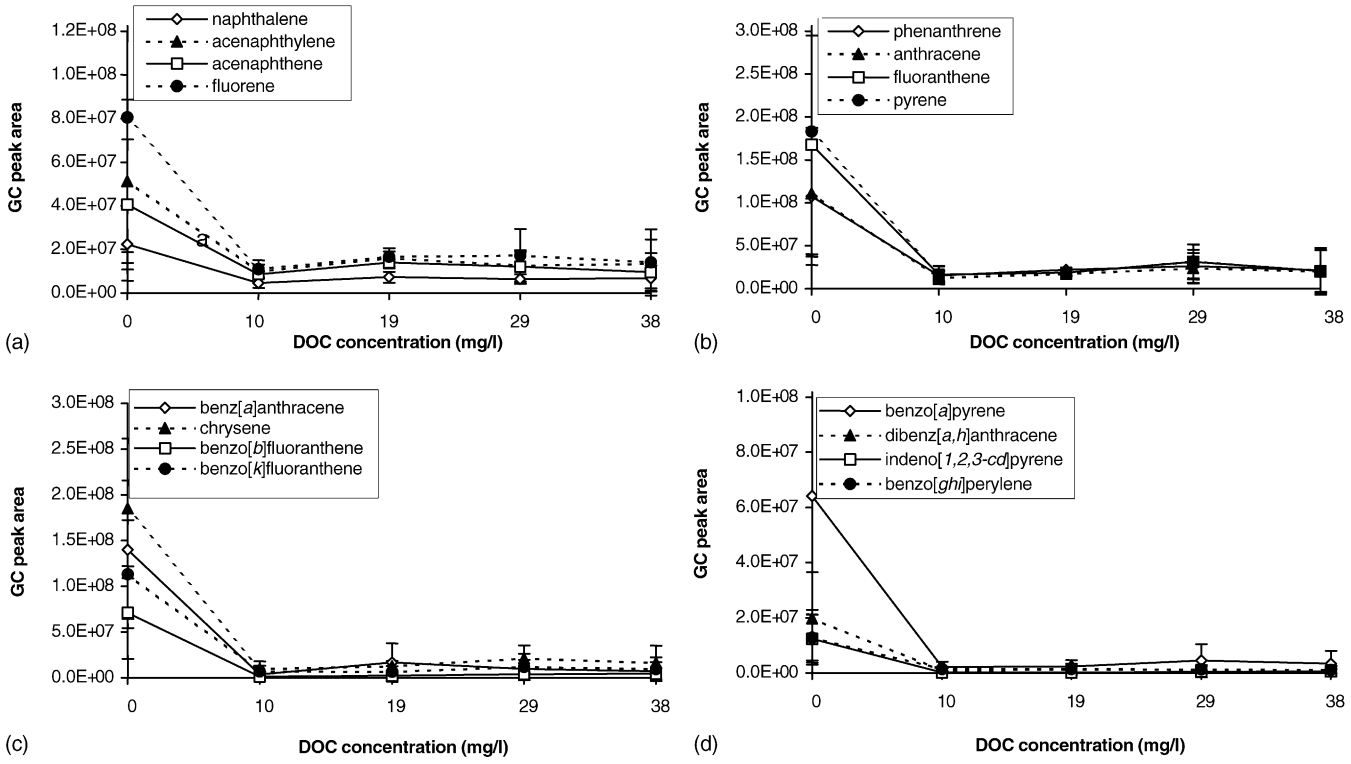

Fig. 3. The effect of sample DOC concentration on the extraction of PAHs by SPME (mean ± S.D.). Aqueous solutions containing 0–38.28% DOC and 10 μg/l 16 PAHs extracted with fibre exposure time of 45 min and agitation by ultrasonication.

Table 2
The limit of detection and linear range for the extraction of PAHs by SPME. Fibre exposure time 45 min with agitation by ultrasonication during extraction for all samples

Compound	LOD (ng/l)	Linear range (μg/l)	Correlation coefficient (r^2)	P
Naphthalene	3	0.01–10	0.76	<0.05
Acenaphthylene	3	0.01–10	0.84	<0.05
Acenaphthene	6	0.01–10	0.85	<0.05
Fluorene	2	0.01–10	0.78	<0.05
Phenanthrene	17	0.02–10	0.86	<0.05
Anthracene	20	0.03–10	0.89	<0.05
Fluoranthene	1	0.01–10	0.78	<0.05
Pyrene	1	0.01–10	0.77	<0.05
Benz[*a*]anthracene	29	0.03–10	0.72	<0.05
Chrysene	5	0.01–10	0.87	<0.05
Benzo[*b*]fluoranthene	27	0.03–10	0.78	<0.05
Benzo[*k*]fluoranthene	13	0.02–10	0.87	<0.05
Benzo[*a*]pyrene	18	0.02–10	0.75	<0.05
Indeno[1,2,3-*cd*]pyrene	21	0.03–10	0.88	<0.05
Dibenz[*a*,*h*]anthracene	14	0.02–10	0.85	<0.05
Benzo[*ghi*]perylene	12	0.02–10	0.82	<0.05

The interaction of PAHs and DOC (as represented by humic acid here) can be described as follows:

$$\mathrm{PAH_{free}} + \mathrm{DOC} \leftrightarrow \mathrm{PAH_{DOC}} \quad (1)$$

where $\mathrm{PAH_{free}}$ is the truly dissolved PAHs, while $\mathrm{PAH_{DOC}}$ is PAHs bound to DOC.

At equilibrium, the distribution coefficient (K_d) of PAHs between colloids and truly dissolved phase can be calculated:

$$K_d = \frac{\mathrm{PAH_{DOC}}}{\mathrm{PAH_{free}}} \quad (2)$$

K_d can be normalised to DOC concentration (kg/l) to derive K_{DOC}:

$$K_{DOC} = \frac{K_d}{\mathrm{DOC}} \quad (3)$$

The results for log K_{DOC} are plotted against log K_{ow}, a measure of compound hydrophobicity (Fig. 4). It is clear that the distribution coefficients for all 16 PAHs declined substantially over the DOC concentrations studied. A similar decrease in distribution coefficients have been reported for PAHs and other hydrophobic compounds such as DDT and PCBs [21]. They attributed such a relationship to the forma-

Table 3
PAH concentration (ng/l) in porewater samples from a sediment core from the Mersey Estuary, determined using SPME, fibre exposure time 45 min with agitation by ultrasonication during extraction

Depth (cm)	Naphthalene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	∑PAHs
0–2.5	67	75	26	58	<20	77	106	409
2.5–5	275	43	29	44	42	62	109	604
5–7.5	<3	46	17	17	<20	28	58	166
7.5–10	<3	66	105	126	<20	100	125	522
10–12.5	27	21	<2	<17	<20	14	32	95
12.5–15	<3	16	28	45	<20	85	86	260
15–17.5	62	16	33	45	<20	75	92	323
17.5–20	33	<6	10	12	57	15	32	159
20–22.5	19	20	6	7	<20	13	32	96
22.5–25	65	23	<2	12	50	15	33	198
25–27.5	29	19	32	<17	<20	111	275	467
27.5–30	69	71	52	94	85	162	189	721
30–32.5	41	20	7	9	<20	18	34	129
32.5–35	35	16	6	10	<20	17	31	116
35–37.5	30	<6	7	15	<20	19	36	107
37.5–40	54	20	<2	6	<20	15	30	126
40–42.5	107	49	35	76	71	181	220	739
42.5–45	<3	<6	<2	<17	<20	73	83	156
45–47.5	159	<6	<2	<17	<20	37	38	234
47.5–50	65	<6	<2	7	<20	26	31	129
50–52.5	268	78	29	74	<20	130	162	742
52.5–55	103	47	<2	<17	<20	100	102	353

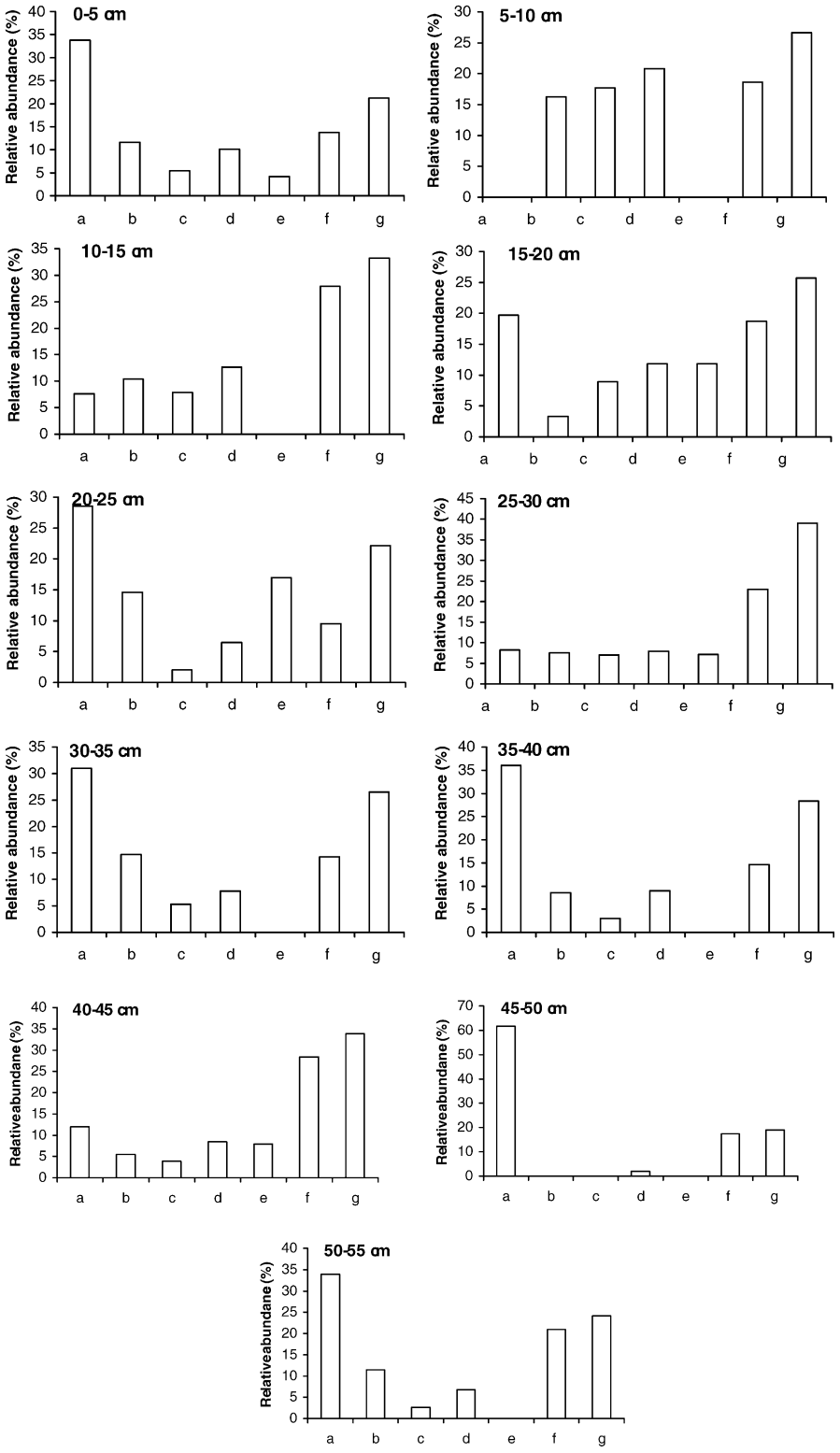

Fig. 5. Changes in the relative abundance (percentage of ∑PAH, ng/l) of (a) naphthalene, (b) acenaphthene, (c) fluorene, (d) phenanthrene, (e) anthracene, (f) fluoranthene and (g) pyrene at 5-cm intervals in porewater samples.

tion of charge–transfer complexes between PAHs and humic acids. Results also show that log K_{DOC} increases with increasing log K_{ow}. This indicates that the degree of interaction with humic acid is related to compound hydrophobicity, with more hydrophobic compounds interacting more strongly with humic material and therefore being removed to a greater extent from the aqueous phase.

3.3. Quality control

It has been shown that SPME fibres should be immersed in samples for 45 min during which the sample should be agitated using ultrasonication, modification to the sample in terms of pH or salinity is unnecessary as is heating during extraction. The fitness for purpose of the technique was then investigated in a series of quality control experiments as shown in Table 2. The linearity of the technique was measured by extractions of a range of standard solutions containing all 16 PAHs. Plots of response against PAH concentration were made and a best fit straight line plotted, values of r^2 were found to be between 0.72 and 0.89. The limit of detection (LOD) of the SPME technique was calculated as three times the standard deviation of the baseline noise from 10 blank desorptions for each compound and found to vary between 1 and 29 ng/l. Precision (given as relative standard deviation (R.S.D.)) for each compound was calculated from 10 extractions and desorptions from standard solutions, with R.S.D. generally < 20%.

3.4. Application of SPME to porewater samples

Following successful method development, SPME was used to extract PAHs from sediment porewater samples collected from the Mersey Estuary. Table 3 shows the depth profiles for the PAH concentrations in porewater through the sediment core. Changes in the relative abundance of the measured compounds at intervals throughout the sediment core are illustrated in Fig. 5. It can be seen that a range of PAHs at varying concentrations were found in the porewater samples. Generally it was the four-ring compounds that were found in the highest concentrations, the largest contribution to this arising from the compounds fluoranthene and pyrene. Naphthalene also dominated in many samples. Concentrations of five- and six-ring PAHs were typically below the limit of detection for the technique, this may be due to a high DOC concentration in the porewater. Total PAH concentration in porewater varied widely with depth in the sediment core and several regions of high concentration can be recognised, the highest (742 ng/l) occurred at between 50 and 52.5 cm.

4. Conclusions

A trace analytical method based on SPME–GC–MS has been developed for the extraction and analysis of 16 priority PAHs, from water samples. There are several factors that can influence extraction efficiency but to varying degrees. Solution properties such as sample pH and salinity have a small influence on the efficiency of extraction while fibre exposure time and the application of sample agitation are critical to the amount extracted, with a fibre exposure time of 45 min shown to provide optimum extraction when the sample is being agitated by ultrasonication. The DOC content of the sample has a crucial role on the availability of PAHs for extraction by SPME, with extraction efficiency decreasing with increasing DOC concentration for all the PAHs studied. The method was applied to sediment porewater samples from the Mersey Estuary, UK, for determining PAH concentrations.

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