

Using solid-phase microextraction to evaluate the role of different carbon matrices in the distribution of PAHs in sediment-porewater systems of the Baltic Sea

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Abstract

Purpose The speciation of polycyclic aromatic hydrocarbons (PAHs) in sediment-porewater systems affects both the chemical fate and bioavailability of these compounds. PAHs may be dissolved or sorbed to sediment particles or dissolved organic carbon (DOC). Furthermore, soot carbon has been shown to control the sorption of PAHs onto particles in natural

waters. The present study investigates the distribution of individual PAHs among these three phases by examining sediments from the western Baltic Sea, focusing on a highly contaminated former dumping area and evaluating the importance of soot-carbon partitioning.

Materials and methods Freely dissolved concentrations of nine PAHs were measured in the porewater of sediment samples using solid-phase microextraction, a cost- and time-efficient method with detection limits in the lower nanogram per liter range. Additionally, total sediment and total porewater concentration were measured in sediments to calculate the distribution of PAHs between the three compartments. Dissolved organic carbon, total organic carbon, and soot content were analyzed for calculation of partitioning coefficients.

Results and discussion Soot-carbon control partitioning between the dissolved and particulate phases and the partition coefficients are orders of magnitude higher than would be expected on the basis of organic carbon/water partitioning alone. The carbon-normalized partition coefficient for the distribution of individual PAHs between DOC and the dissolved phase exhibit no more than a weak correlation with hydrophobicity. This indicates that there are different sorption mechanisms at work in DOC than in particulate organic carbon and soot.

Conclusions The sediment-water partition coefficient is a key parameter in the risk assessment of PAHs in sediments, as it determines the chemical activity of the PAHs in water, which in turn determines bioconcentration. The PAH partitioning observed in this study suggest that partitioning models are of limited value in PAH risk assessment if the sorbents under study differ markedly from those used to develop the model. In such cases, PAH risk assessment should rely on measurements of PAH activity. In this work, we showed how such measurements can be performed in a comparatively simple way.

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1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are some of the most frequently occurring organic contaminants of concern in sediment. The mobility, and consequently the bioavailability, of PAHs associated with sediments depend on the porewater concentration of these compounds. This concentration is controlled by the sorption to the sediment matrix (Schwarzenbach et al. 2003). The PAH sorption affinity can be described with the aid of sediment-porewater partition coefficients (K_D). Non-polar organic compounds like the PAHs are believed to sorb to the sediment particles as a result of partitioning between the porewater and the sediment organic matter (Karickhoff et al. 1979; Schwarzenbach and Westall 1981; Karickhoff 1981). On the basis of measured porewater and sediment concentrations, McGroddy and Farrington (1995) showed that only a fraction of the solvent-extractable PAHs was available for rapid partitioning into the sediment porewater. PAH porewater concentrations of three sediment cores from Boston Harbor (MA) were significantly lower than the values predicted by two and three-phase equilibrium-partitioning models. Furthermore, McGroddy et al. (1996) stated that the source of PAHs affected their partitioning between porewater and sediment. Combustion-derived PAHs appear to be more associated with particles than petrogenic PAHs.

PAHs tend to associate with any dissolved organic matter (DOM) in the porewater. This may enhance their concentrations beyond values predicted by their water solubility (Pörschmann et al. 1998). To calculate K_D , therefore, the freely dissolved porewater concentration must be determined. In this context it should be noted that several properties and effects of organic pollutants in aquatic environments, including transport behavior, environmental fate, bioavailability and toxicity, depend only on their freely dissolved concentration in water. The freely dissolved concentration of PAHs is, for example, available for uptake by benthic organisms or fish via passive diffusion through membranes (Servos and Muir 1989; Black and McCarthy 1988).

The sediment-porewater partition coefficient (K_D) expressed as follows:

$$K_D = \frac{c_S}{c_{\text{free}}} \quad (1)$$

c_{free} Freely dissolved porewater concentration ($\mu\text{g/L}$)

c_S Sediment concentration, available for equilibrium partitioning ($\mu\text{g/kg}$)

Earlier, sorption was normalized to the total organic carbon (OC) content with OC–water distribution ratios (K_{OC}) describing the sorption strength (Karickhoff et al. 1979; Schwarzenbach and Westall 1981; Karickhoff 1981). It has been shown that, in addition to the amorphous organic matter, the soot-like fraction also contributes to the sorption capacity of the sediment (Cornelissen et al. 2006). Gustafsson et al. (1997) included the soot phase in their K_D calculations:

$$K_D = f_{OC}K_{OC} + f_{SC}K_{SC} \quad (2)$$

f_{SC} Soot-carbon weight fraction of solid phase ($\mu\text{g/kg}$ solid)

f_{OC} Organic carbon weight fraction of solid phase ($\mu\text{g/kg}$ solid)

K_D Solid-water distribution coefficient (L/kg)

K_{SC} Soot-carbon-normalized distribution coefficient (L/kg soot)

K_{OC} Organic carbon normalized partitioning coefficient (L/kg organic carbon)

To calculate the partitioning coefficients between water and sediment, the freely dissolved porewater concentration must be measured. Many studies that evaluate partitioning processes between sediment and porewater could not distinguish between the freely dissolved and dissolved organic carbon (DOC) associated phase. If the DOC content was found to be low, some authors neglected the DOC fraction. Other studies used the DOC content to estimate K_{DOC} values in conjunction with predictions of three-phase distribution models in order to estimate the freely dissolved concentrations (McGroddy and Farrington 1995; Mitra et al. 1999; Persson et al. 2002; Accardi-Dey and Gschwend 2003). So the calculated partitioning coefficient can only be an estimate. The measurement of the freely dissolved porewater concentration represents an analytical challenge because of the difficulties in determining this parameter. A number of studies have developed approaches to distinguish between the freely dissolved and sorbed phases, including dialysis (Escher and Schwarzenbach 1996), solubility enhancement (Chiou et al. 1986), fluorescence quenching (Backhus and Gschwend 1990) as well as techniques based on passive partitioning such as semipermeable membrane devices (Huckins et al. 1990; Verweij et al. 2004), C18 empore disks (Södergren 1987), LDPE strips (Booij et al. 2003) and solid-phase microextraction (Pörschmann et al. 1997; Van der Waals et al. 2004, Ossiander et al. 2008).

Nonlinear adsorption of PAHs onto soot or black carbon particles was accurately described in laboratory sorption experiments (e.g., Bucheli and Gustafsson 2000; Accardi-Dey and Gschwend 2003; Jonker and Koelmans 2002; Cornelissen et al. 2005; Hawthorne et al. 2007; Barthe et al. 2008). While these studies from laboratory-spiked experiments were extrapolated to propose that this is also an important process in marine environments only a few studies are available that studied the PAH distribution and the actual influence of black carbon in sediments of the real marine environment (e.g., Gustafsson and Gschwend 1997; Persson et al. 2002; Sánchez-García et al. 2010). The aim of this study is therefore to apply the solid-phase micro-extraction technique to field sediment samples in order to measure the freely dissolved (i.e., bioavailable) concentration of PAHs in sediment, focusing on a highly contaminated dumping area in the western Baltic Sea. On the basis of the freely dissolved porewater concentrations, the site-specific partition coefficients between the dissolved and sediment as well as dissolved organic carbon phases were calculated and the influence of the sediment matrix was evaluated.

2 Experimental section

2.1 PAH source identification

PAH contamination sites are usually the result of anthropogenic processes. Two major anthropogenic sources are known: (1) petroleum, including crude oil and its refined products and coals (petrogenic PAHs) and (2) residues from incomplete combustion of organic matter (pyrogenic PAHs). PAH ratios are widely used to diagnose sources (e.g., Budzinski et al. 1997; Lima et al. 2005). Different diagnostic ratios are employed in this study ($\text{Ant}/[\text{Phe} + \text{Ant}]$, $\text{Fluo}/[\text{Fluo} + \text{Pyr}]$, $\text{BaA}/[\text{BaA} + \text{Chr}]$, Combustion PAH/ Σ 16 US-EPA-PAH (Fig. 1)), which allow us to distinguish pyrogenic versus petrogenic origin (Yunker et al. 2002; Hwang et al. 2003). Source identification was done because one aim of this study was the evaluation of the influence of the PAH source on the mobility of sediment-bound PAHs with regard to a high contaminated dumping area as well as to the impact of the accident of the oil tanker “Baltic Carrier” in the western Baltic Sea (Table 1).

2.2 Sampling stations

2.2.1 Dumping site

This station (dumping site (DS)) is located in the inner part of the Mecklenburg Bight and represents a historical dumping site (Fig. 2, Table 1). Leipe et al. (1998) identified

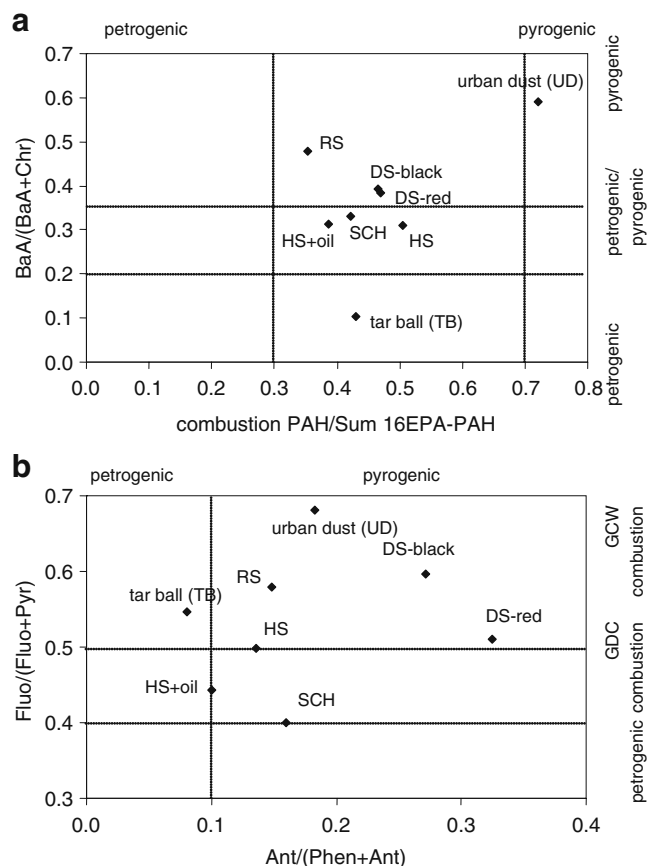


Fig. 1 Source identification using diagnostic PAH ratios: **a** benzo[a]anthracene to benzo[a]anthracene plus chrysene ($\text{BaA}/(\text{BaA} + \text{Chr})$) ratio versus combustion PAHs (sum of Fluo, Pyr, BaA, Chr, BbF, BkF, BaP, Inp) to total PAHs (combPAH/Sum 16 US-EPA PAH); **b** fluoranthene to fluoranthene plus pyrene ($\text{Fluo}/(\text{Fluo} + \text{Pyr})$) versus anthracene to anthracene plus phenanthrene ($\text{Ant}/(\text{Ant} + \text{Phe})$) ratio. Combustion sources: GDC gasoline, diesel, and crude oil; GWC grass, wood, and coal (after Sánchez-García et al. 2010)

this site as a “hot spot” with high pollutant concentrations. In the late 1950s and early 1960s, industrial waste products containing high concentrations of heavy metals and organic pollutants (e.g., PAHs) were dumped at this site. A high resolution acoustic sediment profiling was performed on basis of the assumption, that the dumped material is characterized by a higher density than the surrounding natural muddy sediment (SES 2000, Univ. Rostock). This technique enabled us to follow the sediment layers in the topmost centimeters of the sediment column for selecting suitable core sampling positions. On board the ship, the cores were optically examined for the presence of dumped material. The composition of the waste material can be characterized as a mixture of black carbon substances, partly greasy in the form of heavy oil, tar, and soot mixed with heavy metal oxides (black material, DS-black) and reddish dusts or fine-grained material with mainly iron oxides together with some mixed ashes originating from

Table 1 Characteristics and location of sediment samples

Station	North	East	Dominant PAH source	Sampling method	Description
RS	54°18.94	11°33.02	Pyrogenic	Gravity corer	Reference station
SCH	54°06.08	11°05.96	Petrogenic/Pyrogenic	Gravity corer	Shipping channel
DS-red	54°04.77	10°59.69	Pyrogenic	Gravity corer	Dumping site (red-colored sediment)
DS-black	54°04.78	10°59.69	Pyrogenic	Gravity corer	Dumping site (black-colored sediment)
TB	54°04.79	10°59.69	Petrogenic	Mussel dredge	Dumping area (tar ball from oil contamination from the “Baltic Carrier” accident)
UD	–	–	Pyrogenic	–	Standard material (urban dust material)
HS	–	–	Pyrogenic	–	Standard material (Toronto Harbour standard reference sediment)
HS+oil	–	–	Pyrogenic/Petrogenic	–	Standard material contaminated with “Baltic Carrier” oil spill (1:1, v/v)

various high-temperature industrial processes such as slag from smelting plants and steelworks (red material, DS-red). Both materials were enriched in PAHs as well as in heavy metals (see Table 1). PAHs of pyrogenic origin dominate in the dumped material.

2.2.2 Reference station

This station (reference station (RS)), located in the outer Mecklenburg Bight about 25 nautical miles NE of the dumping site (see Fig. 2), was chosen to compare the data of the material from the dumping site with those of the

adjacent areas which are less polluted but are characterized by similar hydrographic conditions and sediment properties. Pyrogenic sources are dominating the PAH load of this sediment samples.

2.2.3 Shipping channel

This station (shipping channel (SCH)) is located in the center of the Mecklenburg Bight, directly below a shipping lane between Lübeck and Scandinavia. Source identification (see Fig. 1) has identified mixed petrogenic/pyrogenic PAH origin likely due to shipping traffic and discharges of oily waste in this area.

Fig. 2 Characteristics and location of sediment samples



2.2.4 “Baltic carrier” oil samples

One main pathway of PAHs to the marine environment is the release of oil (petrogenic PAH source). On March 29th 2001, the oil tanker “Baltic Carrier” collided with the bulk carrier “Tern” in the western Baltic Sea, near the naval border between Germany and Denmark. Because of the collision, 2,700 tons of bunker oil leaked from the cargo tanks into the western Baltic Sea. To simulate consequences of oil spills on sediments, an oil-contaminated sample was made by mixing the standard harbor sediment (HS) with the crude oil spilled in the “Baltic Carrier” accident (HS+oil). A tar ball (TB) that was found in a mussel dredge collected at the dumping site after the Baltic Carrier accident was also included as representative of a petrogenic source (station: TB; Table 1, Fig. 1).

2.2.5 Standard materials

Two standard materials were included in the investigations: an urban dust (UD) material (NIST, SRM 1649a) and a standard harbor sediment (HS; NWRI-EC-4, Toronto Harbour). The latter was also used to check the accuracy of the analytical procedure. Urban dust material was chosen because most of the PAHs were transported to the Baltic Sea in soot-bonded form via the atmosphere.

2.3 Analytical methods/procedure(s)

2.3.1 Chemicals

All solvents (analytical grade) were purified by distillation. Aluminum oxide and silica gel (MERCK, Darmstadt, Germany) as well as sodium sulfate powder (BAKER, Netherlands) were heated for 9 h in a muffle oven at 850°C, 400°C, and 450°C, respectively. Prior to use, Al₂O₃ and SiO₂ were partly deactivated with 15% and 3.5% deionised water, respectively. An external PAH standard was used for calibration of the gas chromatograph/mass chromatography (GC/MS) system and external standard quantification of the SPME devices (PAH Mix 45, Dr. Ehrensdoerfer). A mixture of deuterated PAHs from PROMOCHEM (naphthalene d-8, phenanthrene d-10, fluoranthene d-10, chrysene d-12, and perylene d-12, benzo(ghi)perylene d-12) was used for internal standard calibration and quantification of the sediment samples and in the total porewater extracts. All chemicals were checked for impurities by GC/MS measurements.

2.3.2 Sediment and total porewater concentration

An aliquot of homogenized sediment (2–3 g) was extracted by accelerated solvent extraction (ASE 200, DIONEX). The

wet samples were mixed and dried with approximately 15 g sodium sulfate, transferred into the ASE cartridges (11 ml) and the internal standard solution (100 µl of a 100 pg/µl PAH solution) was added. The extraction was carried out with 35 ml of an n-hexane/acetone mixture (3:2, v/v). Two static cycles with a temperature of 100°C and a pressure of 140 bar were carried out. The exhaustiveness of the extraction procedures was evaluated by conducting a second and third extraction of the sediment-filled ASE cartridges. A sub-sample of each sediment were freeze-dried (−40°C, 200 mbar vacuum) to analyze the water content of the samples.

Another aliquot of the wet sediment sample was centrifuged in 250 ml polycarbonate centrifuge bottles at 10,000 rpm (GS-6R centrifuge from BECKMAN). The supernatant was filtered through a precombusted 0.45-µm glass-fiber filter. The eluate was extracted twice with 10 ml of n-hexane by agitation for 15 min to measure the total porewater concentration (sum of freely dissolved and colloid bound concentrations).

The concentrated sediment and total porewater extracts (50 µl) were cleaned using solid-phase extraction through a column containing 5 g Al₂O₃ which eluted directly onto a second column containing 3 g silica gel. The elution was performed with 10 ml 50% n-hexane/CH₂Cl₂. After subsequent concentration of the extract to 200 µl, the PAH fraction was isolated by HPLC using a silica gel column (MERCK, LiChrospher Si 100-5; Witt et al. 2001). Elemental sulfur was removed by agitation of the extract with 0.5 g activated copper followed by ultrasonic treatment for 30 min. Cu was activated by using concentrated HCl followed by cleaning with methanol, acetone, and n-hexane. The extracts were subsequently concentrated to approximately 50 µl prior to analysis.

The PAHs were quantified using a gas chromatograph (Trace GC, Thermo Finnigan) coupled to a quadrupole mass spectrometer (Automass, Thermo Finnigan). An XTI-5 capillary column (30 m×0.25 mm, 0.25-µm film thickness) from RESTEK was used for separation. The GC temperature was programmed from 50°C to 190°C at 12°C/min, held at 190°C for 3 min, then held from 190°C to 300°C at 5°C/min and at 300°C for 10 min.

Aliquots of a certified reference material for PAHs in marine sediments (NIST, SRM 1941A) were extracted in triplicate to evaluate the accuracy of the overall method. The measured value ranged between 68% and 125% of the certified values. The quality of the analytical method was evaluated by checking the recovery of the internal deuterated standards. The recovery of the internal standards ranged from 67% to 102%. This was considered satisfactory.

Analytical blanks of the whole analytical procedure were determined using ASE cartridges filled with cleaned Na₂SO₄. The data were blank-corrected. In general, the

blanks were less than the quantities present in the samples by at least a factor of ten.

2.3.3 Measurement of the freely dissolved porewater concentration using matrix SPME and GC/MS

The procedure described in this study is based on that of Arthur and Pawlyszin (1990), who developed a sampling technique called solid-phase microextraction. The SPME device consists of a small fused silica fiber which is coated with an organic phase such as polydimethylsiloxane (PDMS). Extraction with a PDMS phase has the advantage of being a purely absorptive process and no adsorption takes place (Mayer et al. 2000a). The fiber is placed in an aqueous sample where the analytes partition into the coating. The fiber is subsequently thermally desorbed in a GC injector.

The SPME fibers (Fiberguide Industry, Stirling, NJ) used in this study were 100-mm long and 230 μm in diameter (Mayer et al. 1999). The polymethylsiloxane coating was 10-μm thick and the coating volume was calculated to be 0.691 μl for each fiber of these dimensions. The fibers were cleaned twice in methanol in an ultrasonic bath for 10 min and stored in glass tubes in deionised water at 4°C prior to use in the analysis. Cleaned fibers served as blanks, and no detectable amounts of PAHs were found in them.

The concentration of the freely dissolved PAH concentration in the porewater (c_{free}) was calculated from the concentration in the fiber (c_{PDMS}) using previously measured partition coefficient K_{PDMS} (Witt et al. 2009) of the PAH between water and the SPME fiber (Eq. 3).

$$c_{free} = \frac{c_{PDMS}}{K_{PDMS}} \tag{3}$$

Matrix SPME was applied to all the samples listed in Table 1. This approach differs from other SPME methods, because it utilizes the entire sediment matrix as a reservoir for an equilibrium extraction (non depletive extraction), and it is hence called matrix solid-phase microextraction. (Mayer et al. 2000b). The sediment sample was sized to have a sorption capacity of at least 50 times the sorption capacity of the extraction phase. This was in practice achieved by using sediment sample volumes containing at least 50 mg of organic carbon.

$$V_{PDMS} \cdot K_{PDMS,water} \ll m \cdot K_{OC,water} \tag{4}$$

- V Volume
- K Partition coefficient
- m Mass

The SPME extraction was performed with 12-ml vials with polytetrafluoroethylene (PTFE) septum caps. A sus-

pension of 1.5 g of wet sediment and 7.5 ml of centrifuged porewater, or of MilliQ water in the case of the tar ball and urban dust samples, was filled into the vial. Duplicates of each of the sediment samples were used. The samples were poisoned with NaN₃ to inhibit biological activity. Three 100-mm long fibers were inserted into each sample using a syringe needle that pierced the septum. The needle was carefully removed and the position of the fibers was adjusted so that 80 mm of the fiber remained in the vial during extraction. The samples were shaken during the experiment at 300 rpm and room temperature (18°C) in the dark. They were agitated for 500 h until equilibrium was reached for all PAHs. The time to equilibrium was measured in a kinetic experiment to determine the partitioning coefficients (Table 2).

The PAH-loaded SPME devices were introduced manually into the injector of the Saturn 2000 GC and thermally desorbed. The fiber entered the injector through a needle that pierced the injector septum. Due to this injection technique and the injector construction, only the analytes from the lower part of the fiber (70-mm fiber; coating volume, 0.31 μm) were desorbed.

The injector temperature was increased from 50°C to 250°C at 200°C/min to carry out the thermal desorption process from the fiber. A narrow-bore insert liner was used in the injector. Fifteen minutes after sample introduction, the injector was cooled to its initial temperature and was then returned to split mode. The GC temperature was programmed from 60°C (held, 18 min) to 190°C (held, 2 min) at 15°C/min and from 190°C to 300°C (held, 5 min) at 20°C/min and finally to 320°C at 20°C/min. The final temperature was held for 5 min. A DB5 column from J&W Scientific was used (30 m×0.25 mm; film thickness, 0.25 μm). Detection and quantification were based on mass chromatography (SIM-mode) with a VARIAN Saturn 2000 ion trap. The fiber samples were quantified with external PAH standard solution (PAH Mix 45; Dr. Ehrendorfer). Cleaned fibers served as blanks, and no detectable amount

Table 2 PDMS-water partition coefficient, including the standard deviation, compared to the K_{OW} values of Doong et al. (2000)

PAH (abbreviation)	log K_{PDMS}	log K_{OW}
Phenanthrene (Phen)	4.06±0.10	4.46
Anthracene (Ant)	4.19±0.08	4.55
Fluoranthene (Fluo)	4.63±0.10	5.12
Pyrene (Pyr)	4.73±0.06	5.00
Benzo(a)anthracene (BaA)	5.41±0.03	5.74
Chrysene (Chr)	5.33±0.09	5.63
Benzo(b) fluoranthene (BbF)	5.64±0.05	5.78
Benzo(k) fluoranthene (BkF)	5.86±0.05	5.86
Benzo(a)pyrene (BaP)	5.22±0.15	5.91

of target analytes was found on them. The detection limit of the whole fiber method ranged between 10 and 25 pg/ μ l PDMS.

2.3.4 Determination of the PDMS-water partition coefficients

The SPME water partition coefficients used in this study were measured by a kinetic experiment. Briefly, a 0.5-ml solution of PAHs in hexane (20 μ g/ml) was applied to a C18-Empore disk and the solvent was allowed to evaporate. C18 empore disk was used as a reservoir for an equilibrium extraction (non-depletive extraction) to determine PDMS-water partitioning coefficients. Dissolved aqueous concentrations of PAHs were established by partitioning from a C18 Empore disk as described by Mayer and co-workers (Mayer et al. 1999). During the experiment, SPME extractions “consumed” the dissolved concentrations that were “refilled” from the Empore disk. This was carried out with closed vials that were agitated on a rotary shaker at about 200 rpm with an orbit of 3 mm. A 25-mm C18 Empore disk with about 50 μ L of octadecyl (C18) was contaminated with 16 EPA PAHs at about 20 mg/l. Two 2-L bottles (duplicates) were filled with 1800 ml of Millipore water, the contaminated disk was added, and the bottle was closed with a silicone/PTFE septum cap. Bottles were agitated overnight, and stable aqueous concentrations were established within a few hours according to $c_{\text{water}} = c_{\text{C18}}/K_{\text{C18,water}}$ (Mayer et al. 1999). Agitated SPME extractions were conducted for different exposure times while avoiding any direct contact with the Empore disk. Duplicate fibers were sampled after 3, 6, 10, 24, 48, 100, 167, 218, 267, 339, 411, 507, and 640 h. There was no significant difference between the fibers exposed at 507 and 640 h, indicating that equilibrium was reached in the fiber-water system. The fibers were removed, wrapped in aluminum foil, and stored at -20°C until analysis. The water in the bottle was divided into three 500-ml sub-samples which were filtered, spiked with a mixture of deuterated PAHs (surrogate standards), and extracted with n-hexane. The extracts were dried on sodium sulfate, concentrated to 0.05 ml, and analyzed using GC/MS. Table 2 shows the experimental K_{PDMS} values compared to the octanol-water coefficient K_{OW} . The log K_{PDMS} ranged between 4.06 and 5.86 with a mean error of between 0.03 and 0.15 log units.

2.3.5 Dissolved organic carbon

Five milliliters of porewater were sub-sampled from the remaining 10 ml and centrifuged at 10,000 rpm under controlled temperature for 30 min and, after filtration (glass-fiber filter of 0.45- μ m pore size), were analyzed in triplicate with a Shimadzu total organic carbon analyzer (TOC 5000).

2.3.6 Total organic carbon and soot content

Freeze-dried sub-samples were used to measure TOC and soot content. The calculated TOC and soot values are given in Table 3. The total carbon content as well as the total inorganic content was measured using a C/S analyser (Metalyt CS 100 by ELTRA). The total organic carbon content was calculated as the difference of the two measurements.

The method of Gustafsson et al. (1997) was used to measure the soot content (SC). All samples were oxidized at 375°C for 24 h in the presence of air inside a muffle furnace (NABERTHERM). In situ acidification with HCl was subsequently used to remove the inorganic carbon. The composition of the prepared samples was determined using a PE 2400 CHN elemental analyser (Perkin Elmer Corp., Norwalk, CT). Its detection limit (i.e., instrument blank) was about 4 μ g of C. To validate our method, the results of the standard UD material NIST SRM 1649a were compared with measurements of the same material by different authors. The results of this study are very similar to those conducted in other laboratories (Table 4).

3 Results and discussion

3.1 PAH concentration in sediments and porewater

The concentrations of the PAHs in the sediments, in total porewater, and freely dissolved in porewater are given in Tables S1 and S2 of the [Electronic Supplementary Material](#).

In the sediments, the concentration of the sum of the nine selected PAHs (Σ PAH) ranged from 26 to 1,090 μ g/g TOC. The highest concentrations were observed in the sediments from the dumping area (DS-black and DS-red), while the concentrations at the reference site (station RS) were about 30 times lower. The concentration of Σ PAHs in the tar ball (11,000 μ g/g TOC) was much higher than in the

Table 3 Soot and TOC content of the different samples

PAH	RS	SCH	HS	HS+oil	DS-red	DS-black	UD	TB
TOC (mg/g dw)	37.8	52.1	29.0	31.4	81.3	118.3	200.8	900.5
Soot (mg/g dw)	2.6	3.1	4.0	3.1	13.8	51.2	14.8	13.3
Ratio soot/TOC	0.069	0.059	0.138	0.099	0.017	0.433	0.074	0.015

Table 4 Comparison between soot data from the same site of NIST material SRM 1649a to assess the soot isolation method

SRM 1649a	No. of measurements	Soot content (mg/g d.w.)	Soot/TOC ratio
This study	5	14.8±0.05	0.07±0.03
Reddy et al. (2002)	3	14±0.1	0.08±0.01
Massiello (1999)	–	–	0.10±0.01
Mitra et al. (2002)	4	–	0.11±0.03
Gustafsson et al. (2001)	–	13.6±0.7	0.08

– No information available

sediments, reflecting the strong aromatic nature of this sample.

The total (i.e., freely dissolved+colloidal) ΣPAH concentration in the porewater ranged between 920 and 14,800 ng/L. The TB sample was an exception again, with a porewater concentration of 230,000 ng/L. As with the sediments, the ΣPAH concentrations in porewater from the dumping area were more than one order of magnitude higher than in porewater from the reference site.

The concentrations of freely dissolved ΣPAHs in the porewater (10 to 121 ng/L, tar ball 1,080 ng/L) were markedly lower than the total concentrations in the porewater. This indicates that the great majority of the PAHs in porewater were associated with colloidal material. Although the freely dissolved concentrations do not represent a large pool, it is this fraction that partitions into aquatic organisms (Kraaij et al. 2003). If this concentration is depleted by uptake, it will be replenished from the much larger pools associated with the colloids and sediment. The large difference between the total and freely dissolved PAH concentrations in the porewater emphasizes the importance of measuring the freely dissolved concentrations; using the total concentrations in porewater instead would greatly overestimate the ecotoxicological risk posed by the PAHs.

3.2 DOC/water partitioning

The total porewater concentrations (c_{total}) and the freely dissolved concentrations (c_{free}) were used to calculate the dissolved organic carbon/water partition coefficients (K_{DOC}) according to:

$$K_{DOC} = \frac{(c_{total} - c_{free})/DOC}{c_{free}} \quad (5)$$

where DOC is the concentration of dissolved organic carbon in the porewater. The results are shown in Table S3 (Electronic Supplementary Material), and $\log K_{DOC}$ is plotted against $\log K_{OW}$ in Fig. 3.

For the porewater “reconstituted” from purchased standard materials with MilliQ water, namely UD, HS, and the harbor sediment/oil mixture (HS+oil), $\log K_{DOC}$ increased with increasing $\log K_{OW}$, and K_{DOC} was similar in magnitude to K_{OW} . This is broadly consistent with what has been reported for laboratory studies of PAH partitioning

between water and humic and fulvic acids (Georgi and Kopinke 2002) and in porewater from freshwater sediments (Akkanen et al. 2004). For instance, the $\log K_{DOC}$ of pyrene ranged between 4.01 and 5.02 for 11 humic and fulvic acids (Kopinke et al. 2001), while Ter Laak et al. (2005) measured a value of 5.55 in Aldrich humic acid. This compares with the range of 5.06 to 5.20 determined for the standard materials in this study.

The sampled porewater showed a different behavior. In contrast to the reference materials, K_{DOC} was largely independent of K_{OW} . While the K_{DOC} of the more lipophilic PAHs (BaA, Chr, BbF, BkF, and BaP) were similar for the directly sampled and “reconstituted” porewater, the K_{DOC} of the less lipophilic PAHs (Phen, Ant, Fluo, and Pyr) were markedly higher in the directly sampled porewater. This suggests that the porewater contained colloidal matter with a high sorption capacity for these PAH. One explanation for the difference between the sampled and “reconstituted” porewaters could be that the preparation and/or storage of the standard materials resulted in removal of a large portion of the strongly sorbing colloidal fraction.

The K_{DOC} values for the less lipophilic PAHs in the sampled porewater were 1–2 orders of magnitude greater than the K_{OW} values of these compounds. This is consistent with the high K_{OC} values observed for the sediment-water partitioning, which suggests that the same strongly sorbing

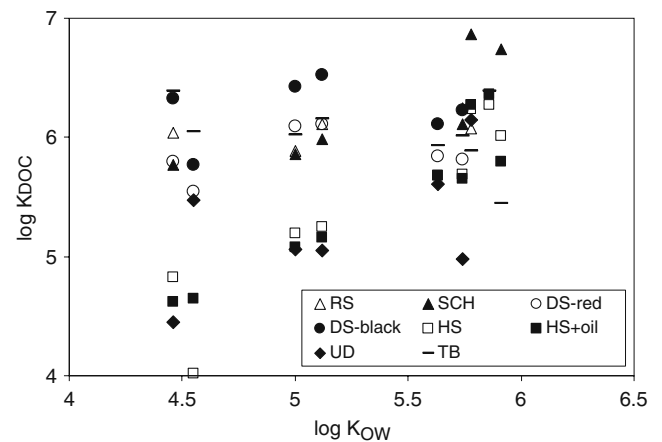


Fig. 3 Logarithm of the field K_{DOC} values of the individual PAHs in the directly sampled (RS, SCH, DS-red, DS-black, TB) and “reconstituted” (HS, HS+oil, TB) porewaters plotted as a function of octanol-water partition coefficients ($\log K_{OW}$)

material may have been present in both the colloidal and solid fractions. However, the fact that K_{OC} was strongly correlated with K_{OW} while K_{DOC} was not suggests that the strongly sorbing material was different in these two fractions.

Previous measurements have yielded similar K_{DOC} values for PAHs in seawater. Næs et al. (1998) determined K_{DOC} of PAHs in seawater at two locations in the North Sea. For both locations they found that K_{DOC} was almost independent of K_{OW} , in agreement with our work, but in stark contrast to the strong K_{OW} dependency of K_{DOC} observed for porewater from freshwater sediments and isolated humic and fulvic acids (see above). At a control station situated in coastal waters influenced by general human activities, but by no point sources, Næs et al. (1998) reported that $\log K_{DOC}$ ranged around 5.5, while at a second station close to an aluminum plant it ranged around 6.5. In our work, the $\log K_{DOC}$ in most of the sampled porewaters ranged around 6, with minimum and maximum values of 5.5 and 6.9, respectively. Together, these two papers suggest that colloid/water partitioning of PAHs in these marine environments is fundamentally different from the partitioning that has been reported for freshwaters and isolated humic and fulvic acids. More data on the colloid/water partitioning of PAHs in marine waters is needed to gain a better understanding of PAH behavior in the marine environment.

3.3 Sediment-water partitioning of the PAHs

The equilibrium partitioning of PAHs is generally described using an organic carbon/water partition coefficient (K_{OC}). The K_{OC} values for the materials studied in this work are shown in Table S4 (Electronic Supplementary Material) and plotted against K_{OW} in Fig. 4.

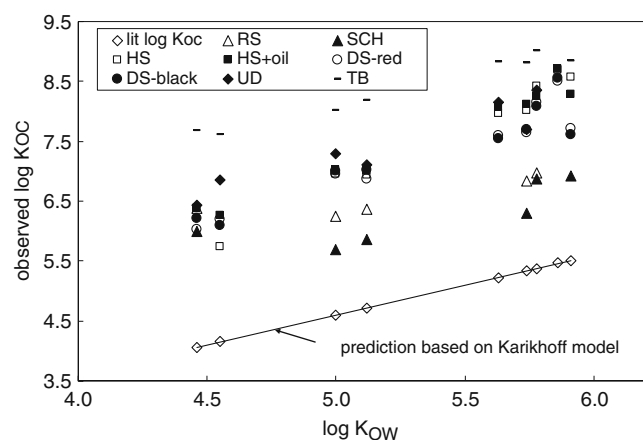


Fig. 4 Logarithm of the field K_{OC} values of the individual PAHs at the different stations and in the standard materials (HS, HS+oil, UD) plotted as function of $\log K_{OW}$. The $\log K_{OC}$ values calculated with the Karickhoff model (Karickhoff, 1981) are also shown

The figure also shows the correlation developed by Karickhoff (1981) and Karickhoff et al. (1979) to predict the K_{OC} of organic chemicals from K_{OW} :

$$\log K_{OC} = 0.99 \log K_{OW} - 0.35 \quad (6)$$

There was good agreement between the inter-chemical variability in K_{OC} and the predictions of the Karickhoff model. K_{OC} increased with the K_{OW} of the chemical in all sediments, and the slope of the K_{OC} vs K_{OW} relationship was similar to the Karickhoff model in all cases. However, the measured K_{OC} values of each of the PAHs were one to four orders of magnitude greater than the K_{OC} value predicted by the Karickhoff model. They were also greater than the K_{OC} values that Karickhoff measured for several of the PAHs and that were part of the dataset that he used to develop his model. These results are consistent with the hypotheses that a significant proportion of the PAHs in sediments is not available for partitioning or that sediments contain materials such as soot carbon that are much stronger sorbents than natural organic material (e.g., Cornelissen et al. 2005).

Another possible explanation for the underestimation by Karickhoff's model is artifacts in the K_{OC} measurement. The porewater in this study was prepared in a manner similar to the water phase analyzed by Karickhoff (centrifugation at 10,000 rpm and filtration through a filter with a 0.45- μm cutoff in this study, versus centrifugation at 20,000 rpm or filtration through a filter with a 2–5- μm pore size by Karickhoff (1981) and Karickhoff et al. (1979)). In this study, the freely dissolved concentrations were one to three orders of magnitude less than the total porewater concentrations (see Tables S1 and S2, Electronic Supplementary Material). Clearly, using total porewater concentrations as opposed to freely dissolved concentrations can lead to an underestimation of K_{OC} . When the K_{OC} values in this study were estimated using the total porewater concentrations, there was much better agreement with the Karickhoff K_{OC} values (Table S5, Electronic Supplementary Material). This might indicate that these latter values for the PAHs were also significantly underestimated. However, the extent of any underestimation will depend on the nature and quantity of the colloidal material present in the porewater, and it cannot be established how comparable these parameters were for the sediments studied here and by Karickhoff. Consequently, no conclusions can be drawn about the relative importance of this artifact compared to the other two hypotheses above in explaining the discrepancies between the measured K_{OC} values and Karickhoff's model.

Another prominent characteristic of the K_{OC} dataset was the large differences in the K_{OC} values of a given PAH between the different substrates. The lowest values were typically measured for HS, while the highest were measured in TB. The range was a factor of 40 to 200 between the different sediments. Clearly, the organic carbon

content is not a good descriptor of the influence of sediment properties on sediment-water partitioning of PAHs. Current models that use the organic carbon content as the only sediment property influencing sediment-water partitioning cannot describe the range of partitioning behavior present in this small area in the western Baltic Sea.

As a consequence of the finding that soot carbon can be a very strong sorbent of PAHs in water, the soot-carbon content of sediment has been suggested as a more appropriate property for describing the variability in sediment-water partitioning of organic contaminants between sediments. Soot-carbon-normalized sediment-water partition coefficients (K_{SC}) were calculated from the experimental data according to:

$$K_{SC} = \frac{(c_s)/SC}{c_{free}} \quad (7)$$

where C_s is the concentration in dry sediment ($\text{mol}\cdot\text{kg}^{-1}$), and SC is the soot-carbon content of the dry sediment ($\text{kg}\cdot\text{kg}^{-1}$). The $\log K_{SC}$ values are plotted as a function of $\log K_{OW}$ for the different PAHs and sediments in Fig. 5.

The range in the K_{SC} values for a given chemical was typically three orders of magnitude. The K_{SC} for the tar ball sample was at least an order of magnitude greater than the remaining samples, but even if TB was neglected, the range in K_{SC} for the remaining samples was approximately 1.5 orders of magnitude. This is comparable to the range observed for the K_{OC} if TB was neglected (see Fig. 3). To further evaluate the importance of the soot matrix, the soot content was correlated with the PAH concentrations of the different locations. A significant positive linear correlation was found for the individual PAHs, with correlation coefficients between 0.89 and 0.97. Compared to these results, the correlation coefficients between the TOC content and the different PAHs ranged below 0.6. These regressions showed that the distribution of PAHs of different origin can be much

better explained by soot than by organic carbon. These results are supported by previous studies where Gustafsson and Gschwend (1997) showed that the distribution of benzo(a) pyrene in surface sediments of the Gulf of Maine was much better explained by soot than by bulk organic carbon.

The observed soot/TOC ratios ranged between 0.09 and 0.51. Apart from the dumped sediments, all other measured soot/TOC ratios are usual for anthropogenically influenced coastal sediments where ratios between 0.02 and 0.2 have been commonly observed by several authors (Gustafsson and Gschwend 1998; Middelberg et al. 1999; Persson et al. 2002; Sánchez-García et al. 2010). Soot/TOC carbon ratios of 0.02–0.03 were found in the surface sediments of the reference stations as well as in the other sediments of the Mecklenburg Bight which are representative of the present pollution level of this area of the Baltic Sea. These ratios were one order of magnitude lower than the soot/TOC content of the Toronto Harbour standard sediment.

Due to variation in specific surface areas and surface chemistries, various soot types may exhibit significantly different distribution coefficients for PAHs. For example carbon black from tire ware may be a big contributor to environmental soot where street runoff is important but this graphite-like soot may not be a strong sorbent. In comparison larger distribution coefficients were found for diesel soot (Accardi-Dey and Gschwend 2003). The comparison of two PAH isomer ratios (BaA/Chr; BbF/BkF) that are typical for PAHs as by-products of incomplete combustion processes with the same PAH ratios observed in sediments indicate that the soot of the dumping area is smelter derived (Mitra et al. 1999). In contrast, the sediments which are normally characteristic of this part of the western Baltic Sea are best associated with the urban dust (UD) sample. This result might indicate atmospheric deposition of pyrogenic-derived PAHs as a major source of

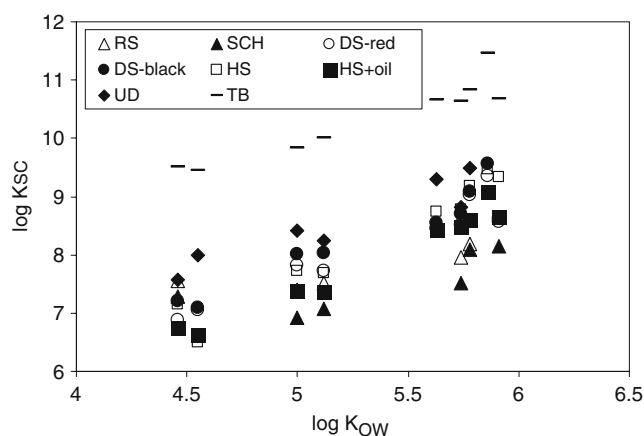


Fig. 5 Logarithm of the field K_{SC} values of the individual PAHs at the different stations and in the standard materials (HS, HS+oil, UD) plotted as a function of $\log K_{OW}$

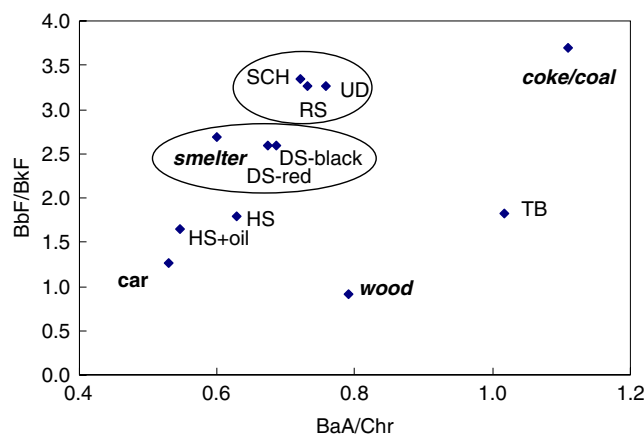


Fig. 6 Comparison of two isomer ratios for high molecular PAHs derived from different combustion sources and those of the sediments investigated

PAHs in sediments of the western Baltic Sea (Fig. 6). This type of soot seems to have a lower sorption strength compared to smelter-derived soot. Nevertheless, a new procedure to quantify the different constituents of the soot fraction is essential to interpret the results in more detail.

The contamination of the standard sediment by the “Baltic Carrier” oil was carried out to assess the impact of spilled oil on the distribution of PAHs in sediment-porewater systems. Surprisingly, the spilled oil has only slightly influenced distribution coefficients between sediment and porewater. The log K_{SC} values of sample HS and HS+oil were very similar (see Fig. 5 and Table S4). It has shown that the presence of soot can cause strong sorption of PAHs in sediments (Bucheli and Gustafsson 2000). We hypothesize that the highly hydrophobic and strongly sorbing soot matrices of the native sediment were able to absorb the petrogenic PAHs in the “Baltic Carrier” crude oil relatively quickly. Due to the strong sorption of PAHs from oil to soot PAHs become non-accessible for equilibrium partitioning. Furthermore, Karapanagioti et al., who have investigated the sorption properties of different kinds of organic matter, showed that soot particles have a very high sorption capacity even when they are present as only a very small fraction of the composite organic carbon (<3%). While soot particles do not dominate the sample f_{OC} , they do dominate the sample reactivity. However, our results suggest that since PAHs have both pyrogenic and petroleum sources, the soot fraction may control the partitioning of the PAHs between sediment and porewater. Furthermore, the results of the sample TB (weathered oil/sediment mixture with a consistency similar to tar) show the most remarkable results. The K_{OC} values demonstrate that the absolute affinity of the PAHs for this material is very high (see Table S4 and S5, [Electronic Supplementary Material](#)). Jonker and Koelmans (2002) report very high sorption affinities of PAHs for weathered oil matrices. Analogously to soot, extreme sorption of PAHs to the weathered tar could occur. As a result of the weathering process, the number of polar groups will be minimized and a highly hydrophobic surface should be developed which has a high affinity for PAHs. In addition, sorption becomes more independent of hydrophobicity (see Fig. 4), an effect that Jonker and Koelmans (2002) also observed for charcoal and activated carbon.

4 Conclusions

The wide range of sorption behavior observed in this study may be attributed to the diverse nature of the sorbents. While they all either occurred in or were relevant to the study area, they ranged from natural sediments to a range of materials of anthropogenic origin. Some contained PAHs that were mainly of pyrogenic origin; others were mainly of

petrogenic origin. The sediment-water partitioning coefficient is a key parameter in the risk assessment of PAHs in sediments, as it determines the activity of the PAHs in water, which in turn determines bioconcentration. Especially Kraaij et al. (2003) have found that steady-state accumulation of hydrophobic organic compounds (HOC) like PAHs in benthic deposit-feeders can be fully reconciled with equilibrium partitioning of rapidly desorbing compounds between sediment, porewater, and deposit-feeders. Taken together, these findings indicate that equilibrium partitioning is a conceptually correct representation of sediment bioaccumulation, provided that sequestration is accounted for. This implies that the risk assessment of sediment-associated HOCs can be significantly simplified: With a method at hand for measuring freely dissolved porewater concentrations of HOCs, it appears that HOCs' body residues in sediment-dwelling organisms can be estimated on the basis of concentrations in porewater and bioconcentration factors.

Finally, the PAH partitioning in this study indicates that partitioning models are of limited values in PAH risk assessment in cases where the sorbents under study differ markedly from those used to develop the model. In such cases, PAH risk assessment should rely on measurements of PAH activity. In this work, we showed how such measurements can be performed in a comparatively simple way.

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