



Matrix solid-phase microextraction for measuring freely dissolved concentrations and chemical activities of PAHs in sediment cores from the western Baltic Sea

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ABSTRACT

Sediment-pore water partitioning of polycyclic aromatic hydrocarbons (PAHs) was studied in sediment cores of a dumping area in the western Baltic Sea and compared to a reference site. Freely dissolved concentrations (C_{free}) of nine PAHs were measured in sediment samples using solid-phase microextraction (SPME), a cost and time-efficient method with detection limits in the lower ng L^{-1} range. Elevated levels of C_{free} were measured at the dumping site, where concentration peaks in the core correlated with the presence of the dumped material, which was conspicuous in its color and consistency. Sediment concentrations of PAHs were three orders of magnitude higher at the dumping site than at the reference site, whereas C_{free} was only one order of magnitude greater. Chemical activities of the PAHs in the sediment cores were calculated from C_{free} to predict the baseline toxic potential of the contaminant mixture. Finally, gradients in C_{free} and chemical activity were used to determine the direction of diffusion within the sediment and to obtain a spatial characterization of the PAH exposure. C_{free} and chemical activity are important exposure parameters for the prediction of bioconcentration and toxicity in sediment organisms, and their measurement should be included in risk-assessment and pollution-management strategies.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are of considerable interest, primarily due to their toxic, carcinogenic and mutagenic potential. PAHs originate from various sources, including oil spills and fossil fuel combustion and are widely distributed in marine environments. Their origin influences their mobility and bioavailability. Thus PAHs from pyrogenic sources are mainly adsorbed onto charcoal and soot particles characterized by high K_D values, whereas those from petrogenic sources are usually sorbed to natural organic material with lower K_D values (Socha and Carpenter, 1987; McGroddy and Farrington, 1995; McGroddy et al., 1996; Naes et al., 1998; Gustafsson and Gschwend, 1999; Jonker et al., 2003; Cornelissen et al., 2005). This is one of several reasons why it remains difficult to assess sediment contamination solely on

the basis of total contaminant concentrations. Investigations by DiToro et al. (1991) and Kraaij et al. (2003), for instance, suggest that freely dissolved concentrations (C_{free}) are a precondition for several diffuse mass transfer processes, including sorption and uptake into macro- and microorganisms. So it is crucial to determine C_{free} in order to understand the distribution processes in sediments and to estimate both bioconcentration and toxicity.

In the past, it was impossible to quantify C_{free} and to distinguish between the PAH fraction that was freely dissolved and the dissolved organic carbon-bound fraction. If the dissolved organic carbon (DOC) content was low, some researchers decided to neglect the DOC fraction. Others have used the DOC content or the estimated K_{DOC} values as well as the predictions of three-phase distribution models to estimate the freely dissolved concentration (McGroddy and Farrington, 1995; Mitra et al., 1999; Persson et al., 2002; Accardi-Dey and Gschwend, 2003). Commonly used techniques such as solvent extraction have the disadvantage of extracting the entire pore-water concentration of the compound present in the sample. The presence of non-extractable residues often leads to further mistakes. The determination of freely dissolved pore-water concentrations therefore represents an analytical challenge. A number of approaches have been developed to distinguish between the freely dissolved and sorbed phases, including dialysis

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(Escher and Schwarzenbach, 1996), solubility enhancement (Chiou et al., 1986), fluorescence quenching (Backhus and Gschwend, 1990) as well as techniques based on passive partitioning in semi-permeable membrane devices (SPMD) (Huckins et al., 1990; Verweij et al., 2004), C18 Empore disks (Södergren, 1987), LDPE strips (Booij et al., 2003), polyoxymethylene plates (Jonker and Koelmans, 2001) and polymer coated glass fibers (SPME) (Pörschmann et al., 1997; Van der Waals et al., 2004).

Arthur and Pawlyszin (1990) developed solid-phase microextraction (SPME) using silica fibers coated with a polymeric organic phase such as polydimethylsiloxane (PDMS). Such fibers can be placed directly into or above an aqueous sample, the analytes then partition into the coating from where they can subsequently be thermally desorbed directly in a GC injector. PDMS is the most frequently applied polymer for the SPME of hydrophobic organics, since it provides well-defined absorptive retention, high permeability and very good thermal stability (Pawlyszin, 1997; Mayer et al., 2000a). Mayer et al. (2000b) evaluated the potential of disposable PDMS-coated fibers to measure the C_{free} of hydrophobic organics by placing them directly in the sediment matrix, and named the method matrix-SPME. The PDMS-coated fiber is equilibrated within the sediment and C_{free} can then be calculated from the concentration in the fiber coating (C_{PDMS}) using a measured PDMS-to-water partition coefficient (K_{PDMS}):

$$C_{\text{free}} = \frac{C_{\text{PDMS}}}{K_{\text{PDMS}}} \quad (1)$$

The aim of the present study was to measure the C_{free} of several PAHs in vertical sediment cores from a highly contaminated dumping area in the western Baltic Sea and from two reference cores by matrix-SPME. The chemical activities of the PAHs were calculated from C_{free} to assess the baseline toxic potential of the PAH mixture. This information is important for assessing the risk of lipophilic organic pollutants such as PAHs in highly polluted sediments. Finally, the vertical gradients in C_{free} and chemical activity within the sediment cores were applied to determine the direction of diffusive mass transfer and to obtain a spatial characterization of the PAH exposure.

2. Materials and methods

2.1. Investigation area

The Baltic Sea is one of the largest semi-enclosed brackish-water regions (415 000 km²) in the world (Matthäus, 1996) and is considered to be an especially sensitive and endangered marine ecosystem (Lozán et al., 1996). The exchange of water masses with the North Sea occurs through only three small channels (the Danish Straits) and is therefore extremely limited. The average residence time of Baltic Sea water is between 25 and 50 years, thus enhancing the accumulation of pollutants (HELCOM, 1989). Additional high-pollutant inputs are the rivers and the atmosphere. HELCOM (1989) identified 132 pollution “hot spots” around the Baltic Sea, which thus requires special and differentiated consideration of its pollutant impacts due to its unique marine ecosystem and high contaminant load.

The study site is located in the Mecklenburg Bight (Fig. SI 1, Supplementary information) between the North Sea and the central Baltic Sea. Local currents are influenced by various processes occurring between both seas. The Bight has a maximum water depth of 25–30 m and consequently belongs to the “shallow water region” of the Baltic. The sediment consists of mud with a total organic carbon content of ~5%.

Sediment cores were collected during an expedition with the research vessel Prof. A. Penck in 2004. Fig. SI 1 (SI = Supplementary

information) shows the investigated areas of the Sea with the sampling stations. Samples consisted of one 30 cm-long sediment core per station. Each core was separated into 2 cm slices and was stored at –20 °C until analysis.

2.2. Sampling stations

2.2.1. Dumping site (DS)

This station is located in the inner part of the Mecklenburg Bight and represents a historical dumping site. Leipe et al. (1998) identified 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 cm of the sediment column for selecting suitable core sampling positions. On board of the ship, the cores were optically examined for the presence of dumped material. Visual inspection was the best opportunity to identify and isolate the 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) and reddish dusts (red material) or fine-grained material with mainly iron oxides together with some mixed ashes originating from various high-temperature industrial processes (such as slag from smelting plants and steelworks). Especially the reddish material was enriched in PAHs as well as in heavy metals (Leipe et al., 2005). The PAH sources are known to be more pyrogenic than petrogenic (Table SI 1).

2.2.2. Reference site (RS)

This station, located in the outer Mecklenburg Bight about 25 nautical miles NE of the dumping site (Fig. SI 1), was chosen to compare the data of the material from the dumping site with those of the adjacent areas which were less polluted but have similar hydrographic conditions and sediment characteristics.

2.2.3. Shipping channel (SCH)

This station is located in the centre of the Mecklenburg Bight, directly below a shipping lane between Lübeck and Scandinavia. Previous investigations (Leipe et al., 2005) have determined more petrogenic PAH sources in this area due to shipping traffic and discharges of oily waste.

2.2.4. History of the cores

The natural sedimentation rate in the Mecklenburg Bight varies between 1 and 3 mm a⁻¹. Dating of an undisturbed sediment core from the reference station (Leipe et al., 2005) by the Gamma Dating Centre, Copenhagen resulted in a sedimentation rate of 1 mm a⁻¹, with a mass accumulation rate of about 300 g m⁻² a⁻¹. The PAH profile of the RS core indicate an undisturbed core due to the decreasing PAH concentrations with depth. Therefore we can suggest a similar sedimentation rate like the other RS core.

On the other hand the highly dynamic environment of the 20 m deep seafloor of the Mecklenburg Bay includes various forms of sedimentation and mixing processes caused by bioturbation, wave and current induced hydroturbation, and anthropogenic impacts (fishery, shipping) to the sediment. Both other cores are disturbed and older layers are mixed with newer layers. Therefore it is not possible to find a time line in these cores.

2.3. Analytical method

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, the Al₂O₃ and SiO₂ were partly deactivated with 15% and 3.5% of deionised water respectively. An external PAH standard was used for calibrating the GC–MS system and for the external standard quantification of the SPME devices (PAH Mix 45 of Dr. Ehrendorfer). A mixture of perdeuterated PAHs from PROMO-CHEM (naphthalene-*d*₈, phenanthrene-*d*₁₀, fluoranthene-*d*₁₀, chrysene-*d*₁₂ and perylene-*d*₁₂, benzo(*g,h,i*)perylene-*d*₁₂) was used for the internal standard calibration and quantification of the sediment samples. All chemicals were checked for impurities.

2.3.2. Sediment concentration

Some 2–3 g of sediment were extracted using an accelerated solvent extractor (ASE 2000, DIONEX). The freeze-dried samples were transferred to the ASE cartridges and the internal standard solution was added. The extraction was carried out with 35 mL of a *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 concentrated sediment extracts (50 µL) were pre-cleaned using solid-phase extraction. The concentrated extract was pre-cleaned 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 separation of the extract and subsequent concentration to about 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 with concentrated HCl_(aq), then cleaned with methanol, acetone and *n*-hexane. The solvents were subsequently concentrated to approximately 50 µL for preliminary analyses.

The PAHs were quantified using a gas chromatograph (Trace GC, Thermo Finnigan) coupled to a quadruple mass spectrometer (Automass, Thermo Finnigan). An XTI-5 capillary column (30 m × 0.25 mm, 0.25 µm film thickness) from RESTEK was used. The GC temperature was programmed from 50 °C to 190 °C at 12 °C min⁻¹, held at 190 °C for 3 min and from 190 °C to 300 °C at 5 °C min⁻¹ and then held at 300 °C for 10 min.

2.3.3. TOC and soot measurements

The total carbon content (TC) and the total inorganic carbon content (TIC) were measured using a C/S analyzer (Metalyt CS 100 by ELTRA), and the total organic carbon content (TOC) was calculated as the difference between the two measurements. The soot content was calculated as the difference between the remaining carbon content after thermal oxidation (375 °C, 24 h, 20% O₂) and the measured TIC. The soot content was also measured with the method of Gustafsson et al. based on the removal of the inorganic carbon by acidification with HCl (Gustafsson et al., 1997). This published method yielded many very low or negative results for the soot content, and the results of the thermal oxidation method were thus used in the present study.

2.3.4. Measurement of the freely dissolved pore-water concentration with SPME

The procedure described in this study is based on that of Arthur and Pawlyszin (1990), who developed a sampling technique called solid-phase microextraction (SPME). 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 pure absorptive process involving no adsorptive processes (Mayer et al., 2000a). The fiber is placed in an aqueous sample, and chemicals partition into the coating and are subsequently 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., 2000b). The polymethylsiloxane (PDMS) coating was 10 µm thick and the coating volume was calculated to be 0.691 µL for every fiber of this size. 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.

The concentration of the freely dissolved PAH concentration in the pore water (C_{free}) was calculated from the concentration on the fiber (C_{PDMS}) using a measured partition coefficient K_{PDMS} of the PAH between the water and the SPME fiber see Eq. (1).

Matrix-SPME was applied to all the samples listed in Table SI 2. The sediment matrix was used as a reservoir for the equilibrium extraction in order to avoid depletion of the pore water (Mayer et al., 2000b). The SPME extraction was performed with 12 mL vials with PTFE septum caps. A suspension of 1.5 g of wet sediment and 7.5 mL of centrifuged pore water was filled into the vial. Duplicates for each of the sediment samples were used. The samples (volume: 8 mL) were spiked with 1 mL of a 10 mM NaN₃ solution to inhibit biological activity. In each sample, three 100 mm long fibers were inserted 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 at room temperature (18 °C) in the dark. They were then agitated for 500 h until equilibrium was reached for all PAHs. The time to equilibrium was measured in the experiment to determine the partitioning coefficients (Table SI 2).

Each SPME fiber loaded with PAH was 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⁻¹ to assure thermal desorption from the fiber. A narrow-bore insert liner was used in the injector. 15 min after sample introduction, the injector was cooled to its initial temperature and was returned to split mode. The GC temperature was programmed from 60 °C (held: 18 min) to 190 °C (held: 2 min) with 15 °C min⁻¹ and from 190 °C to 300 °C (held: 5 min) at 20 °C min⁻¹ and finally to 320 °C at 20 °C min⁻¹. 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). The detection and quantification were based on mass chromatography (MS, SIM-mode) with a VARIAN Saturn 2000 ion trap. The fiber samples were quantified with the external PAH standard solution (PAH Mix 45, Dr. Ehrendorfer).

Six fibers were analyzed for each sediment sample to determine C_{free} . The latter's standard deviation ranged between 2.8% and 12% for phenanthrene; 4.5% and 12.9% for anthracene; 3.4% and 18% for fluoranthene; 1.7% and 17.2% for pyrene; 2.5% and 8.9% for benzo(*a*)anthracene; 4.1% and 17.6% for chrysene; 4.1% and 19.1% for benzo(*b*)fluoranthene; 9.7% and 18.2% for benzo(*b*)fluoranthene and 6.1% and 20.0% for benzo(*a*)pyrene.

2.3.5. Determination of the PDMS-water partition coefficients

The SPME water-partition coefficients used in this study were measured as follows. A solution of PAHs in hexane was applied to a C18-Empore disk and the solvent was allowed to evaporate. The Empore disk was placed in a glass bottle containing 2 L of MilliQ water and allowed to equilibrate. Ten of the SPME fibers were

then placed in the bottle, which was sealed and stored at room temperature. After 647 h, the fibers were removed, cleaned with MilliQ water as well as a lint free tissue and finally wrapped in aluminum foil and stored at -20°C until analysis (as described above). 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 SI 2 shows the experimental K_{PDMS} values compared to the octanol–water coefficient K_{OW} (Table SI 2). The $\log K_{\text{PDMS}}$ value ranged between 4.06 and 5.86 with a mean error of between 0.03 and 0.15 log units. The SPME water–partitioning coefficient of naphthalene, acenaphthene, acenaphthylene and fluorene could not be calculated from the sixteen EPA PAHs due to the poor reproducibility of the fiber measurements.

Equilibrium was established within 400 h for most of the substances of lower molecular weight, whereas the equilibration time of benzo(*ghi*)perylene, dibenzo(*a,h*)anthracene and indeno(1,2,3-*cd*)pyrene exceeded 500 h. The latter were consequently not included in these studies.

3. Results and discussion

3.1. Sediment profiles and distribution pattern of C_{free}

The sediment profile measurements of C_{free} at the three stations are presented in Fig. 1. The values of C_{free} in the surface sediments (0–2 cm) were very similar for all three stations and ranged between 53 and 82 ng L^{-1} (sum of 9 PAHs). This indicates that the present input of PAHs is dominated by a diffuse contamination of the entire area. The vertical profiles at the three stations were

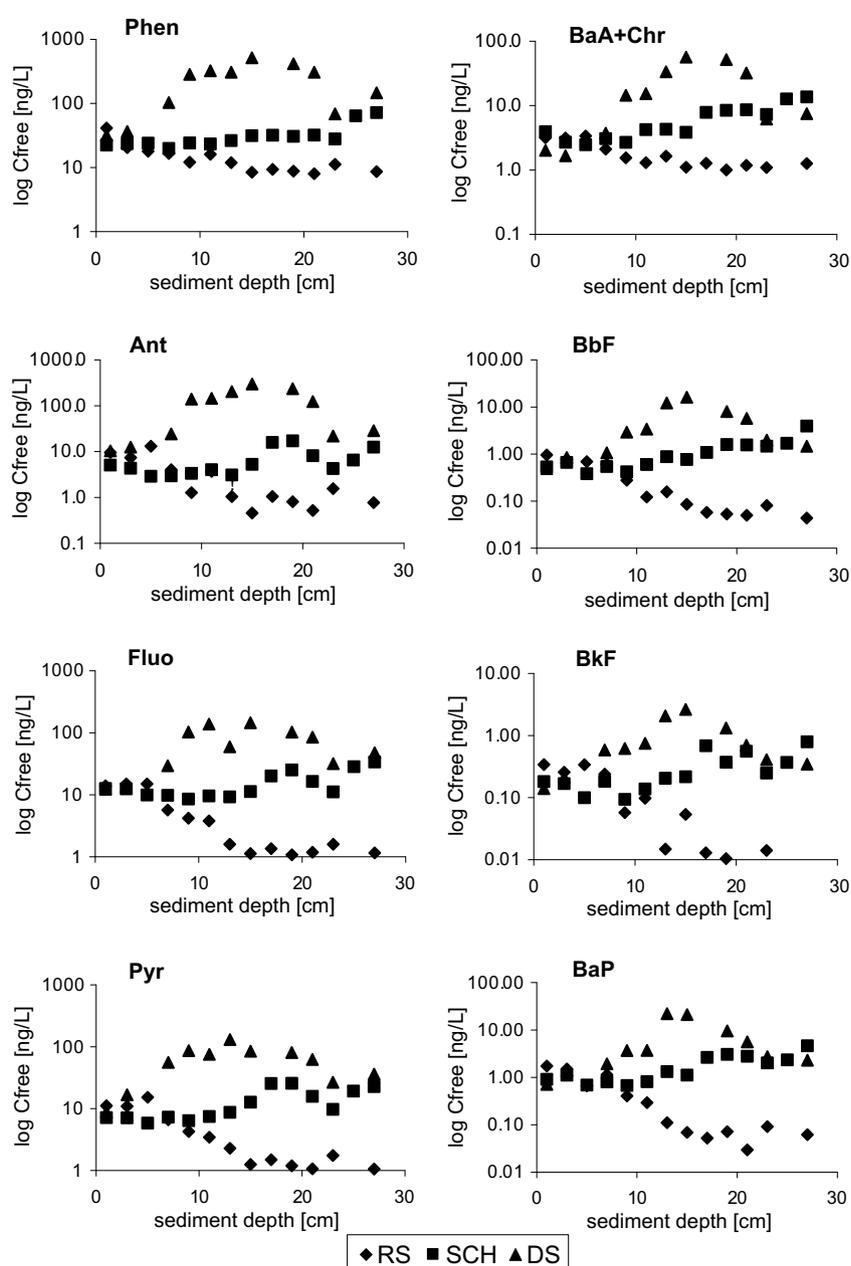


Fig. 1. Measured freely dissolved pore water concentration of PAHs (C_{free}) in ng L^{-1} from the reference sites (RS), dumping sites (DS) and shipping channel (SCH).

markedly different, which can be explained by differences in their sedimentation and contamination history.

Profiles at the reference station (RS) showed a vertical decrease in C_{free} (ng L^{-1}) in correlation with a decrease of sediment concentration (C_{sediment} in ng g^{-1} dry weight, see Fig. SI 2). Although the decrease of the PAHs of lower molecular weight could be explained by biodegradation, the decrease was most pronounced for the PAHs of higher molecular weight. This strongly suggests that the historic increase of diffuse PAH contamination is the main reason for the observed gradient as already described by Gschwend and Bohnke (1981), for example. The effect of aging would only explain the decrease in C_{free} but not the decrease of sediment concentrations.

Profiles of the dumping site (DS) showed elevated PAH levels of C_{free} and C_{sediment} at 10–25 cm below the sediment surface, with maximum peaks between 16 cm and 19 cm. The concentration peaks in the sediment core from this site correlate with the presence of the dumped material layer, which was reddish in color and had an oily consistency.

Profiles of the shipping channel station (SCH) were different from those of the dumping site sediment core, but peaks of concentration maxima were also found in this core. C_{free} of all measured compounds except phenanthrene and benzo(b)fluoranthene had two concentration maxima at depths of 16–22 cm and 26–28 cm. Phenanthrene and benzo(b)fluoranthene showed a higher concentration peak at a depth of 26–28 cm. These concentration peaks could be a result of shipping activities e.g. the release of oily wastes or oily water from ships. Moreover, Leipe et al. (2005) observed a spreading of the dumped material since 1980. To date, a part of the material also reached the SCH station.

3.2. PAH exposure of sediment organisms

Fig. 1 shows that PAH exposure can vary with sediment depth. At the reference station, both C_{free} and C_{sediment} decrease with depth (see also Fig. SI 2). This suggests that organisms moving into deeper sediment layers would experience reduced PAH exposure. The opposite is the case for the two other sites, where the movement of an organism into the deeper sediment layers would be associated with a marked increase in exposure. The high PAH levels of C_{sediment} and C_{free} in the deeper sediments at station DS and RS are less accessible to organisms living on the sediment surface or the water column, such as mussels and fish.

These matrix-SPME measurements can be applied to the exposure assessment of the PAHs in the sediment in three different ways:

- [i] The measured C_{free} of a contaminant can be multiplied by its bioconcentration factor (BCF) to predict its body residue in sediment worms (Kraaij et al., 2003), for instance. The measured C_{free} can also be related directly to the effective concentration (e.g. EC-50) derived from aquatic toxicity tests of individual compounds.
- [ii] A second approach applies the measured PAH concentrations in the PDMS coating of the SPME fiber to estimate the body burden, and this approach is well suited to derive the total body burden of a complex mixture (Leslie et al., 2002; Osslander et al., 2008).
- [iii] Finally, the baseline toxic potential of the PAHs can be assessed on the basis of the chemical activities of the PAHs, which can be deduced from C_{free} (Reichenberg and Mayer, 2006). This very recent approach will be described in more detail below.

3.3. Chemical activity and baseline toxicity

Hydrophobic pollutants such as PAHs accumulate in biological membranes, possibly disturbing their structure and function. This

mode of acute toxic action is called baseline toxicity or narcosis (Escher and Schwarzenbach, 2002). Although baseline toxicity is the minimal toxicity that a compound may elicit, it is relevant for assessing the risk of complex mixtures in the environment. In particular for large numbers of compounds, all of which are present below the threshold level for specific toxicity, the underlying baseline toxicity can determine the overall toxic effect because it is concentration-additive (Escher et al., 2002).

The partitioning of lipophilic organic substances into lipid membranes is a spontaneous process and can be better described by chemical activity than by the concentration in the exposure medium (Reichenberg and Mayer, 2006). In this study, chemical activities (a) of PAHs were calculated from C_{free} and the subcooled liquid solubility S_L :

$$a = \frac{C_{\text{free}}}{S_L} \quad (2)$$

S_L : Subcooled liquid solubilities were calculated by a SPARC on-line calculator (<http://ibmlc2.chem.uga.edu/sparc/index.cfm>, 2006-02-20).

The mixture toxicity of PAHs is concentration-additive (Lan-drum et al., 2003) and the sum of chemical activities is an indicator of the baseline toxic potential of the mixture (Di Toro et al., 2000). Fig. 2 shows the sum of chemical activities of nine PAHs for the various sampling sites and sediment depths. The gray area represents the chemical activity range of 0.01–0.1, where baseline toxicity is lethal (Reichenberg and Mayer, 2006). The chemical activity was below the baseline toxic limit at all sampling stations and sediment depths. In some cases, however, the sum of chemical activities was only a factor of ten below a 50% effect activity (EA50) for lethality. This may be considered a very high contamination level because the contaminated sediment contains many substances other than the nine measured PAHs, some compounds might exert excess toxicity and lethality is a very severe toxicological endpoint. The contribution to the baseline toxicity of the material dumped at

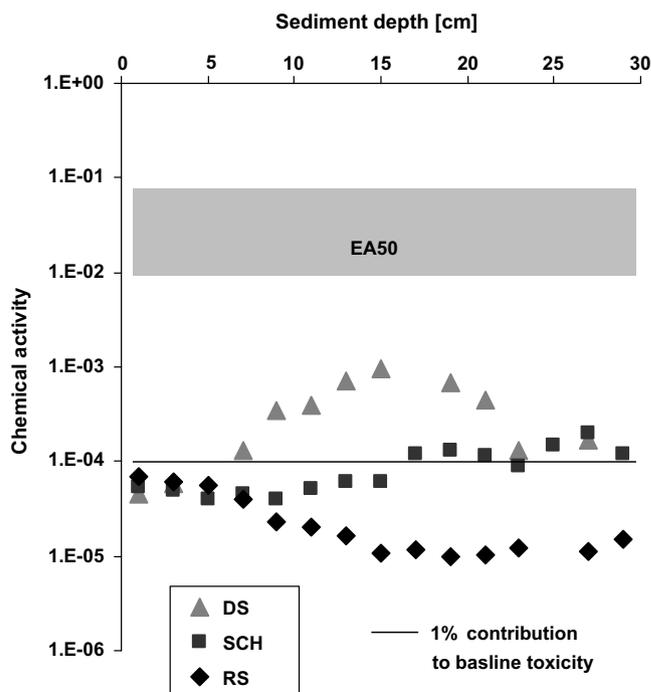


Fig. 2. Comparison of the chemical activities of the different sampling sites of the PAH mixture (sum of 9 PAHs). Grey zone indicates risk for lethal baseline toxicity (EA50).

station DS at a depth of 12–22 cm in particular is up to 100 times higher than in the reference station.

The chemical activities of phenanthrene and benzo(a)pyrene are shown as a function of sediment depth in Fig. 3, which also includes a line representing the 1% contribution to baseline toxicity as recently suggested (Mayer and Reichenberg, 2006). Chemical activities are more evenly distributed among the measured PAHs than freely dissolved concentrations. Although the freely dissolved concentration of these two PAHs is very different (see Fig. 1) their chemical activity and thus their contribution to the baseline toxicity is rather similar (Fig. 3). This can be explained by the general decrease of EA50 for the baseline toxicity with increasing $\log K_{OW}$, and benzo(a)pyrene ($\log K_{OW} = 5.91$) thus requires a lower C_{free} than phenanthrene ($\log K_{OW} = 4.46$) to show the same chemical activity and thus make a similar contribution to the baseline toxicity.

3.4. Direction of diffusive mass transfer

Measurements of C_{free} or chemical activity (a) give direct information about the direction of the diffusive mass transfer, which always takes place from areas of high to low chemical activity (and fugacity) (Reichenberg and Mayer, 2006). The chemical activity of phenanthrene at the dumping site increases with sediment depth within the first 15 cm, and this implies a diffusive phenanthrene flux towards the sediment surface, with the surface sediment acting as a diffusion and sorption barrier (Fig. 3). The chemical activity of benzo(a)pyrene shows a steeper slope, which is in good agreement with the fact that it is less mobile than phenanthrene due to its higher K_{OC} value. This low mobility due to sorption is the precondition for the long-term conservation of PAH gradients. For PAHs, the surface sediment at station DS acts as a seal between the contaminated sediment and the water column.

The activity gradient of benzo(a)pyrene at the reference site has the opposite direction, indicating diffusion from the upper sediment layers down to the deeper layers. The gradient of benzo(a)pyrene is again much steeper compared to phenanthrene, which can also be explained by its lower mobility.

A very important question remains. Does the sediment act as a diffusive source or as a diffusive sink for the PAHs in the water column? Or is a given sediment in thermodynamic equilibrium with the overlying water? These questions call for the determination of the chemical activity of PAHs in the overlying water, which can be measured by field equilibrium sampling, preferably using the same sampling material (Cornelissen et al., 2008).

3.5. Sorption of PAHs to the sediment matrix

Sorption coefficients are often used to describe the equilibrium distribution of a chemical between sediment and water. The observation that sorption of hydrophobic organic chemicals (HOC) generally increases with increasing organic carbon content of the sediment and with increasing hydrophobicity of the chemical has led to the application of sorption coefficients normalized with respect to organic carbon (K_{OC}) (Karickhoff et al., 1979; Karickhoff, 1981; Doucette, 2003). Generic K_{OC} coefficients are often estimated with the Karickhoff regression:

$$\log K_{OC} = 0.99 \log K_{OW} - 0.35 \quad (3)$$

Several recent field investigations have shown that such generic K_{OC} values overestimate the actual sediment to water distribution of HOCs by one to two orders of magnitude (Naes et al., 1998; Gustafsson and Gschwend, 1999; Persson et al., 2002), which can in turn lead to a significant overestimation of C_{free} in pore water and body residues in sediment organisms. Such underestimation of sorption and overestimation of C_{free} has recently been explained by the presence of soot and other forms of black carbon characterized by strong adsorption and non-linear isotherms for PAHs (Cornelissen et al., 2005, 2006).

We determined the ratio of the estimated and measured values of C_{free} and plotted these against the measured soot content of the sediment. Fig. 4 presents data for three representative PAHs in all three sediments. The estimates of C_{free} were based on PAH concentrations, the dry weight content and the OC fraction of the dry weight, all measured in the sediment. These were combined with K_{OC} values calculated with Eq. (3) and Table SI 2. The deviation between the estimated and measured C_{free} values is within one order of magnitude at low soot concentrations of 1–3 mg g⁻¹ dry weight, and the average ratio is close to unity. The observed scatter can be attributed to the sum of errors in the input data of the estimated as well as the measured freely dissolved concentrations, the main uncertainty being the variation of the sorptive properties of the organic carbon of the sediment. The latter type of variation is excluded with SPME, as this applies the same partitioning phase (i.e. PDMS) to all samples. A systematic overestimation by up to two orders of magnitude is apparent at higher soot concentrations. This observation is in good agreement with the recent literature (e.g. Cornelissen et al., 2005).

These observations lead to the conclusion that measuring rather than estimating C_{free} will improve the precision of data at low soot concentrations and reduce analytical work, whereas such measure-

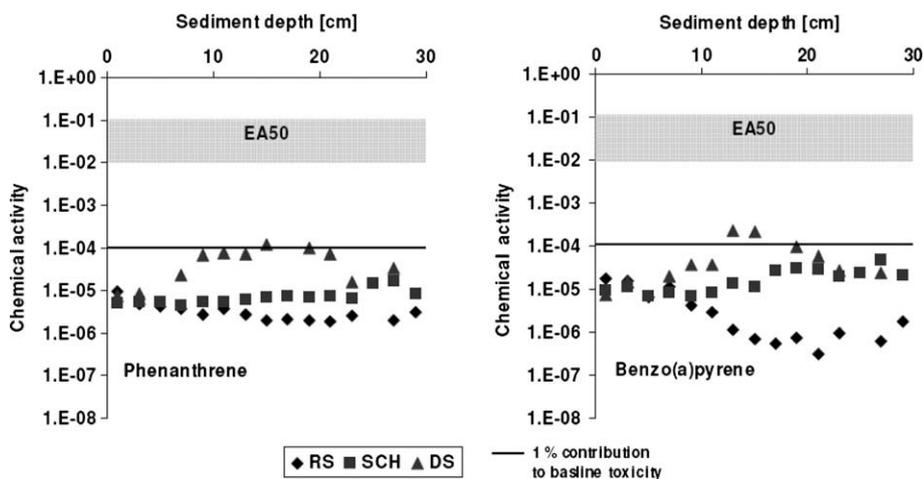


Fig. 3. Comparison of the chemical activities of phenanthrene and benzo(a)pyrene at the different sampling sites and at different sediment depth.

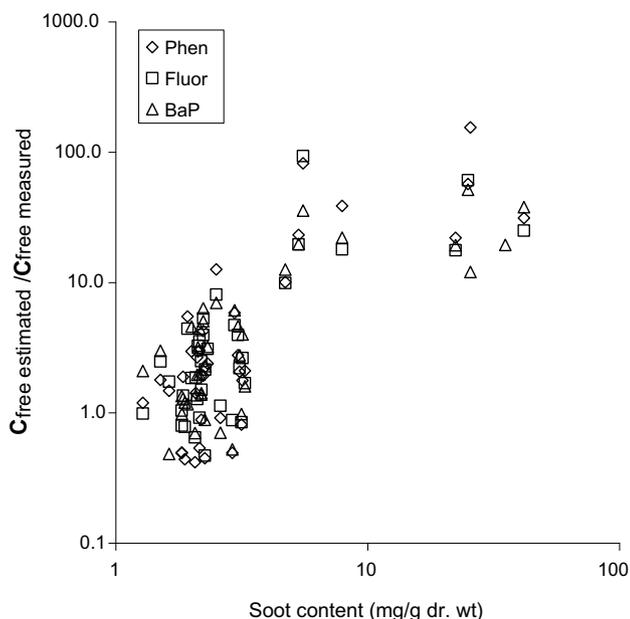


Fig. 4. Ratio of estimated and measured C_{free} for three PAHs with different hydrophobicity plotted against the measured soot content of the sediment.

ments are actually necessary at higher soot concentrations. Like the measurement of the soot content, the measurement of C_{free} may re-establish the relationship between sediment quality criteria and biological uptake in risk assessments.

4. Conclusions

In contrast to total sediment concentrations, freely dissolved concentrations and chemical activities are directly related to the bioconcentration in sediment organisms (Kraaij et al., 2003). The SPME technique used in this study offers an efficient method to measure C_{free} and to assess the site-specific risks of sediment pollution. The calculation of the chemical activity from C_{free} is useful for a comprehensive discussion of bioavailability and for predicting the baseline toxic potential. Although sediment concentrations of PAHs at the dumping site were more than three orders of magnitude higher than at the reference sites, the pore-water concentrations were higher by only one order of magnitude. Highly hydrophobic substances such as benzo(a)pyrene were characterized by low levels of C_{free} and rather high levels of chemical activity. This means that the contribution of such substances to the pool of freely dissolved molecules is often negligible, whereas their contribution to the baseline toxic potential may be significant.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2008.09.073.

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