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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.

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 (Pawliszyn, 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}):

$$C_{\mathrm{free}} = \frac{C_{\mathrm{PDMS}}}{K_{\mathrm{PDMS}}} \tag{1}$$

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 (415000 km^2) 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.