



## Equilibrium passive sampling as a tool to study polycyclic aromatic hydrocarbons in Baltic Sea sediment pore-water systems

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### ABSTRACT

Solid Phase Microextraction (SPME) was applied to provide the first large scale dataset of freely dissolved concentrations for 9 polycyclic aromatic hydrocarbons (PAHs) in Baltic Sea sediment cores. Polydimethylsiloxane (PDMS) coated glass fibers were used for ex-situ equilibrium sampling followed by automated thermal desorption and GC–MS analysis. From the PAH concentrations in the fiber coating we examined (i) spatially resolved freely dissolved PAH concentrations ( $C_{free}$ ); (ii) baseline toxicity potential on the basis of chemical activities (a); (iii) site specific mixture compositions; (iv) diffusion gradients at the sediment water interface and within the sediment cores and (v) site specific distribution ratios. Contamination levels were low in the northern Baltic Sea, moderate to elevated in the Baltic Proper and highest in the Gulf of Finland. Chemical activities were well below levels expected to cause narcosis to benthos organisms. The SPME method is a very sensitive tool that opens new possibilities for studying the PAHs at trace levels in marine environments.

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### 1. Introduction

The Baltic Sea is one of the largest brackish water regions in the world and nearly completely surrounded by the European littoral states. As a shallow semi-enclosed sea it is only connected to the open ocean through the North Sea. Hence, water exchange is dominated by seasonal inflow events through the Kattegat and Skagerrak region and the fresh-water influx is limited to river inputs. Due to its geographical location (including the geological, hydrographical and physico-chemical conditions), the Baltic Sea is globally one of the heaviest polluted marine areas (Lozán, 1996).

Polycyclic aromatic hydrocarbons (PAHs) are primary components of Baltic Sea sediment contamination (Witt and Trost, 1999; HELCOM, 2010). Combustion processes are responsible for the majority of PAHs that enter the marine environment of the Baltic Sea via the atmosphere. PAHs are also constituents of coal, crude oil and tar and include numerous natural sources. Through atmospheric deposition and municipal as well as industrial waste water discharges, hydrophobic organic contaminants (HOCs) like PAHs are distributed in the marine environment and finally enriched in the sediment due to their ability to bind to particulate

matter. In recent decades many hydrophobic organic contaminants, such as PAHs, PCBs, dioxins and dibenzofuranes (PCDDs, PCDFs) and pesticides (lindane, DDT), have become important in environmental sciences and toxicology because they are major pollutants of sediments. In addition this class of contaminants causes a variety of adverse health effects in organisms; some of them are carcinogenic and mutagenic. As a result PAHs were defined as priority pollutants by the US-EPA in the 1980s and are the focus of many national and international laws and policies.

Marine environmental monitoring programs (European Union Marine Strategy Framework Directive (MSFD) and HELCOM; e.g. Baltic Sea action plan (2007), Baltic Sea Monitoring Program) have been implemented over the last 50 years and have focused on the characterization and improvement of the ecological state of the Baltic Sea (Backer et al., 2010). As a result a large pool of data exists describing the condition of organic contamination in sediments on the basis of total concentrations (Witt and Trost, 1999; Baumard et al., 1999; Blanz et al., 1999; Konat and Kowalewska, 2001; Pikkarainen, 2007 and Dabroska et al., 2013). In most cases, field studies have been restricted to localized areas of the Baltic Sea and cover different years, using a variety of sampling and analytical methods, which makes a comparison of data, in particular for their spatial and historical trends, more difficult.

Traditional solvent extraction techniques used to study the behavior of organic contaminants in sediments should now be supplemented by

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a range of passive sampling methods (Zygmunt et al., 2001 and Jahnke et al., 2014), because ecologically relevant processes such as bioavailability (Escher et al., 2002), bioconcentration in sediment organisms (Kraaij et al., 2003) and baseline toxicity (Mayer and Reichenberg, 2006) are more closely related to the freely dissolved concentrations than to total concentration of HOCs ( $C_{\text{total}}$ ) in the sediment. Despite this potential, sediment quality guidelines (SQGs) based on  $C_{\text{total}}$  are applied in most regulatory jurisdictions. The use of  $C_{\text{total}}$ -based SQGs often overestimates risks from sediment contaminants, because it ignores factors that are known to limit or reduce chemical bioavailability.

Differences in freely dissolved concentrations ( $C_{\text{free}}$ ) and chemical activity (a) drive diffusion and partitioning processes, that determine if sediments act as a source or sink for HOCs (Reichenberg and Mayer, 2006). The chemical activity describes the energetic state of a substance, whereas  $C_{\text{free}}$  generally are the effective concentrations for diffusive uptake into aquatic and benthic organisms (Di Toro et al., 1991 and Reichenberg and Mayer, 2006). This makes  $C_{\text{free}}$  and chemical activity more relevant as exposure parameters for assessment and management of contaminated sediments.

The rapid development of various passive sampling techniques in the last decade, applying a variety of polymers for a broad range of HOCs provides novel approaches for measuring rather than calculating  $C_{\text{free}}$  and chemical activity (Booij et al., 2003; Cornelissen et al., 2008; Hawthorne et al., 2008; Bondarenko and Gan, 2009; Lydy et al., 2014 and Mayer et al., 2014). However, to date only a few studies exist that deal with passive sampling of HOCs in sediment-pore water of the Baltic Sea. The first study concentrating on  $C_{\text{free}}$  of PCDD/Fs and PCBs in marine sediments at a pristine location of the Baltic Sea was published by Cornelissen et al. (2008). Recently Jahnke et al. (2012) and Witt and co-workers (2009 and 2010) focused on PCBs and PAHs at the regional scale in the Baltic Sea area. To date no large-scale evaluation of PAH exposure in Baltic Sea sediment cores using passive sampling methods exists. Solid phase micro extraction (SPME) was introduced as a solvent free extraction technique in Analytical Chemistry by Arthur and Pawliszyn, 1990. Ten years later, SPME was applied for non-depletive equilibrium sampling with disposable glass fibers to determine freely dissolved concentrations of hydrophobic organic chemicals in sediments (Mayer et al., 2000). More recently, this approach was further developed by combining equilibrium sampling in sediment with automated thermal desorption and GC-MS (Witt et al., 2013). There are several other equilibrium sampling techniques that operate on a similar principle, such as silicone coated glass jars (Jahnke et al., 2012), silicone rubber sheets (Yates et al., 2013), polyethylene devices (PEDs) (Lohmann, 2012 and Gschwend et al., 2011) and polyoxymethylene (POM) (Cui et al., 2013). The main reason for choosing the SPME technique for the present study is that thermal desorption in contrast to most other methods transfers the entire analyte onto the analytical system, which means that trace level determination are feasible even with a very small sampler containing less than 1 mg of polymer phase. This in turn allows non depletive equilibrium sampling even on small sediment samples, which is important when taking sub-sections of sediment cores. Presumably another advantage that could be highlighted is faster kinetics of thin PDMS fibers versus other PS options thus facilitating practicality of shorter lab equilibration times for ex-situ analysis. Additional reasons for using the SPME approach are (1) high throughput analysis based on automated thermal desorption, (2) the approach is largely solvent free and (3) close alignment with the analytical instrument. This study was designed to apply and assess SPME as a method to study environmental exposure and distribution of PAH contamination in the main sedimentation basins of the Baltic Sea. The aim was to comprehensively study exposure, fate, partitioning, bioavailability, and baseline toxicity of selected PAHs. It also makes substantial contribution to the assessment of sediment characteristics in terms of providing the first large-scale investigation of 9 PAHs with an equilibrium sampling approach in Baltic Sea sediments identifying (i) large scale horizontal gradients of  $C_{\text{free}}$  and chemical activity; (ii) gradients within sediment cores and at the

sediment-water interface that drive diffusive mass transfer; (iii) site specific distribution ratios ( $K_D$ ) and (iv) the baseline toxic potential.

## 2. Experimental section

### 2.1. Study sites and sediment sampling

Sediment samples were collected at eleven locations across the Baltic Sea region in June and July 2008 on a cruise with the research vessel MARIA S. MERIAN. The sediment cores were sampled with a multicorer, cut into 2 cm thick slices and stored at  $-18\text{ }^{\circ}\text{C}$  in pre-cleaned aluminum boxes until analysis. A total core length of 20 cm was analyzed from each sampling station. Bottom water was sampled at the same time with an in situ pump system (Petrick et al., 1996). A map showing the sampling locations is given in Fig. S1. Details, geographical positions of the sampling stations, the sampling depth, salinity and temperature of the bottom water are given in SI, Table S1. Method description and results of the bulk sediment concentration measurements are given in text S2 and of the bottom water concentrations in text S3 of the SI.

### 2.2. Equilibrium sampling with SPME

The study included the investigation of 9 PAHs with a log  $K_{\text{OW}}$  range from 4.46–6.38 (Doong and Chang, 2000). Standards, chemicals and materials for measurement of freely dissolved concentrations are given in text S1.

Solid phase micro extraction experiments were carried out for the determination of freely dissolved sediment-pore water concentrations ( $C_{\text{free}}$ ) of target PAHs (Witt et al., 2010). Equilibrium passive sampling experiments with SPME were conducted with commercially available glass fibers with a nominal PDMS coating of 10  $\mu\text{m}$  (Fiberguide Industries, Stirling, NJ, USA). However, the actual fiber coating thickness was 12.7  $\mu\text{m}$  (inner radius of 103.6  $\mu\text{m}$ ; outer radius 116.3  $\mu\text{m}$ ) as measured with laser scanning confocal microscopy (Witt et al., 2013), and this measured thickness was used for the calculation of polymer volume. The fibers were cut into 10 cm pieces and cleaned by treating twice with methanol and ultrapure water in an ultrasonic bath. Approximately 10 g (wet weight) homogenized sediment was placed in a cleaned 9 mL glass vial and closed with polytetrafluoroethylene (PTFE) lined caps. The septum was pierced with a syringe needle to place 10 cm pieces of the clean fiber into the vial. Three fibers were inserted into each vial. The vials were shaken on an end-over-end shaker for 240 h until equilibrium was reached (Witt et al., 2010). The equilibrated fibers were rinsed with ultraclean water (MilliQ) and gently wiped with lint free tissue. The exposed as well as cleaned, unexposed fibers (blanks) were wrapped in cleaned aluminum foil and stored at  $-18\text{ }^{\circ}\text{C}$  until analysis via GC-MS (gas chromatography-mass spectrometry).

### 2.3. Fiber analysis by GC-MS

Approximately 9 cm of equilibrated and blank fibers were transferred and stored contamination-free in separate GC liners (ALEX liner tray, Gerstel) for analysis. Prior to loading, the liners were plugged with deactivated glass wool, rinsed twice with both acetone and hexane and pre-heated at 250  $^{\circ}\text{C}$  for 19 min under helium flow in the GC injector to remove organic residues. The fiber loaded liners were automatically placed in the injector (MultiPurpose Sampler, MPS 2XL, Gerstel) and thermally desorbed in a Cooled Injection System (CIS). The injector temperature was increased from 50  $^{\circ}\text{C}$  to 250  $^{\circ}\text{C}$  at 12  $^{\circ}\text{C s}^{-1}$  and held for 15 min to assure thermal desorption from the fiber. Then the desorbed sample was transferred splitless to the column and the injector purge flow to the split vent was set at 50  $\text{mL min}^{-1}$ . The GC (7890A, Agilent Technologies) contained a DB-5 fused silica gel column (325  $^{\circ}\text{C}$ : 30  $\text{m} \times 250\ \mu\text{m} \times 0.25\ \mu\text{m}$ , J&W Scientific) with helium (average linear velocity 37  $\text{cm s}^{-1}$ ) as the carrier phase. The temperature program of the GC oven was: (1) 60  $^{\circ}\text{C}$  held for 15 min, (2) 195  $^{\circ}\text{C}$  (ramp: 15

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