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Equilibrium sampling of polychlorinated biphenyls in River Elbe sediments – Linking bioaccumulation in fish to sediment contamination

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Highlights

Application of equilibrium sampling in routine sediment monitoring.
Freely dissolved concentrations ($c_{\text{free}}$) of PCBs in sediments.
Determining PCB concentrations in lipids at equilibrium with sediment ($c_{\text{lip/sed}}$).
Close link between sediment contamination and fish bioaccumulation.
Cross validation of two independent monitoring programs.

Graphical Abstract

2 independent monitoring programs = 1 relationship

Abstract

Equilibrium sampling can be applied to measure freely dissolved concentrations ($c_{\text{free}}$) of hydrophobic organic chemicals (HOCs) that are considered effective concentrations for diffusive uptake and partitioning. It can also yield concentrations in lipids at thermodynamic equilibrium with the sediment ($c_{\text{lip/sed}}$) by multiplying concentrations in the equilibrium sampling polymer with lipid to polymer partition coefficients. We have applied silicone coated glass jars for equilibrium sampling of seven ‘indicator’ polychlorinated biphenyls (PCBs) in sediment samples from ten locations along the River Elbe to measure $c_{\text{free}}$ of PCBs and their $c_{\text{lip/sed}}$. For three sites, we then related $c_{\text{lip/sed}}$ to lipid-normalized PCB concentrations ($c_{\text{bio/lip}}$) that were determined independently by the German Environmental Specimen Bank in common bream, a fish species living in close contact with the sediment: (1) In all cases, $c_{\text{bio/lip}}$ were below $c_{\text{lip/sed}}$, (2) there was proportionality between the two parameters with high $R^2$ values (0.92–1.00) and (3) the slopes of the linear regressions were very similar between the three stations (0.297; 0.327; 0.390). These results confirm the close link between PCB bioaccumulation and the thermodynamic potential of sediment-associated HOCs for partitioning into lipids. This novel approach gives clearer and more consistent results compared to conventional approaches that are based on total concentrations in sediment and biota-sediment accumulation factors. We propose to apply equilibrium sampling for determining bioavailability and bioaccumulation potential of HOCs, since this technique can provide a thermodynamic basis for the risk assessment and management of contaminated sediments.

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1. Introduction

Sediments are an essential, integral and dynamic part of aquatic ecosystems (Salmons and Brils, 2004). They can also act as a major sink for organic chemicals that are released to surface waters and then tend to bind to sediments. Of particular concern are persistent organic pollutants (POPs) that, due to their persistence, can accumulate at high levels in sediments, which then become a reservoir for POPs. While in many cases the sources of POPs have been reduced in the last few decades and water quality is improving at most places in industrial countries, sediments act today as important secondary sources for POP contamination.

Sediment-associated chemicals can directly affect benthic life as well as pose deleterious effects on other organisms, via bioaccumulation and subsequent transfer through food webs (Arnot and Gobas, 2006). Monitoring chemicals in biota is an essential part of regulatory programs that assess the chemical status of water bodies. In Europe, the focus on bioaccumulation has recently been strengthened by setting new Environmental Quality Standards for priority substances that have to be monitored in aquatic biota (EC, 2013). There are other monitoring programs on regional and national scales such as the German Environmental Specimen Bank (ESB). In freshwater environments, the ESB samples aquatic biota such as common bream (Abramis brama), a fish species living in close contact with the sediment, to monitor for chemicals (UBA, 2008, 2014). Though bioaccumulation and sediment contamination are closely linked, they are traditionally assessed separately.

When monitoring sediment contamination, total concentrations ($c_{\text{total}}$) of chemicals are usually quantified by conventional chemical analyses. However, $c_{\text{total}}$ is a poor descriptor of chemical bioavailability in sediments. Equilibrium partitioning models were, hence, developed to estimate freely dissolved concentrations ($c_{\text{free}}$), which are often considered the effective concentration for diffusive uptake and partitioning (Di Toro et al., 1991; Kraaij et al., 2003). When applying equilibrium partitioning models for hydrophobic organic chemicals (HOCs), concentrations in sediments are normalized to organic carbon (OC) content as major binding phase. Research over the last two decades has clearly demonstrated that the combination of $c_{\text{total}}$ measurements and OC-based normalization approaches is inadequate to accurately characterize contaminant binding to sediments, and contaminant bioavailability remains a key uncertainty in the risk assessment of contaminated sediments (Eilers and Luthy, 2003; Hawthorne et al., 2006).

Passive equilibrium sampling can directly quantify $c_{\text{free}}$, which makes it a promising tool for sediment-management decision making (Kraaij et al., 2003; Parkerton and Maruya, 2014). In equilibrium sampling, a thin polymer is brought in contact with the sediment sample until equilibrium partitioning of the chemicals between the sediment and the polymer is attained (Mayer et al., 2000, 2014). $c_{\text{free}}$ can then be calculated by dividing measured concentrations in the polymer ($c_{\text{pol}}$) with chemical-specific polymer to water partition coefficients ($K_{\text{pol,wa}}$) (Mayer et al., 2000). The measured concentrations in the polymer can further be multiplied with lipid to polymer partition coefficients ($K_{\text{lip,pol}}$) in order to obtain the equilibrium partitioning concentrations in biota lipid ($c_{\text{lip,bi}}$) (Jahnke et al., 2008; Määenpää et al., 2011).

Various equilibrium sampling devices for HOCs have been described in the literature (Mayer et al., 2000; Jonker and Koelmans, 2001; Meloche et al., 2009; Smedes et al., 2013; Witt et al., 2013). They can be applied in situ in order to insure measurements of $c_{\text{free}}$ at field conditions (Fernandez et al., 2009; Witt et al., 2013) or ex situ which is generally more favorable for routine sediment monitoring since deployments are performed and equilibrium can be attained in the laboratory. Silicone coated jars, glass jars with the inner vertical walls coated with a few μm of silicone, were originally developed for contaminated soils (Reichenberg et al., 2008). In recent studies, silicone coated jars have been applied for the quantification of HOCs in marine and limnic sediments (Määenpää et al., 2011; Jahnke et al., 2012, 2014a). A major advantage of this approach is the parallel sampling with varying silicone coating thicknesses for validating equilibrium sampling and confirming the presence of potential artifacts such as surface abrasion of the silicone coating. By applying silicone coated jars to sediment from the Baltic Sea and a Swedish lake and comparing the data to bioaccumulation in fish, Jahnke et al. (2012) and (2014a,b) have shown that lipid-normalized PCB concentrations in fish were near or below $c_{\text{lip,bi}}$. Consequently, these fish appeared at or below the equilibrium partitioning level relative to the sediment.

In the present study, silicone coated jars were applied for equilibrium sampling of POPs while aiming at the integration of bioavailability and bioaccumulation parameters in environmental monitoring programs. Silicone coated jars were directed at monitoring sediment total concentrations ($c_{\text{total}}$) of POPs in sediment interstitial water and (2) equilibrium partitioning concentrations in lipids ($c_{\text{lip,bi}}$). The technical hypothesis of the study was that the silicone coated jars are sufficiently sensitive, precise and practical enough to offer new opportunities for the monitoring of HOCs in sediments. The scientific hypothesis was that PCB bioaccumulation in bream is closely linked to sediment contamination and that equilibrium sampling can be used to measure site-specific bioaccumulation potential based on equilibrium partitioning concentration in model lipids ($c_{\text{lip,bi}}$). Recent studies (Jahnke et al., 2012 and 2014a,b) linked $c_{\text{lip,bi}}$ to lipid-normalized concentration ($c_{\text{lip,bi},\text{lip}}$) in biota sampled in the same ecosystem, whereas we show in the present study that $c_{\text{lip,bi}}$ can even be used to assess site-specific bioaccumulation of PCBs in common bream within a river ecosystem.

2. Experimental

2.1. Sampling and exhaustive extraction of sediments

As part of a yearly monitoring campaign, sediment samples were taken in the German part of the River Elbe in July 2012 (Text S1) at ten sampling stations between Prossen (km 13.3) close to the Czech border and Geesthacht (km 584.5) near Hamburg and situated before the tidal River Elbe (Fig. 1, Table S1). At each sampling site, several sediment grab samples (top layer 0–20 cm) were taken with stainless steel van Veen type samplers, collected in stainless-steel bins and thoroughly homogenized using stainless-steel rakes. Color, smell and consistency of each sediment was recorded and samples were stored in polystyrene jars at 4°C until further processing.

Total analyte concentrations ($c_{\text{total}}$) in sediments were determined by exhaustive extraction and subsequent analysis by GC–MS as described in Text S2. Furthermore, physico-chemical parameters of sediment such as total organic carbon (TOC) content, dry residue and grain size fractions as well as elemental composition of carbon, nitrogen, and sulfur were measured (Text S2, Table S2–3).

2.2. Equilibrium sampling of sediments

Equilibrium sampling was performed as described previously (Reichenberg et al., 2008; Määenpää et al., 2011; Jahnke et al., 2012, 2014a) with minor modifications: Glass jars were internally coated on their vertical sides with silicone (DC 1-2577) from Dow Corning (Midland, USA) (Text S3). In the laboratory, sediment that had been transported and stored for up to several months in one
liter polystyrene jars was again homogenized. 70–80 g of wet, native sediment was weighed in a silicone coated, pre-cleaned and dried glass jar, and 20 mL bi-distilled water was added to insure thorough mixing of sediment during incubation. For each sediment sample, three subsamples were weighed in coated jars with 2, 4 and 8 μm silicone thickness (n = 1), respectively, to validate equilibrium sampling. For sediments from the sampling stations Prossen and Wittenberg three replicates per coating thickness (n = 3, N = 9) were incubated. Jars were sealed with lids and rolled on their sides at 60 rpm on a tumbling roller mixer (Ten Roller Tube Roller Mixer, Ratek Instruments Pty. Ltd., Australia) at room temperature (22 ± 1°C) for two weeks. For each incubation series, three coated jars with 2, 4 and 8 μm silicone coatings were left empty and used as blanks (a total of 15 glass jars).

2.3. Extraction of silicone coated jars, clean-up and analysis

After incubation, sediment and water was poured out of each silicone coated jar, which was rinsed in several steps with a total volume of 20 mL bi-distilled water. The silicone coating was carelessly wiped with lint-free tissues to remove remaining sediment and water. 3 mL of n-heptane was added and analytes were extracted on the roller mixer for 30 min (60 rpm). Extraction was repeated twice and extracts were combined. 50 μL of internal standard solution (PAH Mix 33 containing acenaphthene D10, chrysene D12, 1,4-dichlorobenzene D4, naphthalene D8, perylene D12, phenanthrene D10 with 500 pg/μL each in n-heptane; PCB 185, p,p’-DDE D8, p,p’-DDT D8 with 105 pg/μL each in n-heptane; Dr. Ehrensdorfer GmbH, Augsburg, Germany) and PCB 185 (Dr. Ehrensdorfer GmbH, Augsburg, Germany) to which PCB 118 (Dr. Ehrensdorfer GmbH, Augsburg, Germany) and PCB 185 (Dr. Ehrensdorfer GmbH, Augsburg, Germany) were added.

To minimize matrix effects of sediment components, extracts were submitted to cleanup by aluminium oxide columns. Glass columns were prepared with two pre-cleaned glass fibre filters (Type A/E-glass, 1.0 μm, Pall corporation, Michigan, USA). 2 g pre-heated (220°C, over night) neutral aluminium oxide (Merck KGaA, Darmstadt, Germany) were deactivated with 200 μL bi-distilled water, filled into glass column and sealed with another glass fibre filter. The glass column was rinsed twice with 3 mL of n-heptane, the sample extract was added and eluted with 6 mL of n-heptane. The extract volume was reduced to approx. 0.5 mL in a concentration station (Turbo Vap 2 Concentration Workstation, Zymark, Soatax, Allschwill, Switzerland), pipetted into a GC vial and reduced to 200 μL under a gentle stream of nitrogen.

All extracts were analyzed for 7 ‘indicator’-PCBs (PCB 28, 52, 101, 118, 138, 153, 180) by gas chromatography coupled to tandem mass spectrometry (GC–MS/MS). The system was a 7000 GC–MS/MS coupled to a 7890 GC-System and a GC sampler 80 (Agilent Technologies, Santa Clara, USA) and equipped with a HP 5 MS column (30 m length × 0.25 mm diameter × 0.25 μm film thickness, Agilent J&W, GC columns, USA). The calibration standard was a solution of 36 compounds for EN ISO 6468 (CERTAN®, Promochem, Wessl, Germany) to which PCB 118 (Dr. Ehrensdorfer GmbH, Augsburg, Germany) and PCB 185 (Dr. Ehrensdorfer GmbH, Augsburg, Germany) were added. PCB 185 was used as internal standard. The combined calibration standard solution was diluted to concentrations of 0.25, 0.5, 2.5, 5, 10, 25, 50, 100, 200 pg/μL for each compound in n-heptane. For all analytes the lowest standard that could be quantified was 0.5 pg/μL.

Method detection and method quantification limits (MDLs and MQLs, respectively) of the silicone coated jar approach were calculated as described previously (Jahnke et al., 2012). With a final extract volume of 200 μL MQL was approximately 5.88 μg kg⁻¹ silicone for equilibrium samplers with the thinnest silicone thickness (2 μm, minimum weight 17 mg). MDL was around three times lower (1.96 μg kg⁻¹ silicone) than MQL.

2.4. Performance parameters and calculation of endpoints

To determine the potential loss and the exact mass of silicone, the silicone coated jars were weighed before pre-cleaning as well as after drying of the silicone following equilibrium sampling and solvent extraction of silicone. Analyte mass in silicone (pg) was plotted against respective silicone mass (mg). Proportionality of analyte mass versus silicone mass confirmed equilibrium sampling as after drying of the silicone following equilibrium sampling and solvent extraction of silicone. Analyte mass in silicone (pg) was plotted against respective silicone mass (mg). Proportionality of analyte mass versus silicone mass confirmed equilibrium sampling (Reichenberg et al., 2008). The analyte concentration in silicone (c_{sil}) in μg kg⁻¹ was obtained by the slope of the linear regression forced through the origin. For the linear regression of analyte mass in silicone versus silicone mass, standard errors were calculated. c_{sil} (μg kg⁻¹ silicone) was converted to μg L⁻¹ silicone by dividing by silicone density of 0.903 kg L⁻¹.

Freely dissolved concentration (c_{free}) in sediment interstitial waters was calculated with analyte-specific silicone to water partition coefficient (K_{sil,aq}) as:

\[ c_{\text{free}} = \frac{c_{\text{sil}}}{K_{\text{sil,aq}}} \]
The \( K_{\text{sil,aq}} \) for the silicone DC1-2577 (Dow Corning, Midland, USA), \( K_{\text{DC,aq}} \) that was applied in the present study, were obtained by multiplying silicone to silicone partition coefficients, \( K_{\text{sil,sil}} \), and more specifically \( K_{\text{DC,Altesi}} \) obtained from Gilbert et al. (2015) with \( K_{\text{Altesil,aq}} \) for the silicone Altesil obtained from Smedes et al. (2009):

\[
K_{\text{DC,aq}} = K_{\text{DC,Altesi}} \cdot K_{\text{Altesil,aq}}. \tag{2}
\]

For MDL and MQL, \( c_{\text{free}} \) can be obtained by dividing respective values in silicone (\( \mu \text{g kg}^{-1} \) silicone) with silicone to water partition coefficients. Since mean water temperatures in the River Elbe measured at 14 stations between km 13.2 and 584.5 were around 22 °C in the sampling period from the 2nd to 12th of July 2012 (German Federal Waterways and Shipping Administration (WSV) communicated by multiplying silicone to silicone partition coefficients, \( K_{\text{sil,sil}} \), and silicone-specific lipid to silicone partition coefficients (\( K_{\text{lip,sil}} \)) was calculated according to Määenpää et al. (2011), and silicone-specific lipid to silicone partition coefficients (\( K_{\text{lip,sil}} \)) as

\[
c_{\text{lip,sil}} = c_{\text{sil}} \times K_{\text{lip,sil}} \tag{3}
\]

\[
K_{\text{lip,sil}} \text{ were obtained by}
\]

\[
K_{\text{lip,SSP}} = \frac{K_{\text{lip,SSP}}}{K_{\text{DC,SSP}}} \tag{4}
\]

with \( K_{\text{lip,SSP}} \) being the partition coefficient between lipid and SSP M-823 PDMS membranes published by Jahnke et al. (2008) and \( K_{\text{DC,SSP}} \) being the partition coefficient between DC-1 2577 from Dow Corning and SSP obtained from Gilbert et al. (2015).

3. Results and discussion

3.1. Equilibrium sampling method test

For each sediment sample, the mass of analytes in the silicone (\( m_{\text{ana}} \), pg) was plotted versus the silicone mass (\( m_{\text{sil}} \), mg) (Fig. S1), since proportionality between these parameters indicates valid equilibrium sampling (i.e. equilibrium between sediment and silicone, negligible depletion and no surface related artifacts) (Reichenberg et al., 2008). Linear regressions forced through the origin yielded, in almost all cases, \( R^2 > 0.9 \) and for the majority of data series \( R^2 > 0.97 \) (Table S4). Due to non-equilibrium of PCB 180 in coated jars of 8 l analyzed only for coated jars with 2 and 4 l, in all cases, \( R^2 > 0.97 \) was found in sediment from Prossen, Dessau and Geesthacht. An \( R^2 \) value of 0.89 was found in sediment from Prossen for PCB 180. Blanks (\( N = 15 \)) showed very low levels of PCBs, with the exception of one replicate.

The proportionality between \( m_{\text{ana}} \) and \( m_{\text{sil}} \) confirmed that equilibrium partitioning between sediment and silicone had been established. This is in agreement with studies on PCBs in marine and limnic sediments (Määenpää et al., 2011; Jahnke et al., 2012, 2014a) and shows that the method is well suited to measure PCBs at background levels also in river sediments. From the slope of the linear regressions, \( c_{\text{sil}} \) at equilibrium were calculated for all analytes and sampling stations (Table S5). In general, the data were very precise with mean relative standard errors <5%. In only one sample \( c_{\text{sil}} \) of PCB 28 and PCB 52 were below MQL in coated jars with the lowest silicone thickness.

3.2. Freely dissolved (\( c_{\text{free}} \)) and total concentrations (\( c_{\text{total}} \)) in sediment

Freely dissolved concentrations (\( c_{\text{free}} \)) were determined for each station and analyte (Table 1, Figs. S2 and S3a), and ranged for individual PCB congeners from the low to intermediate pg L\(^{-1}\) range. There are distinct spatial differences in \( c_{\text{free}} \) that can clearly be discriminated partly due to low standard errors (selected analytes in Fig. S3a). This very high precision (mean relative standard errors < 5%) is not affected by the error associated with the determination of \( K_{\text{sil,aq}} \), which, however, will affect the accuracy of the \( c_{\text{free}} \) measurements. We expect the \( c_{\text{free}} \) measurements to be accurate within a factor of 1.5 or less, and more research is needed to address and quantify the accuracy of equilibrium sampling methods.

As previously reported, levels of PCBs in River Elbe sediments are high at the Czech-German border (Heinisch et al., 2006) and there is no clear trend for \( c_{\text{free}} \) along the course of the German part of the River Elbe (Fig. S2, linear regression of analyte \( c_{\text{free}} \) vs. Elbe-km, \( p > 0.05 \)). The main Elbe tributaries, Schwarze Elster, Mulde, Saale and Havel, do not show a clear impact on \( c_{\text{free}} \) of PCB.

\( c_{\text{free}} \) in sediments from the River Elbe ranged from 20 to 280 pg L\(^{-1}\) for the sum of seven PCBs (1.0 for PCB 180 to 100 pg L\(^{-1}\) for PCB 52) and are in the same order of magnitude as data from the Stockhol Archipelago in the Baltic Sea obtained with the same technique (Jahnke et al., 2012). The measured \( c_{\text{free}} \) values were up to two orders of magnitude lower compared to more contaminated sites (Mayer et al., 2000; Gschwend et al., 2011; Määenpää et al., 2011) and up to one order of magnitude higher compared to more pristine background locations (Cornelissen et al., 2008; Jahnke et al., 2014a). Consequently, the PCB contamination of the River Elbe can be characterized as elevated but on a moderate level.

\( c_{\text{total}} \) (Table S6, Fig. S3b) determined by exhaustive extraction of sediment ranged from 7 to 130 \( \mu \text{g kg}^{-1} \) dry weight for the sum of seven PCBs. Differences in sum of seven PCBs between stations were more pronounced for \( c_{\text{total}} \) (maximum factor 20) than for \( c_{\text{free}} \) (maximum factor 14). Boizenburg (km 560.8) had the lowest PCB level on both \( c_{\text{total}} \) and \( c_{\text{free}} \) basis (Table S6, Fig. S3b). The highest \( c_{\text{free}} \) values were found in Wittenberg (km 216.4) and Hitzacker (km 523.1), whereas the greatest \( c_{\text{total}} \) were detected in the upstream station Elster (km 200.3). Similar to \( c_{\text{free}} \), there is no clear spatial trend for \( c_{\text{total}} \) in sediments along the course of the River Elbe (Fig. S3b). For the more hydrophobic PCBs, PCB 138, PCB 153 and PCB 180, there was a decreasing trend downstream the river, which was not statistically significant (linear regression of analyte \( c_{\text{total}} \) vs. Elbe-km, \( p > 0.07 \)).

Sorption of chemicals in sediments from the River Elbe was investigated in more detail by sediment to water distribution coefficients \( K_{D} \). Site- and analyte-specific \( K_{D} \) values were calculated by dividing \( c_{\text{total}} \) by \( c_{\text{free}} \) and are presented and discussed in the supporting information (Text S4, Table S7, Figs. S4–S6).

3.3. Equilibrium status between sediment and biota

Equilibrium partitioning concentrations in lipids (\( c_{\text{lip,sed}} \)) were determined as product of the equilibrium concentration in the silicone (\( c_{\text{sil}} \)) and analyte-specific lipid to silicone partition coefficients (\( K_{\text{lip,sil}} \) (Table S8). The high precision was again conserved during the conversion from \( c_{\text{sil}} \) to \( c_{\text{lip,sil}} \). We expect a better accuracy for \( c_{\text{lip,sed}} \) compared to \( c_{\text{free}} \) since \( K_{\text{lip,sil}} \) are numerically much smaller and less prone to experimental errors compared to \( K_{\text{sil,aq}} \). Since actually measured lipid-normalized concentrations in fish are available from the German Environmental Specimen Bank (ESB) we compared these data with \( c_{\text{lip,sed}} \). Common bream (\( A. \) brama) is considered to be ideal for monitoring chemicals in
freshwater and sediment since it has a small migration radius and permanent direct contact with sediments. Fish were sampled by the ESB in the River Elbe in August 2012. Three of the sampled stations, namely Prossen (km 13), Barby (km 296) and Cumlosen (km 470), coincide or are very close to the sediment sampling stations investigated in the present study. From these stations, PCB concentrations and lipid content in muscle tissue of bream were kindly provided by the ESB (Table S9, UBA, 2014). Details on fish and concentrations and lipid content in muscle tissue of bream were kindly provided by the ESB (Table S9, UBA, 2014). Details on fish and sediment contamination and bioaccumulation of PCB in A. brama has previously been identified by Lopes et al. (2011). Investigating three freshwater fish species the authors identified the feeding location as an important factor for PCB concentrations in fish. Fish length, PCB concentration of the sediment and individual foraging habitat explained 80% of variability in PCB concentrations in fish.

In Fig. 2 all three slopes were <1 and all measured concentrations in fish were well below the 1:1 line, which mainly shows that bream, for all seven PCB congeners, was under-equilibrated relative to the sediment. This is in agreement with findings from Jahnke et al. (2012) and (2014a,b) comparing equilibrium sampling of PCB in sediment with lipid-normalized PCB concentrations in herring, eel, duck mussels, roach, pikeperch, perch and pike. Consequently, equilibrium sampling and subsequent calculation of equilibrium partitioning concentrations in lipids seem to be more conservative than actual PCB bioaccumulation in biota, which is in good agreement with several other recent studies (Mayer et al., 2000; Mäenpää et al., 2011; Jahnke et al., 2012, 2003). The close link between sediment contamination and bioaccumulation of PCB in A. brama has previously been identified by Lopes et al. (2011). Investigating three freshwater fish species the authors identified the feeding location as an important factor for PCB concentrations in fish. Fish length, PCB concentration of the sediment and individual foraging habitat explained 80% of variability in PCB concentrations in fish.

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We also plotted PCB concentrations in biota against OC-normalized total sediment concentrations in Fig. S7 for each station. Linear regressions yielded high R² values for Prossen, Barby and Cumlosen of 0.95, 0.87 and 0.84, respectively. However, the slopes of the linear regressions were within a much broader range of 1.8–7.9, and the differences between them were statistically significant (comparison of linear regression models, our best knowledge not been published before. Adult A. brama are carnivorous and feed on benthic invertebrates in particular mussels and oligochaetes (Marth et al., 1997; Koponen et al., 2003). The close link between sediment contamination and bioaccumulation of PCB in A. brama has previously been identified by Lopes et al. (2011). Investigating three freshwater fish species the authors identified the feeding location as an important factor for PCB concentrations in fish. Fish length, PCB concentration of the sediment and individual foraging habitat explained 80% of variability in PCB concentrations in fish.

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Fig. 3. Activity ratios (a) and biota-sediment accumulation factors (BSAFs) (b) of PCBs at the three stations Prossen (km-13), Barby (km-296) and Cumlosen (km-470) in the River Elbe.
3.4. Final remarks and future development
We applied equilibrium sampling to determine bioavailability
HOCs in sediments and correlated the data with PCB concentra-
tions in bream derived from an independent monitoring program.
The close correlation between contamination of sediments and PCB
bioaccumulation in fish demonstrates the major impact of sedi-
ments on PCB bioaccumulation. It further shows that equilibrium
sampling of sediments can be used for determining the thermody-
namic potential for the bioaccumulation of sediment-associated
PCBs. The equilibrium partitioning levels were somewhat higher
than the actual concentrations in bream and consequently
appeared to be conservative to the PCB concentrations in biota.
This novel approach gives more clear and consistent results than
conventional approaches that are based on total concentrations of
chemicals in sediments and BSAFs. Hence, equilibrium sampling
can help to understand the bioavailability of sediment-
associated HOCs in this fish species and potentially in other ben-
thic organisms.
This study was combined with a routine sediment monitoring
campaign. Thereby, ex situ equilibrium sampling of sediments in
the laboratory was advantageous, since field deployment and
retrieval of passive samplers was avoided and PCB mass transfer
from the sediment to the polymer was easily enhanced by contin-
uous rolling of silicone coated jars. In the future, silicone coated
jars can be applied to assess the bioavailability and bioaccumula-
tion potential of HOCs in, e.g., dredged sediments. In this way,
equilibrium sampling is a promising tool for risk-assessments on
dredged materials and, ultimately, for sediment management
decisions.

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Appendix A. Supplementary material
Supplementary data associated with this article can be found, in
the online version, at http://dx.doi.org/10.1016/j.chemosphere.2015.08.032.

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