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ARTICLE *in* ENVIRONMENTAL SCIENCE & TECHNOLOGY · FEBRUARY 2011

Impact Factor: 5.33 · DOI: 10.1021/es1029969 · Source: PubMed

Equilibrium Sampling of Persistent and Bioaccumulative Compounds in Soil and Sediment: Comparison of Two Approaches To Determine Equilibrium Partitioning Concentrations in Lipids

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Received September 1, 2010. Revised manuscript received November 23, 2010. Accepted November 30, 2010.

The equilibrium sampling in silicone is increasingly applied to measure freely dissolved concentrations and chemical activities within bioaccumulation research of hydrophobic organic chemicals. Two equilibrium methods were applied to PCB-contaminated soil and sediment, and directly calibrated with respect to equilibrium partitioning concentrations in lipids ($C_{\text{lipid,partitioning}}$): (i) Solid phase microextraction in the headspace above the sample (HS-SPME) required optimization for its application to PCBs, and it was calibrated above external partitioning standards in olive oil. (ii) Equilibrium sampling with internally coated glass jars with varying thicknesses of silicone (PDMS) resulted in proportionality between coating and analyte mass, which confirmed several validity criteria. $C_{\text{lipid,partitioning}}$ was here determined as product of PDMS concentration and PDMS to lipid partition ratio. The results of the two methods were in good agreement and thus validated each other. Finally, the coated glass jar method was applied to field sediment containing invertebrates, which lead to $C_{\text{lipid,partitioning}}$ that were about two times higher than measured lipid-normalized concentrations in the organisms. Temperature differences and animal lipid structure were discussed as possible reasons for this discrepancy. Both methods combine high analytical performance, reduced equilibration times and new calibration possibilities, which makes them suited for bioaccumulation research and environmental monitoring.

Introduction

In soils and sediments contaminated by hydrophobic organic compounds, the total concentrations are less indicative of potential exposure and distribution than the associated freely dissolved concentrations (C_{free}) or chemical activities (*1*, *2*). A wide range of equilibrium sampling devices have been developed and applied for the measurement of C_{free} and chemical activity in soils and sediments (*1*). Such devices include silicone-coated SPME fibres (*3*, *4*), low-density polyethylene strips (*5*), polyoxymethylene plates (*6*), thin ethylene vinyl acetate (EVA) films (*7*), silicone microtubes (*8*), and silicone- and EVA-coated vials (*9*, *10*). Most of these sampling formats are based on a thin polymer layer that is equilibrated by being placed in a sample or in the field. The analyte concentrations in the polymer (C_{polymer}) are then measured and converted into C_{free} using analyte-specific polymer to water partition ratios ($K_{\text{polymer,water}}$) (*11*):

$$C_{\text{free}} = \frac{C_{\text{polymer}}}{K_{\text{polymer,water}}} \quad (1)$$

A number of challenges remain for such equilibrium sampling of hydrophobic organic chemicals in soils and sediments. (I) It can be a challenge to establish a thermodynamic equilibrium within a practical time span, and it can be time-consuming and expensive to confirm such an equilibrium. (II) Equilibrium sampling is increasingly applied to contaminated soils. The actual sampling is in most cases performed in soil slurries, and methods are needed that can also be applied to unsaturated soils. (III) The validation and quality assurance of equilibrium sampling methods is still poorly developed. In complex and analytically dirty matrices such as sediment and soil, it is particularly important to ensure that the matrix does not lead to fouling of the polymer surface (*12*).

Two equilibrium sampling approaches were recently developed in an attempt to improve on these issues. The first approach is based on headspace solid phase microextraction (HS-SPME), where the SPME coating is equilibrated within the headspace above the sample (*13*). This analytical approach can also be applied to dry matrices, and fouling is nonexisting due to the lack of contact between sample and polymer. The limitation of this method has so far been its restricted usage domain, which was constrained to rather volatile analytes such as BTEX, alkanes and naphthalene (*13*). In the present study we extended the usage domain of the HS-SPME method to less volatile analytes by choosing SPME fibres with a thinner PDMS coating and enhancing the mass transfer conditions. The second approach is equilibrium sampling with internally coated glass jars of multiple coating thicknesses (*9*). This approach provides the confirmation of important validity criteria such as equilibrium partitioning, negligible depletion, and the absence of fouling effects based on parallel sampling in polymer layers of different thicknesses (*9*). A comparison of these two approaches is summarized in Table 1.

Measurements of C_{free} can be multiplied by an appropriate bioconcentration factor (BCF) in order to predict the bioconcentration in, for example, soil and sediment invertebrates (*14*):

$$C_{\text{organism}} = C_{\text{free}} \cdot \text{BCF} \quad (2)$$

By measuring C_{free} with SPME, concentrations of HOCs in organisms have been successfully estimated in earthworms exposed to contaminated soil (*15*) and oligochaetes exposed to sediment (*16*). A main advantage of this approach is that it takes the matrix specific sequestration into account, which improves the accuracy of the bioconcentration prediction compared to traditional equilibrium partitioning calculations based on total concentrations and generic K_{D} values (*14*). A

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10.1021/es1029969
Published on Web 12/21/2010

TABLE 1. Characteristics of Headspace Solid-Phase Microextraction (HS-SPME) and Equilibrium Sampling with Silicone-Coated Glass

	HS-SPME	Coated glass
working principle	equilibration of SPME fiber within head space above sample, followed by thermal desorption and analysis of fiber	PDMS coatings on inside of glass jar are equilibrated with sample, followed by solvent extraction and extract injection on instrument
special features	applicable to dry samples, very easy to get started in manual mode and high throughput potential in automated mode	combines micrometer thin coatings with rather high polymer mass
usage domain—analytes	applicable to volatile and semivolatile analytes. The approach works best with GC, volatiles can be measured with auto sampler (*13*), whereas semivolatile analytes require manual SPME operation (present study)	mainly applicable to semivolatile and nonvolatile analytes, the method yields solvent extracts, which gives very high flexibility with regard to further analytical steps and instrumental analysis
sampling kinetics	equilibrium has to be confirmed, e.g., by time series measurements	no time series are needed, equilibrium is confirmed by proportionality between mass of analyte and polymer (QA/QC)
surface fouling, analyte adsorption and polymer abrasion	no physical contact between sample and fiber, thus applicable even to extremely dirty samples	the absence of significant artifacts is indicated by the same proportionality (QA/QC)

possible disadvantage of this approach is that it proceeds in two steps via measurements of C_{free}. On a conceptual level, this has the drawback that the bioconcentration process then appears to be limited to diffusion and partitioning via the aqueous phase, thereby ignoring mass transfer through air, which is particularly problematic for unsaturated soils. This approach is also less well suited to describe and study mass transfer by direct contact between matrix and organism. On a practical level, it has the drawback of requiring several input parameters, each with its associated error. This is particularly the case for highly hydrophobic organic chemicals with very high partition ratios and high bioconcentration factors, which can be difficult to determine with high accuracy (*17*).

The present study consequently includes a complete calibration for the determination of equilibrium partitioning concentrations in lipids ($C_{lipid,partitioning}$). Such concentrations will be in good agreement with lipid normalized concentrations in organisms ($C_{lipid,normalized}$), if the organism is in equilibrium and bioconcentration is dominated by partitioning to lipids. Equilibrium sampling measurements of $C_{lipid,partitioning}$ are particularly useful in this scenario, where they will be good predictors of actual biota concentrations. Another situation is biota concentrations below the equilibrium partitioning level, which would indicate a kinetic uptake phase or biotransformation. Finally, lipid normalized biota concentration above the equilibrium partitioning level would indicate protein binding or biomagnification. Consequently, measurements of $C_{lipid,partitioning}$ should not necessarily be understood as accurate predictors of actual body burdens, but as useful and well-defined reference values.

The specific objectives of the study were to extend the usage domain of HS-SPME to PCBs by increasing its sampling kinetics and then to measure $C_{lipid,partitioning}$ with external partitioning standards in olive oil; to sample field contaminated sediment with silicone-coated glass jars and then to measure $C_{lipid,partitioning}$ as product of C_{PDMS} and lipid to silicone partition ratios; to compare the results predicted by the two analytical approaches with each other and with actually measured concentrations in biota.

Materials and Methods

Sediments, Soil, and Reagents. The PCB-contaminated sediments originated from Lake Kernaalanjärvi, Finland. They were composite-sampled from different sites collected using Ekman dredge, and are referred to in the text as sediments S1−S5. Few studies that relate to the same contaminated lake had been conducted earlier (*18*). The sediments were stored at +4 °C until use.

The PCB-contaminated soil originates from Lhenice, Czech Republic, and was kept at +4 °C until use. Soil from the same site had been studied earlier for microbial- and phytodegradation of PCBs (*19, 20*).

The following analytical standards served as the model compounds in HS-SPME: PCB-28, PCB-31, PCB-52, PCB-101, PCB-105, PCB-138, and PCB-153. The analytical standards included in the coated glass jar sampling were PCB-28, PCB-31, PCB-44, PCB-49, PCB-52, PCB-99, PCB-101, PCB-105, PCB-110, PCB-118, PCB-128, PCB-138, PCB-149, PCB-151, PCB-153, PCB-156, PCB-170, PCB-180, PCB-187, PCB-188, PCB-194, PCB-209, and hexachlorobenzene (HCB) (PCB numbering according to IUPAC). The solvents used were of analytical grade, and commercial olive oil was used and described earlier by Jahnke et al. (2008) (*21*).

Static HS-SPME Method Development to Measure PCBs from Sediment and Soil. SPME fiber assemblies were purchased from Supelco (Bellefonte, PA). The fibres had a nominal length of 10 mm and a polydimethylsiloxane (PDMS) coating of 7 μm. The volume of the coating was 0.026 μL (*22*). A total of thirty fibres were used in manual sampling, seven of which were measured for length with a binocular microscope. The average length of the fiber was 10.096 mm (SD 0.128 mm, RSD% 1.265, $n = 7$) and thus a maximum of 0.95% difference is expected in PDMS volume between fibres, which was considered to have a negligible effect on the results. Prior to use, the new fibres were rinsed briefly in hexane and then cleaned according to the manufacturer's instructions.

A time series was performed to determine the time to equilibrium between the PDMS sampler and the sediment or soil, and to determine the ECD signal strength for the PCBs. The method was developed for sediment S1 and soil, and subsequently applied to additional sediment samples

(S2 and S3). SPME sampling was generally operated manually (both exposure of the SPME fibres and the injection) and some measurements were performed with a Combi PAL autosampler (CTC Analytics, Zwingen, Switzerland).

Several 20 mL airtight glass vials with PT-FE septum were half-filled (6−10 g fresh weight) with sediment or soil and the fiber was exposed to the headspace air. In manual sampling, the vials were positioned horizontally to increase the surface area of the matrix. All samplings were performed at 35 °C and static mode with three replicates per time point (0, 1, 2, 4, 7/8, 14/16, and 32 days). The fiber was thermally desorbed at 315 °C in the GC injection port equipped with Merlin Microseal septum (Agilent J&W) and SPME Injection Sleeve linear (i.d. 0.75 mm, Supelco). The analytes were separated using a 60 m DB-5 column (i.d. 0.25 mm, film thickness of 0.25, Agilent J&W), and detected using an HP5890 Series II GC with an electron capture detector (ECD) at 325 °C. The GC oven temperature program was 40 °C (10 min), 25 °C/min to 180 °C (2 min), 1.5 °C/min to 238 °C (2 min) and 3 °C/min to 285 °C (10 min). The initial pressure for hydrogen was set to 140 kPa (2 mL/min), and the flow was kept in splitless mode.

Prior to its use for the next extraction, the fiber was cleaned by agitating it for 5 min in acetone at 45 °C and then thermally desorbed for 5 min at 315 °C in the injection port of the GC. The cleaning steps were repeated twice. Generally, no carry over was detected after these cleaning steps, except in some fibres that were used to sample highly polluted soil. These were not used for further samplings.

A first-order one-compartment model (GraphPad Prism 4, GraphPad Software, San Diego, CA) was used to fit the peak area (PA) as a function of the extraction time (t, days):

$$\mathrm{PA}(t) = \mathrm{PA}_{\mathrm{eq}}(1 - e^{-kt}) \quad (3)$$

where k is the rate constant (day^{-1}) and $\mathrm{PA}_{\mathrm{eq}}$ is the peak area at equilibrium. The time to equilibrium was confirmed by visual inspection of graphs and by calculating the extraction time required to reach 90% of the equilibrium peak area ($t_{90\%}$):

$$t_{90\%} = \frac{\ln 10}{k} \quad (4)$$

SPME fibres were then equilibrated for 10 and 20 days in the headspace above sediments from three different locations (S1, S2, and S3) from Lake Kernaalanjärvi and one soil sample from Lhenice. Two replicate measurements were made for each time point.

External Calibration of HS-SPME Analysis. A new calibration principle was introduced on the basis of external partitioning standards in olive oil. The SPME fibres were equilibrated above PCB standard solutions in olive oil prepared by the addition of solid PCB congeners and subsequent dilution with olive oil. Ultrasonication in a warm-water bath was used to enhance the dissolution. Time series measurements confirmed that equilibrium between the spiked olive oil and the PDMS coating was reached within 3 days for all measured PCBs.

Calibration curves were established for four concentrations covering 2.1 orders of magnitude using a sampling time of nine days. Nonspiked olive oil served as a blank, and two replicate samples were measured for each concentration. A linear regression (GraphPad Prism) was used to fit the peak area at equilibrium ($\mathrm{PA}_{\mathrm{eq}}$) as a function of the PCB concentration in olive oil (C_{oil}). This regression was then applied to the HS-SPME of soil and sediment samples yielding direct estimates of "equilibrium partitioning concentrations in lipids ($C_{\mathrm{lipid,partitioning}}$)".

HS-SPME Method Detection Limits (MDL). The MDLs and relative standard deviation (%) were determined by the equilibrium measurement of four replicate samples of the lowest calibration level (*23*). The MDLs were determined by multiplying Student's t value ($p = 0.05$, df = 3, 2.353) by the standard deviation of the replicate measurements.

Coated Glass Jars. Several 20 mL clear glass and 120 mL amber glass jars were coated with nominal 2, 4, 8, and 16 μm layers (0.017, 0.035, 0.072, and 0.149 g) of the silicone polydimethylsiloxane (PDMS) (Silastic, Dow Corning Corporation, Midland, MI). The coating procedure of the glass with silicone has been described in detail by Reichenberg et al. (2008) (*9*).

The jars were filled with sediment S1 (79 ± 9 g fresh weight, 120 mL jar) or S2 (15 ± 2 g fresh weight, 20 mL jar), sealed with aluminum foil and capped airtight. The analytes were allowed to equilibrate between the polymer and sediment for two weeks at room temperature (+21 °C). Two different treatments were used during the equilibration time: static and rolled. Static jars were allowed to stand still ($n = 3$ per coating thickness), while another set of jars was rolled constantly ($n = 2$ per coating thickness). Additionally, in order to determine the temperature effect on the sediment to PDMS partitioning, sediment S4 was incubated in the coated jars at both 10 and 20 °C.

After two weeks, the sediment was poured off and the jars were rinsed with 4 mL of distilled water, then cleaned and dried with lint-free tissue. The analytes were extracted from PDMS with hexane by rolling the solvent in a capped jar for 30 min. The extraction was repeated three times and the aliquots were combined. 300 μL of iso-octane (keeper) were added to the extracts, which were then evaporated under gentle nitrogen flow. An injection standard (PCB-53 + PCB-155) was added and the final extract volume was adjusted to 1 mL by addition of iso-octane. The solvent extracts were analyzed by dual column gas chromatography with an electron capture detector (GC-ECD). The analytical method and the quality control of the GC analyses have been described in detail by Vorkamp et al. (2004) (*24*). The quantification limit of the method was set at the lowest external standard that was within ±7.5% of the assigned value. The lowest external standard solutions of the present study were 0.5 pg/μL, which met this quality criterion.

Calibration of Coated Glass Jar Analysis. The GC analysis of the solvent extract yielded PCB concentrations in the PDMS coating (C_{PDMS}). These were then multiplied by lipid to PDMS partition ratios from Jahnke et al. (2008) (*21*) in order to obtain $C_{\mathrm{lipid,partitioning}}$. Additionally, C_{PDMS} was also divided by PDMS to water partition ratios from Smedes et al. (2009) (*25*) in order to determine freely dissolved concentrations analogous to the principles of matrix-SPME (*4*). The applied partitioning ratios from Smedes et al. (2009) (*25*) were determined on the same PDMS material used for the coating of the vials.

Biota Measurements. The Tubificidae worms collected from sediment S2 (10 worms divided among 2 pooled samples) were allowed to purge their gut for 6 h on moist glass Petri dishes. The worms were then placed in vials containing 2 mL of hexane and 0.5 mL PDMS (*26*) before being mailed to the National Environmental Research Institute (NERI, Aarhus University, Roskilde, Denmark) for chemical analysis. The analytical method used for the worms followed the procedure described in Vorkamp et al. (2004) (*24*). The Chironomidae larvae were collected from sediment S5 and were allowed to purge their gut for 6 h on moist Petri dish. The larvae were extracted for PCBs with acetone:hexane using internal standard method. The detailed procedure of extraction is given in the Supporting Information. Subsamples of larvae were analyzed for total lipid content with micro-gravimetric method according to Parrish (1999) (*27*), with the exception that iso-propanol was used instead of chloroform in the extraction.

Results and Discussion

HS-SPME. The equilibrium sampling into the PDMS coating was achieved within a reasonable time span (Supporting Information Figure S1, Table S1). The time to reach 90% of equilibrium for the model PCB congeners varied from 0.3 to 5.7 days in sediment, from 8 to 11 days in soil, and from 0.8 to 2.4 days in olive oil. As expected, the time to equilibrium was shorter for the lower chlorinated PCB congeners than for the higher chlorinated ones (Supporting Information Figure S1). The congener-specific rate constants generally varied by less than a factor of 5 between olive oil, sediment, and soil, and the reduced kinetics of the higher chlorinated PCBs in soil and sediment could be explained by local depletion below the sample-to-headspace interface. We tried to minimize this effect by placing the vials close to a horizontal position, which increased the exchange area between sample and headspace.

The calibration with external partitioning standards in olive oil was very simple. The PCB concentrations in the oil were entered into the software as external standard concentrations and the calibration then yielded direct measurements of $C_{lipid,partitioning}$ (Supporting Information Figure S2).

The MDLs on a lipid basis and the relative standard deviations (RSD) are given in Supporting Information (Table S2). The MDLs remained lower than the concentrations of the lowest calibration standards, with the exceptions that the MDL of PCB-52 was close to equal and that of PCB-153 was slightly higher than the concentration of the lowest calibration standard. The RSDs for olive oil were generally around 10% (6−16%) and somewhat higher for PCB-153 (23%). These RSD values are slightly higher than reported earlier for semivolatile compounds sampled with HS-SPME (*13*).

Equilibrium Sampling with Coated Glass Jars. The method of using internally coated glass with multiple thicknesses to sample PAHs from contaminated soil was recently developed and validated (*9*). In the current study, the same method was utilized to sample the sediment S1 for PCBs. The application of the silicone coating was highly reproducible, showing low jar-to-jar variation of the resulting PDMS mass (%RSD 0.7−2.8, $n = 5$).

After two weeks incubation during the rolled jar treatment, the mass of all measured analytes was proportional to the PDMS mass, which confirmed a thermodynamic equilibrium between PDMS and the sediment (Figure 1 and S3). This confirms that PDMS-coated glass jars can be used for equilibrium sampling of even the most hydrophobic PCBs within a sampling time of two weeks, and possibly less. With the static treatment, equilibrium was reached only for hexachlorobenzene (HCB) and rolling of the jars was thus found to be necessary.

The analyte concentrations in the PDMS were characterized by low standard deviations between vials and even between the different coating thicknesses. Relative standard deviations between vials of the same coating thickness ranged from 3.7% (PCB-180) to 11.3% (PCB-194), whereas relative standard deviations between vials of all four coating thicknesses ranged from 15% (PCB-153) to 24% (PCB-194). This leads to very precise best estimates of the analyte concentrations in the PDMS, which can be calculated in two different ways (*28*). A concentration average from eight jars leads to relative standard errors ranging from 5.8% (PCB-153) to 8.9% (PCB-194). The analyte concentration in the PDMS can also be determined as the slope of the linear regression in Figure 1 (*28*), which leads to very similar concentration estimates, but with much smaller relative standard errors ranging from 1.9% (PCB-153) to 2.9% (PCB-128). These estimates were used for all further calculations.

The quantification limits of the liquid injection analysis were approximately 0.5 pg/μL iso-octane, which translates to 15 ng/g PDMS for the thinnest coating and 1.7 ng/g PDMS for the thickest coating. Quantification limits on a lipid basis are 1−2 orders of magnitude ($K_{lipid,PDMS}$) higher, while being 5−7 orders of magnitude ($K_{PDMS,water}$) lower for freely dissolved concentrations. These quantification limits can be further reduced with more sensitive instruments, a reduced final extract volume or large volume injections.

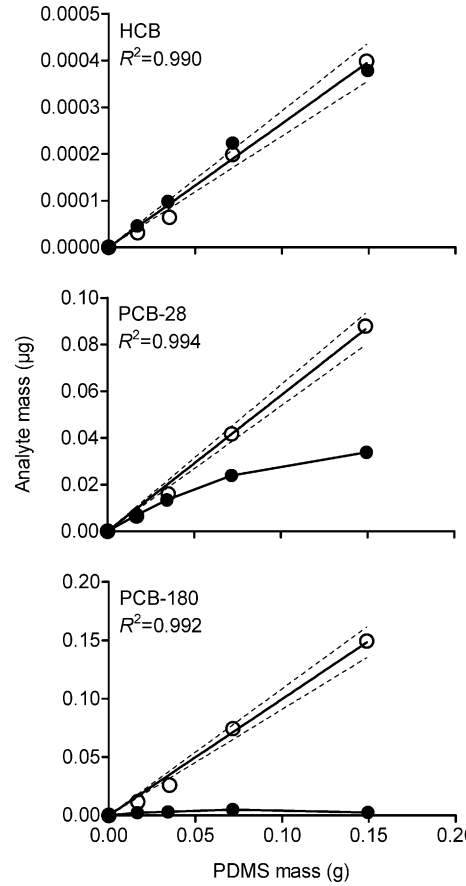

FIGURE 1. Mass of PDMS vs mass of selected analytes in four thicknesses of polymer in silicone-coated glass equilibrated with sediment S1. The linear regression (95% confidence intervals) and coefficient of determination (R^2) are shown for rolled glass treatment (open circles). Static treatments (closed circles) are shown as an example of reaching equilibrium for hexachlorobenzene (HCB) but not for PCBs.

The measured C_{PDMS} (Supporting Information Table S3) can be applied in many ways. First, the freely dissolved concentration can be determined as the ratio of C_{PDMS} and the analyte-specific PDMS to water partition ratio ($K_{PDMS,water}$) (*25*). The chemical activities can be determined using analyte-specific activity coefficients ($\gamma_{analyte}$) (*9*). In this study, in addition we converted the C_{PDMS} to equilibrium partitioning concentration in lipids ($C_{lipid,partitioning}$) by multiplication with recently reported lipid to PDMS partition ratios ($K_{lipid,PDMS}$) (*21*) (Supporting Information Table S3).

Equilibrium Partitioning Concentrations in Lipids ($C_{lipid,partitioning}$). To the best of our knowledge, this is the first study to present equilibrium partitioning sampling methods for soil and sediment that are fully calibrated toward equilibrium partitioning concentrations in lipids. Two different equilibrium sampling methods yielded nearly equal values of $C_{lipid,partitioning}$ for the model congeners, so the methods validated each other well (Figure 2).

Olive oil was chosen as the model partitioning medium in the present study for two reasons: it has already served as the partitioning medium in classical toxicological studies (*29*), and recent studies have shown the partitioning proper-

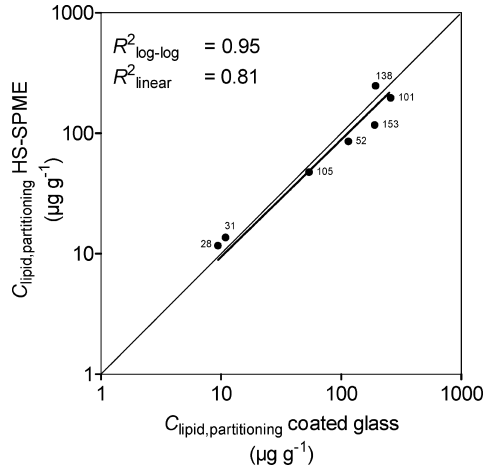

FIGURE 2. Comparison of equilibrium partitioning concentrations of PCBs in olive oil ($C_{lipid,partitioning}$) between silicone-coated glass and headspace solid-phase microextraction (HS-SPME) methods in sediment S1. Coefficient of determination (R^2) is shown for linear regression of log−log transformed and linear data.

ties of lipids from different trophic levels (vegetable oil, fish oil, and seal oil) to be rather similar for both halogenated organics (including PCBs) and PAHs (*21, 30*). The two methods provide measurements of $C_{lipid,partitioning}$ that give an estimate of the PCB levels to be expected in the lipids of organisms in equilibrium with the matrix, and such equilibrium partitioning predictions had already been shown to be successful (*14, 16, 31, 32*). $C_{lipid,partitioning}$ can also be used as a reference for comparisons with actual lipid-based concentrations in organisms, which can be determined either by lipid normalization of the total concentration or by in tissue equilibrium sampling (*33*). Measurements below the equilibrium level would then be an indication of the kinetic uptake phase or biotransformation, whereas higher measurements could indicate biomagnification. Further, lipid based concentrations can be used in a more general way as synoptic multimedia indicators of contaminant levels and trends in aquatic and other ecosystems (*34*).

$C_{lipid,normalized}$ in Biota Versus $C_{lipid,partitioning}$ in Sediment. Equilibrium sampling measurements of the sediment were compared with lipid normalized concentrations in Chironomidae larvae that were collected from the same sediment sample (Figure 3). The larvae were analyzed for total lipids (1.8−3.4%) and PCBs. Measurements of $C_{lipid,partitioning}$ were approximately 2.4 fold or 0.4 log units higher than $C_{lipid,normalized}$ in the larvae (Figure 3A). Plotting $C_{lipid,normalized}$ against C_{PDMS} yielded a linear regression with a slope of 10.7, which is somewhat less than the $K_{lipid,PDMS}$ reported earlier for PCBs (*21*) (Figure 3B). Thus this finding supports the result of $C_{lipid,partitioning}$ being slightly overestimated. Further, another data set with Tubificidae worms confirmed this observation of $C_{lipid,partitioning}$ being somewhat higher than $C_{lipid,normalized}$ measured in biota (Supporting Information Figure S4).

One explanation for the discrepancy could be that the invertebrates actually were under-equilibrated by being in the kinetic uptake phase or due to biotransformation. It could also be a minor bias of the partitioning methods, for instance due to differences in the partitioning properties of the polymers or due to temperature differences between laboratory and field. Another explanation could be the high fraction of phosholipids in lean invertebrates. Phospholipids have been reported to have a lower bioaccumulation potential when compared to storage lipids (*35, 36*). While it is very simple to apply various types of vegetable and animal oils for the calibration of the methods, it seems more difficult to calibrate with phospholipids, which are in solid state at

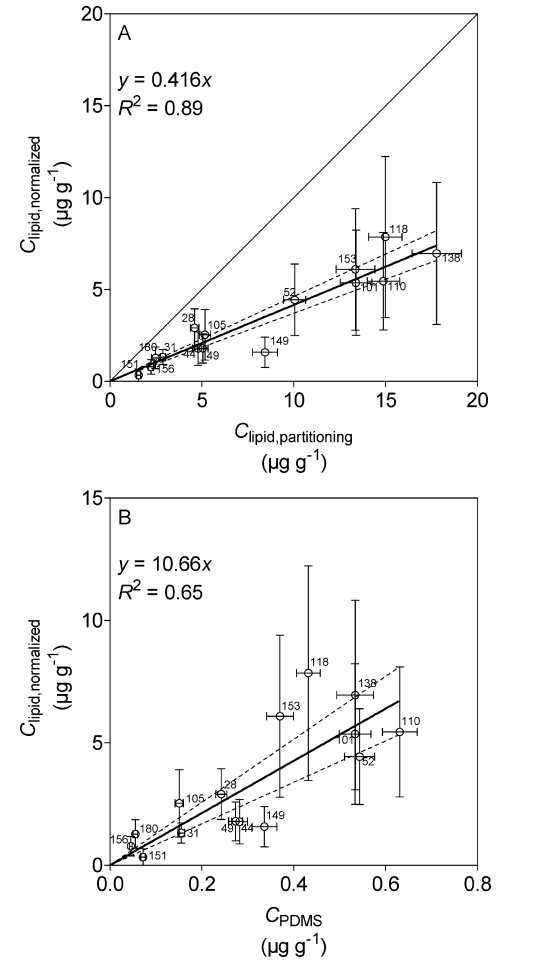

FIGURE 3. Comparison of equilibrium partitioning concentrations in lipids ($C_{lipid,partitioning}$) (A) and in silicone (C_{PDMS}) (B) with measured lipid normalized PCB concentrations in Chironomidae larvae ($C_{lipid,normalized}$) in sediment S5. The sediment was sampled with the silicone coated glass method and C_{PDMS} was converted to $C_{lipid,partitioning}$ using partition ratios $K_{lipid,PDMS}$ (*21*).

ambient temperature. More research is needed in this area in order to extend the calibration methods to phospholipids. This is important for toxicological research, where phospholipid membranes often are considered the target for toxic action. Within bioaccumulation research this is likely of less importance, where storage lipids in most cases dominate the partitioning. More research and more experience with these new analytical tools are needed, which will either reduce the observed discrepancy or will help to explain the observed differences. It should be noted that the observed discrepancy between prediction and measurement of lipid based concentrations hardly would have been visible in many earlier studies that were limited to log−log plot and to linear correlations.

Proportionality was found between PCB concentrations in the PDMS of the coated glass and the concentrations in biota (Figure 3B and Supporting Information Figure S4), with a linear regression forced through origin yielding an R^2 of 0.65 and 0.93. Similar results were reported for polyethylene (PE) samplers that correlated well with Polychaeta PCB concentrations when exposed to contaminated sediment (*37*). The concentration ratio between biota and polymer seems to be sufficiently constant in both cases to allow the polymers to be used as a biomimetic phase for the accumulation of PCBs in sediment biota. However, the slope of such regressions can change with the chemical group (*38*), and the

regression obtained should consequently not be applied to other groups of chemicals. The calibration of the present study with respect to equilibrium concentrations in lipids is a strategy designed to solve this problem, since it takes the analyte-specific partitioning into account.

A recent study by Van der Heijden and Jonker (2009) (*39*) suggests that SPME-based body burden predictions of PAHs in sediment worms can be improved by deploying the SPME fibres in situ rather than in the laboratory. A potentially important difference between field deployment and laboratory sampling is the temperature. Muijs and Jonker (2009) (*38*) have shown that both water to PDMS partitioning of PAHs and their bioaccumulation in sediment worms decreased significantly with increasing temperature (*38*). We expect a reduced temperature dependency in our new approach, where we avoid water in the partitioning measurements and calculations. The reason for this is that water has fundamentally different solvation properties for hydrophobic organic chemicals when compared to organic matter, PDMS and lipid. The sediment to PDMS partitioning during the sampling was indeed rather insensitive to temperature, since concentrations in the PDMS on average only increased by 14% for a temperature increase from 10 to 20 °C (Supporting Information Figure S5). The temperature dependency of the second partitioning step from PDMS to the lipid partitioning requires further research. Depending on the results there will be different ways to deal with this issue. (i) A minor bias due to temperature differences between field and laboratory might be accepted, (ii) the HS-SPME approach could be calibrated at environmental temperature, or (iii) temperature specific lipid to PDMS partition coefficients could be determined and applied for the coated jar approach.

In summary, two equilibrium sampling techniques for PCBs in soils and sediments were developed. They combine simplicity with good analytical performance and were specifically designed for their application to very complex media. Equilibration times for PCBs were in the order of one to two weeks for both methods, which is rather short compared with other passive samplers. Finally, both methods were calibrated with respect to $C_{\text{lipid,partitioning}}$, leading to good agreement between the methods, which are now ready to be used in bioaccumulation research, environmental monitoring and exposure assessments.

Acknowledgments

We thank Annegrete Ljungqvist for performing the GC analyses on the coated glass jar and worm samples, Wesley Hunter for the initial work with the headspace SPME method, Thomas Macek and Ulrich Karlson for providing soil samples and Margit Fernquist for her laboratory assistance. The study was funded by the Academy of Finland project no. 123587 and the EU FP7 project "Model Driven Soil Probing, Site Assessment and Evaluation" (MODELPROBE no. 213161).

Supporting Information Available

Additional information, figures and tables for extraction procedure of the larvae, uptake of PCBs by different matrixes, calibration of HS-SPME, coated glass experiment and calculations of C_{lipid} and C_{free}, biota plotted against $C_{\text{lipid partitioning}}$ and C_{PDMS}, and comparison of two temperatures in coated glass extraction of sediment. This material is available free of charge via the Internet at http://pubs.acs.org.

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ES1029969

Supporting information for:

Equilibrium sampling of persistent and bioaccumulative compounds in soil and sediment – comparison of two approaches to determine equilibrium partitioning concentrations in lipids

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Number of pages: 11
Number of tables: 3
Number of figures: 5

Extraction of PCBs from Chironomidae larvae

The glassware were rinsed with hexane before use. First, an internal standard (PCB-30) was added on the weighed biota sample in the test tube. Five ml of acetone:hexane 1:1 (v:v) was added and sample was homogenized using sonicator (ultrasound) homogenizer for 2-3 minutes or until tissues looked diffused. Between the samples, the ultrasound rod was cleaned by sonicating in clean hexane. Sonication was continued in the ultrasound bath for 20 minutes. The sample was then centrifuged 665 g for 3 minutes and the solvent phase was transferred through drying funnel (sodium sulfate, Na_2SO_4) to a new 20-ml test tube. The extraction was repeated twice with 3 ml of acetone:hexane solution, and the solvent phases were combined. Finally, the drying funnel was rinsed three times with 2 ml of hexane.

Next, solvent was evaporated approximately to 2 ml under gentle nitrogen flow. Then, 1 ml of concentrated sulphuric acid (H_2SO_4) was added and the sample was shaken gently. The sample was centrifuged again 665 g for 3 minutes, and the solvent phase was transferred to a new 10-ml test tube. The acid phase was rinsed with 2 ml hexane by shaking gently, and centrifuged 665 g for 3 minutes, and the solvent phase combined with the sample. Next, 1 ml of concentrated H_2SO_4 was added in the sample, shaken gently, and centrifuged 665 g for 3 minutes. The acid phase was removed using Pasteur pipette. Fifty µl of nonane (keeper) was added and the sample was evaporated to dryness under gentle nitrogen flow until only nonane drop was left. The sample was dissolved in 500 µl of iso-octane and a little bit of Na_2SO_4 was added to bind the rest of the possible acid. Finally, the sample was transferred in GC-vial inner tube being careful not to transfer any Na_2SO_4.

Table S1. Rate constants (k_{static} day^{-1}) and standard errors (*SE*) for olive oil, sediment S1 and soil from headspace solid-phase microextraction (HS-SPME) sampling.

PCB congener	Olive oil k_{static} (day^{-1})±*SE*	Sediment S1 k_{static} (day^{-1})±*SE*	Soil k_{static} (day^{-1})±*SE*
PCB-31	1.97 ±0.53	7.34 ±2.58	NQ
PCB-28	1.45 ±0.31	8.73 ±7.99	NQ
PCB-52	2.79 ±1.63	8.52 ±2.99	NQ
PCB-101	2.38 ±0.82	2.27 ±0.86	NQ
PCB-153	1.13 ±0.23	0.48 ±0.09	0.21 ±0.05
PCB-105	1.14 ±0.24	0.57 ±0.15	0.28 ±0.07
PCB-138	0.96 ±0.19	0.40 ±0.07	0.20 ±0.05

NQ = Not Quantified due to oversaturation of the detector.

Table S2. The calibration data of external standard mixtures in olive oil by headspace solid-phase microextraction (HS-SPME) for model compounds

Model compound	Calibration curve	R^2	Concentration range (μg g^{-1})	MDL^1 (μg g^{-1})	%RSD^2
PCB-31	y=4418x	0.986	2-298	0.996	7.2
PCB-28	y=6578x	0.988	2-190	0.611	7.8
PCB-52	y=4041x	0.989	2-222	1.768	14.6
PCB-101	y=4467x	0.989	2-271	1.753	15.7
PCB-153	y=4301x	0.991	3-356	3.796	23.1
PCB-105	y=4174x	0.990	5-635	1.903	6.0
PCB-138	y=4475x	0.990	3-362	1.579	11.2

[1]Method detection limit, [2]Relative standard deviation%.

Table S3. Measured concentrations of chemicals in polydimethylsiloxane (C_{PDMS}) (*SE* = standard error, n=8) by the silicone-coated glass method applied to sediment S1. C_{PDMS} is multiplied by olive oil to PDMS partition ratios ($K_{olive,oil,PDMS}$) (Jahnke et al. 2008), and divided by the PDMS to water partition ratios ($C_{PDMS,water}$) (Smedes et al. 2009) to obtain equilibrium partitioning concentrations in lipids ($C_{lipid,partitioning}$) and freely dissolved concentrations in water (C_{free}) respectively.

Analyte	$C_{PDMS} \pm SE$ (µg g^{-1})	$C_{lipid,partitioning}$ (µg g^{-1})	C_{free} (ng L^{-1})
HCB	0.0027 ±0.0001	0.04	0.02
PCB-28	0.58 ±0.01	11.05	2.09
PCB-31	0.68 ±0.02	12.72	2.69
PCB-44	3.41 ±0.09	57.99	5.99
PCB-49	2.32 ±0.06	42.90	3.55
PCB-52	7.09 ±0.18	131.20	12.75
PCB-99	4.66 ±0.12	117.04	2.31
PCB-101	11.77 ±0.29	295.43	7.17
PCB-105	1.84 ±0.04	63.21	0.89
PCB-110	10.56 ±0.28	249.22	6.00
PCB-118	5.10 ±0.11	177.04	2.47
PCB-128	1.60 ±0.05	44.72	0.32
PCB-138	6.67 ±0.16	221.94	1.38
PCB-149	5.95 ±0.16	149.45	1.48
PCB-151	1.35 ±0.03	29.19	0.37
PCB-153	5.88 ±0.11	212.41	1.30
PCB-156	0.71 ±0.02	34.64	0.17
PCB-170	0.57 ±0.02	22.06	0.05
PCB-180	1.00 ±0.03	44.64	0.12
PCB-187	0.53 ±0.01	15.56	0.08
PCB-188	0.54 ±0.01	10.60	-
PCB-194	0.07 ±0.004	4.08	-

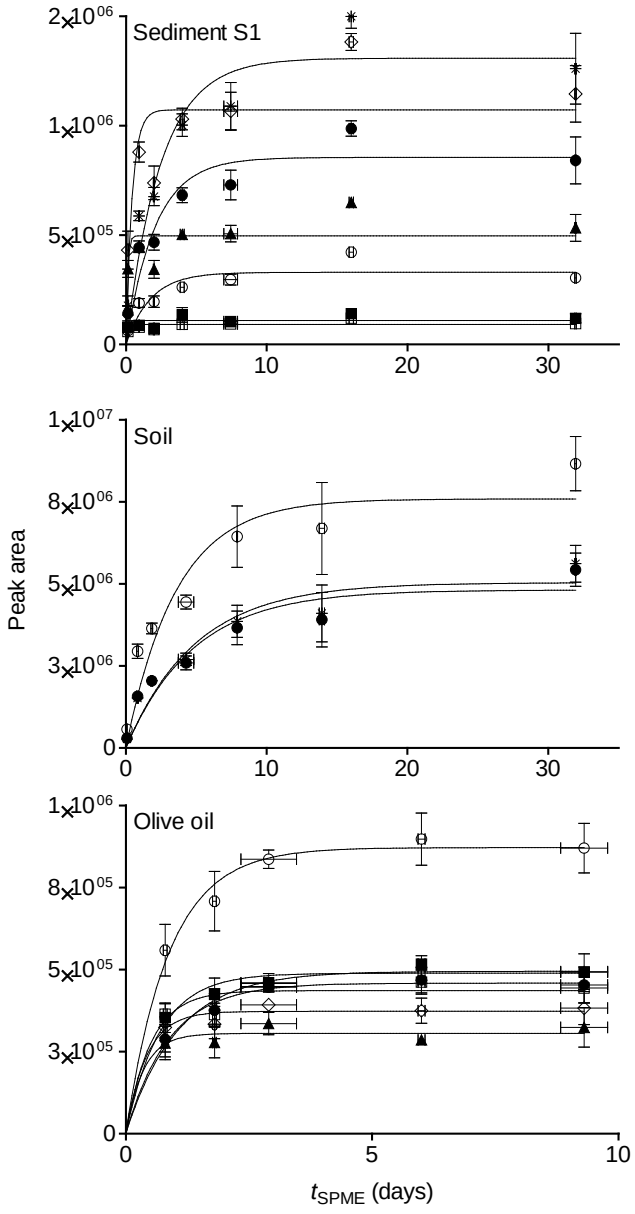

Figure S1. Headspace solid-phase micro-extraction (HS-SPME) sampling kinetics of selected PCB congeners from field-contaminated sediment (S1) and soil, and spiked olive oil. The measurements were conducted under static conditions at 35 °C using HS-SPME fibre with PDMS coating of 7 μm. The peak area against sampling time is fitted to equation (3). The symbols with error bars denote an average and standard error of three replicate samples (PCB-31 □, PCB-28 ■, PCB-52 ▲, PCB-101 ◊, PCB-153 ●, PCB-105 ○, PCB-138 ∗).

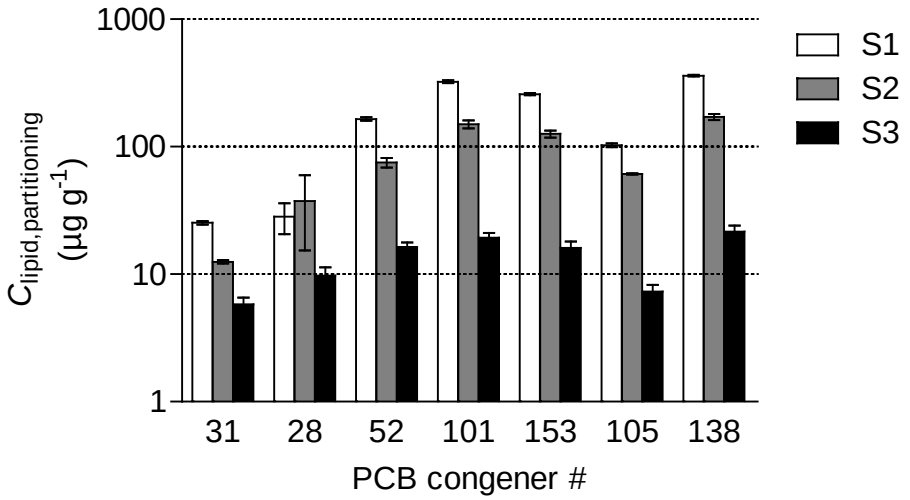

Figure S2. Equilibrium partitioning concentrations in lipids ($C_{lipid,partitioning}$) (mean ± *SE*, *n* = 4) of model compounds in field-contaminated sediments (S1, S2 and S3).

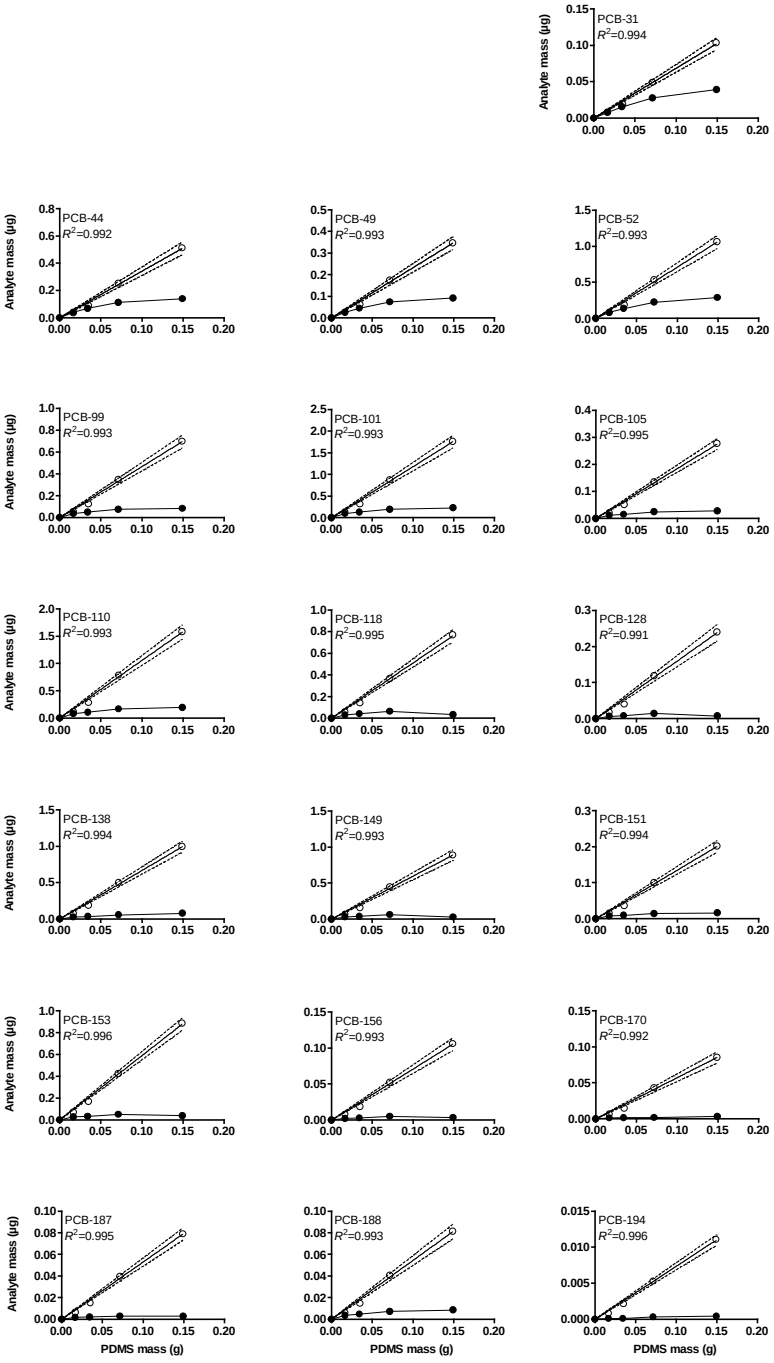

Figure S3. Mass of PDMS vs. mass of analytes in four coating thicknesses of silicone of coated glass applied to sediment S1. Each dot with error bars represents an average of replicate samples (open circle ○ = rolled vial treatment , n = 2, closed circle● = static treatment , n = 3). Linear regressions (95% confidence intervals) are shown for the rolled vial treatment.

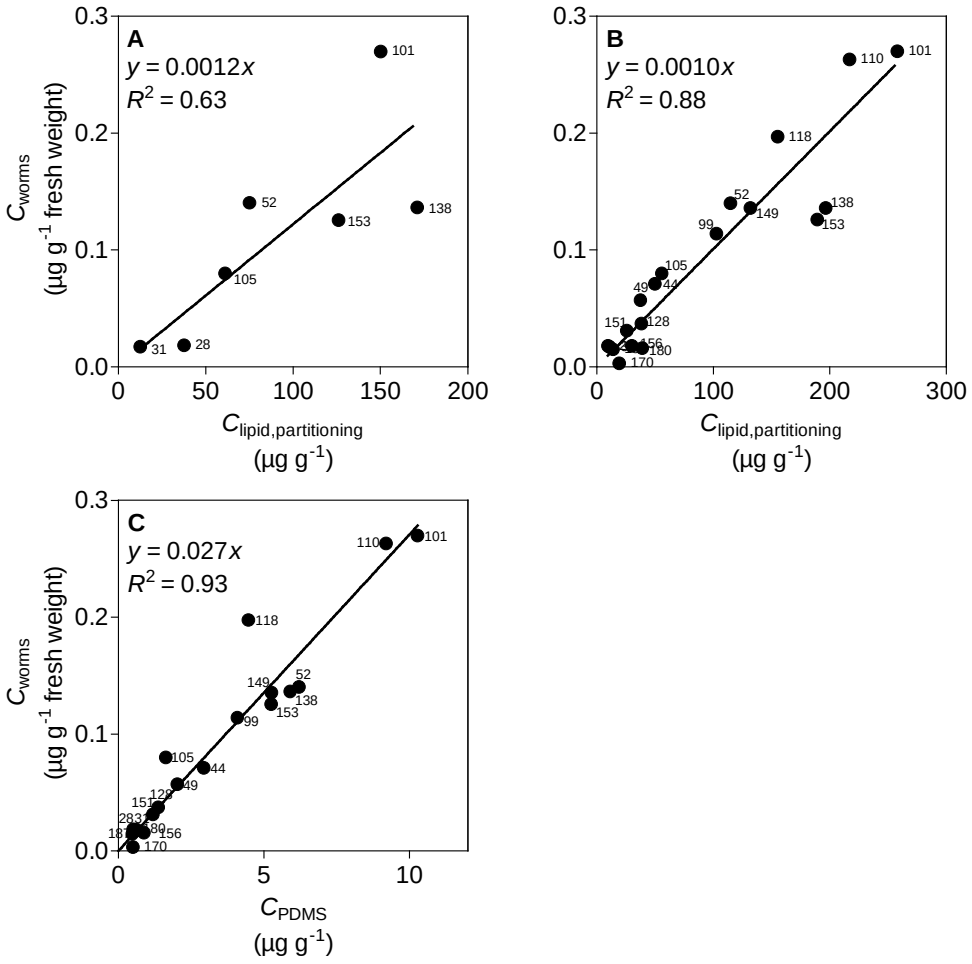

Figure S4. Comparison of equilibrium partitioning concentrations in lipids ($C_{lipid,partitioning}$) with measured PCB concentrations in Tubificidae worms (C_{worms}) by the two equilibrium sampling methods for field contaminated sediment: A) headspace solid phase microextraction (HS-SPME), and B) silicone-coated glass with various thicknesses of silicone (PDMS). Panel C shows PCB concentrations in PDMS (C_{PDMS}) from coated glass experiment vs. C_{worms}. PCB congeners are numbered beside the dots. Unfortunately, the number of worms in the sample was insufficient to enable lipid analysis. However, the slope of a perfect fit line in Figure A and B would yield the lipid content of the worms, but the slope of the regression (0.001-0.0012 g olive oil/g fresh weight) is somewhat lower than was expected.

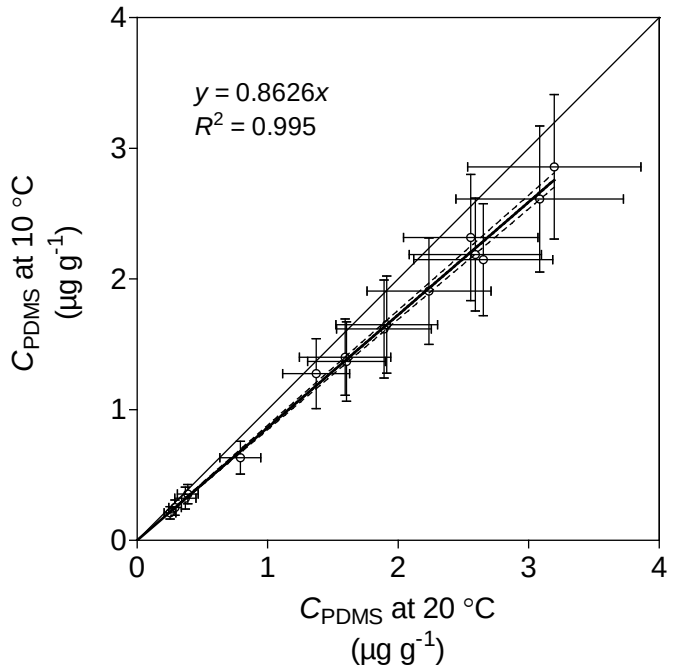

Figure S5. Equilibrium partitioning concentrations of PCBs in the PDMS (C_{PDMS}) after sampling field contaminated sediment (S4) at two temperatures with coated glass-jar method.

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