

ASSESSING EXPOSURE OF SEDIMENT BIOTA TO ORGANIC CONTAMINANTS BY THIN-FILM SOLID PHASE EXTRACTION

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Abstract—Differences in bioavailability among sediments are a source of variability and uncertainty in sediment quality assessment. We present three sets of studies designed to test a thin-film solid phase extraction technique for characterizing the bioavailability of organic chemicals in sediments. Laboratory studies with spiked natural sediments reveal highly reproducible thin-film extractions for chemicals with octanol–water partition coefficients between $10^{4.5}$ and $10^{8.5}$, with 95% equilibration times between 1 and 600 h. Studies with field-collected sediments illustrate that method detection limits are sufficiently low for field application at contaminated sites. Bioaccumulation studies with clams (*Macoma balthica*) show excellent correlations between thin-film and animal tissue concentrations. We conclude that thin-film extraction provides an ecologically relevant, fugacity-based measure of chemical exposure that can be expected to improve sediment quality assessments.

Keywords—Benthic invertebrates Fugacity Hydrophobic organic chemicals Partitioning Sediment

INTRODUCTION

A common strategy in assessing the potential impact of contaminated sediments on aquatic life is to compare measured contaminant concentrations to sediment quality guidelines (SQGs). Concentrations in excess of SQGs can trigger regulatory or voluntary efforts to address the apparent contamination problem. However, it is widely recognized that the bioavailability of contaminants in sediments can vary substantially among locations due to differences in organic carbon content and type, particle size distribution, history of contamination (aging), pH, salinity, and other factors [1]. This variability adds considerable uncertainty when interpreting chemical concentrations in terms of effects or risks to wildlife and humans. In many cases, the comparison of concentrations among sediments or between ambient sediments and SQGs is effectively a comparison between apples and oranges because of differences in bioavailability. Empirical SQGs are also subject to this problem, as they are often derived from a combined data set including sediments of various sources and types, potentially with different chemical bioavailabilities.

One way to account for variation in bioavailability is to express exposure in terms of chemical fugacity rather than concentration. Several authors have argued that substantial improvements in sediment quality assessment can be achieved when total chemical concentrations in sediments are replaced by fugacity or some other direct measure of bioavailable concentrations [2–5]. Similarly, mechanistic SQGs derived from equilibrium partitioning theory [6] effectively account for differences in bioavailability by relating the exposure of organ-

isms to chemical fugacity (as equilibrium is, by definition, equifugacity). Recent advances in solid phase microextraction with polymer-coated fibers [3,4,7,8] or polymer thin films [9,10] have demonstrated the utility of passive sampling with surrogate materials to make empirical measurements of the fugacity of hydrophobic organic chemicals in sediments, effectively sensing the exposure of sediment biota. Chemical fugacity is directly related to bioconcentration [6], biomagnification [11,12], and toxicity and is therefore a useful and meaningful measure of the bioavailability of chemicals in sediment.

Thin-film solid phase extraction (TF-SPE) is a simple and inexpensive technique that has been used to measure fugacities in biological tissues [13], air [14], and sediment [9,10]. It is based on the premise that, due to a large surface area-to-volume relationship, chemicals in environmental media (sediments in the present study) can relatively quickly achieve an equilibrium distribution with the thin-film solid phase (ethylene vinyl acetate [EVA] in the present study). Equilibrium is achieved when the fugacity (f_E) of the chemical in the thin film equals that in the sediment (f_S). Therefore, at equilibrium, f_S can be determined from f_E , which in turn can be determined from the measured concentration (mol/m^3) of the chemical in the thin film (C_E) and the sorptive capacity ($\text{mol} \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}$) of the thin film, Z_E , for the chemical (i.e., $f_S = f_E = C_E/Z_E$). In turn, Z_E for the chemical can be determined via measurement of a thin film–air equilibrium partition coefficient, K_{EA} (for relatively volatile substances) [13] or a thin film–octanol partition coefficient, K_{EO} (for substances with little capacity to partition into the gaseous phase) [9]. Since K_{EA} equals Z_E/Z_A , and Z_A equals the inverse of the product of the gas constant R ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) and temperature T

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(Kelvin), the fugacity of a chemical in sediment can be calculated from the measured chemical concentration in the thin film as

$$f_s = \frac{C_E RT}{K_{EA}} \quad (1)$$

Likewise, as K_{EO} equals Z_E/Z_O , and Z_O is the product of the octanol-air partition coefficient K_{OA} and Z_A (or $1/RT$), the fugacity of a chemical in sediment can be calculated from the measured chemical concentration in the thin film as

$$f_s = \frac{C_E RT}{K_{EO} K_{OA}} \quad (2)$$

While the calculations in Equations (1) and (2) are useful in expressing concentrations in terms of fugacities, they are not always necessary. The measured concentration in the thin film can itself be a useful surrogate for fugacity. A higher concentration in thin films exposed to sediment A compared to a thin film exposed to sediment B implies a higher fugacity of the chemical in sediment A compared to sediment B, as Z_E for the films exposed to sediments A and B is the same. A higher ratio of thin-film concentration to bulk sediment concentration implies a lower sediment sorptive capacity, Z_s , and hence a higher fugacity at a given concentration.

Here we present a threefold validation of TF-SPE to measure f_s for sediment quality assessment. First, we demonstrate that chemical equilibrium is achieved between the thin-film solid phase and the spiked natural sediment in a practical time frame and with negligible depletion of the original sediment concentration. Second, we demonstrate that the method is sufficiently sensitive to be applicable to real-world contaminated sites. Third, we demonstrate the ecological relevance of f_s by showing that measured chemical fugacities in sediment relate to the concentrations and fugacities of chemicals in organisms residing in the sediment.

MATERIALS AND METHODS

Thin-film preparation

A 6,210 mg/L EVA solution was prepared by dissolving 0.621 g of EVA (Elvax 40W, DuPont, Wilmington, DE, USA) in 100 ml of dichloromethane. Glass scintillation vials (20 ml) were cleaned with lab-grade detergent, followed by solvent rinses with acetone and hexane. To coat the vials, 150 μ l of the EVA solution was added to each scintillation vial, and the uncapped vials were rolled to allow the dichloromethane to evaporate. This formed a thin film of EVA on the vial interior. Each vial contained 1.0 μ l (0.93 mg) of EVA, producing a film with an average thickness of 0.27 μ m and a surface area to volume ratio of 3,770 mm^{-1} . Approximate uniformity of film thickness resulting from this procedure was confirmed by visual inspection of vials coated with an EVA solution containing the red dye Sudan IV (Sigma-Aldrich, St. Louis, MO, USA).

Sediment collection and characterization

Four sediment types were used. Surficial marine sediment (top 1 cm) was collected at low tide from Port Moody Arm (PM), British Columbia, Canada. Sediments from Roberts Bank (RB) and Boundary Bay (BB), British Columbia, were collected at low tide by staff from Environment Canada's Pacific Environmental Science Centre. Sediment from Sydney Harbor (SH), Nova Scotia, Canada, was collected by staff from

Environment Canada's Atlantic Environmental Science Centre using a 0.1-m² Van Veen grab. Sediments were stored in washed and solvent-rinsed glass jars and frozen until use.

Particle size analysis (by sieving) characterized the PM and SH sediments as silty and the RB and BB sediments as sandy. The total organic carbon content (g of organic carbon per g dry wt) of the sediments was measured at the Institute for Ocean Sciences using a Leeman's 440 elemental analyzer (Teledyne Leeman Labs, Hudson, NH, USA) following Van Iperen and Helder [15] and was 3.77% for PM, 0.35% for RB, 16.5% for SH, and 0.20% for BB sediment. Sediments used in thin-film extractions were adjusted to a 50 to 51% moisture content by adding small amounts of deionized water.

Spiked sediment study

The PM and RB sediments were spiked in the lab with 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene (Aldrich Chemical, Milwaukee, WI, USA) and polychlorinated biphenyl (PCB) congeners 52 and 155 (AccuStandard, New Haven, CT, USA); RB sediments were additionally spiked with PCB congeners 101, 180, and 194 (AccuStandard). Spiking of PM and RB sediments involved preparing a spiking solution by dissolving the test chemicals in 10 ml of hexane; adding the spiking solution to 850 g of sediment (wet wt); and mechanically stirring for 8 h to evenly distribute the chemicals and to allow evaporation of hexane. Once spiked, sediments were stored at 4°C until needed. Before each uptake experiment, sediments were manually stirred. Chemical concentrations in the sediments are listed in Table S1 (<http://dx.doi.org/10.1897/08-081.S1>).

We conducted TF-SPE uptake experiments after aging periods of 21 and 102 d for PM sediments and 17 and 52 d for RB sediments. After aging, 20 ml of sediment was added to EVA-coated scintillation vials. Chemical concentrations in EVA were then sampled after a series of exposure times up to 75 h. Triplicate analyses of at least 10% of samples were performed to test for reproducibility. In addition, three vials were filled with unspiked sediment, incubated for 24 h, and extracted as a method blank.

At the end of each exposure time, sediment was poured from the vials, and the EVA film was rinsed twice with approximately 10 ml of distilled water to remove remaining sediment particles. The vials were then centrifuged for 2 min at 3,500 rpm and residual water was removed with a Hamilton syringe (Hamilton Company, Reno, NV, USA). Chemicals were extracted from the EVA thin film using two 0.5-ml volumes of hexane and vigorous shaking of the vials on a vortex mixer. The extraction efficiency was close to 100%, as a third extraction revealed no measurable traces of the test chemicals. The two extracts were removed from the scintillation vial using a Hamilton syringe, pooled, and stored in a preweighed 2-ml autosampler vial until chemical analysis.

Hexane extracts were injected directly into a Hewlett-Packard 5890 series gas chromatograph (Hewlett-Packard, Mississauga, ON, Canada) equipped with an electron capture detector and a 30 m \times 0.53 mm \times 2.65 μ m (film thickness) HP-5 column (Supelco, MO, USA). Helium was used as a carrier gas at a flow rate of 1 ml/min. Injections of 1 μ l were made manually, with a temperature program of 40 to 270°C at 20°C/min. The temperature increase rate was altered to 15°C/min for the RB extract to separate the coeluting peaks for PCB congeners 155 and 101. Peaks were integrated using ChemStation software (Hewlett-Packard).

To obtain estimates of equilibrium analyte concentrations in EVA films, nonlinear regression (SPSS® 11.0, SPSS, Chicago, IL, USA) of the observed thin-film concentrations, C_E ($\mu\text{g/ml}$), versus time, t (h), was performed using a one-compartment model:

$$C_E(t) = C_E(\text{eq})(1 - e^{-kt}) \quad (3)$$

where $C_E(\text{eq})$ is the concentration in the thin film at equilibrium and k is a rate constant (h^{-1}), and using a two-compartment model following [16–18]:

$$C_E(t) = C_{E(\text{fast})}(1 - e^{-k_{\text{fast}}t}) + C_{E(\text{slow})}(1 - e^{-k_{\text{slow}}t}) \quad (4)$$

where $C_{E(\text{fast})}$ and $C_{E(\text{slow})}$ are the analyte concentrations in the thin film reflecting equilibrium in the apparent fast and slow compartments, and k_{fast} and k_{slow} are the corresponding rate constants describing the kinetics in these compartments. The more suitable model for the observed data was determined by comparing r^2 values and by examination of residuals.

Field sediment study

The SH sediment was manually stirred, 20 ml was added to EVA-coated scintillation vials, and vials were incubated at room temperature (in duplicate) for 0.25, 1, 4, 8, 24, and 75 h. Three empty EVA-coated vials were extracted as a method blank. An aliquot of SH sediment was sent to AXYS Analytical (Sidney, BC, Canada) for analysis of PCB congeners using high-resolution gas chromatography/high-resolution mass spectrometry [19]. Briefly, sediments were spiked with labeled extraction standards, Soxhlet-extracted in dichloromethane, and diluted as necessary for quantification. The extracts were then spiked with labeled quantification standards, solvent-exchanged into hexane, passed through a 2% deactivated Florisil column (Supelco, MO, USA), and treated for sulfur with activated copper. The extracts were cleaned up using alumina and an acid–base silica column, reduced in volume, and spiked with labeled internal recovery standards.

Thin films were extracted as described earlier and analyzed at the Institute for Ocean Sciences (Sidney, BC, Canada) by high-resolution gas chromatography/mass spectrometry to identify and quantify individual PCB congeners [20]. Before analysis, film extracts were spiked with ^{13}C -labeled PCB congeners 15, 18, 52, 118, 136, 181, and 209 (AccuStandard) and then concentrated under nitrogen and transferred to microvials using toluene, at which time a ^{13}C -PCB 111 internal standard was added (AccuStandard). Concentration data were analyzed by nonlinear regression as described earlier.

Bioaccumulation study

Twelve kilograms of BB sediments were spiked with an 18.75-ml solution of Aroclor 1254 (Ultra Scientific, North Kingstown, RI, USA) at a nominal concentration of 3,750 $\mu\text{g/kg}$ (dry wt) and aged for 30 d. Control sediments were prepared in the same way, but no test chemicals were used. The sediment was then used in side-by-side 28-d TF-SPE and 28-d *Macoma balthica* bioaccumulation tests following the U.S. Environmental Protection Agency [21]. Duplicate EVA-lined scintillation vials were filled with 20 ml of the spiked sediment on day 0, incubated for 28 d at 15°C, and then rinsed and extracted as described earlier. Clams and control sediment were collected by Environment Canada staff on April 22, 2004, from Moose Cove, Bay of Fundy, Canada. Three replicates of approximately 1.5 L of sediment and 2.5 L of clean overlying seawater were prepared for each of the control and spiked treatment

groups. The overlying water was aerated with oil-free compressed air at a rate of approximately 150 ml/min. Subsamples of the sediment (day 0) from all treatments were frozen for PCB analyses. Upon test initiation, 48 clams were added to each of the spiked and control sediment replicates. An additional group of 48 clams was used for the initial preexposure PCB tissue sample. Testing was performed at $15 \pm 1^\circ\text{C}$, under a 16:8-h light:dark photoperiod, with lighting provided by overhead fluorescent fixtures at an intensity of 400 to 600 lux. Water quality parameters were monitored three times per week in one replicate from each treatment, and approximately 50% of the overlying water was renewed with clean seawater in each test vessel. A sample of overlying water was taken at the start and end of the test for ammonia analysis. After 28 d, final sediment samples from all treatments were frozen for PCB analysis. The contents of each test vessel were sieved through a 0.5-cm sieve, and the number of mortalities was recorded. Live clams were depurated for 24 h in their native control sediment, recovered, shucked, and frozen for PCB analysis.

Analysis of sediment, tissue, and hexane extracts from the EVA thin films was performed by AXYS Analytical using high-resolution gas chromatography/high-resolution mass spectrometry [19]. Tissue samples of approximately 10 g were spiked with labeled quantification standards and were Soxhlet-extracted using dichloromethane; additional sample cleanup was conducted using gel permeation, silica, and alumina and Florisil chromatography columns. Thin-film extracts were spiked with 29 labeled surrogate PCBs and cleaned up using alumina and acid–base silica columns. Samples were then reduced in volume and spiked with a labeled recovery standard.

RESULTS

Spiked sediment study

Figure 1 illustrates the thin-film concentrations of analytes over time for PM and RB spiked sediments. Coefficients of variation among triplicate thin-film extractions ranged between 1.4 and 10.9% and averaged 6.2% in PM sediments aged 102 d, and 6.9% for RB sediment aged 52 d. Tetra- and pentachlorobenzenes, the lowest- K_{OW} chemicals tested, reached equilibrium within the time frame of the experiment for both aging periods (Fig. 1). The PCB congeners 180 and 194 did not reach equilibrium. Hexachlorobenzene and PCB congeners 26, 52, 101, and 155 appear to have reached equilibrium within 300 h in RB sediments aged for 17 d but not in RB sediments aged for 52 d.

The two-compartment model provided a better fit to the data than the one-compartment model, with the exception of tetrachlorobenzene and pentachlorobenzene in RB sediments aged for 17 d, for which both models fit equally well (Table S2; <http://dx.doi.org/10.1897/08-081.S1>). Residuals from the one-compartment model were strongly structured in all cases, whereas the two-compartment model residuals appeared to be approximately symmetrically distributed. A two-compartment model was therefore used to derive rate constants for exchange in the fast (k_{fast}) and slow (k_{slow}) compartments, EVA concentrations reflecting equilibrium with the fast ($C_{E(\text{fast})}$) and slow ($C_{E(\text{slow})}$) compartments, and the estimated time to reach 95% of equilibrium (t_{95} , approximated as $3/k_{\text{slow}}$; Table S3). Rate constants for k_{fast} ranged from 0.2 to more than 3 h^{-1} , whereas k_{slow} ranged from 0.13 to 0.005 h^{-1} . Because equilibrium between thin film and PM sediments aged for 21 d was reached within the first few extractions (in less than 1 h), k_{fast} could not be calculated for all test chemicals in these sediments.

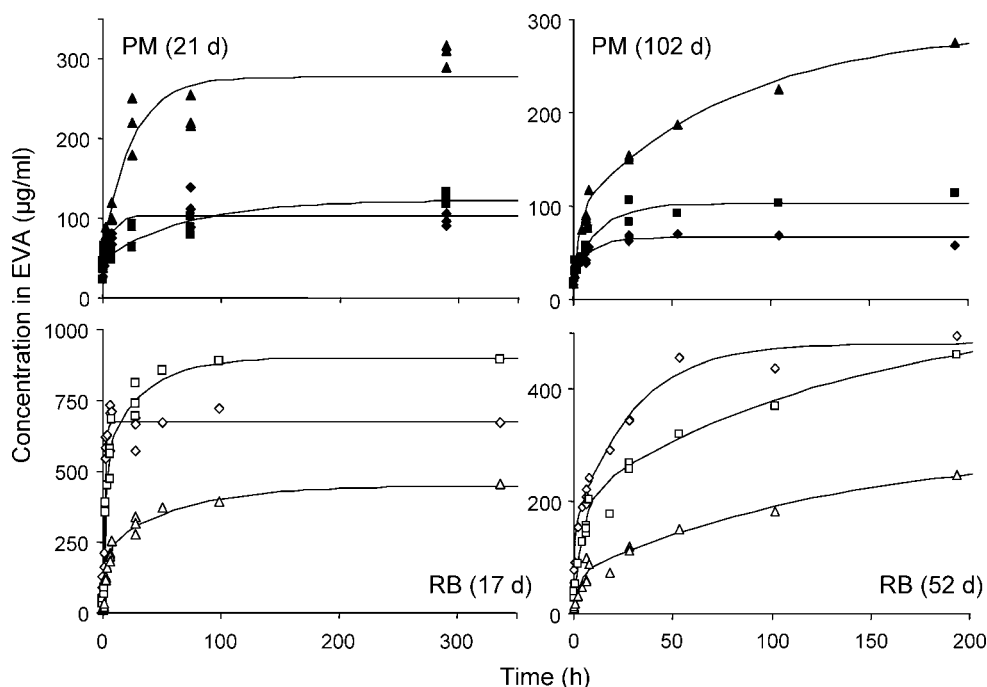


Fig. 1. Uptake curves for tetrachlorobenzene (◆), hexachlorobenzene (■), and polychlorinated biphenyl (PCB) congener 52 (▲) in Port Moody (PM) sediment (British Columbia, Canada) after aging periods of 21 and 102 d and for pentachlorobenzene (◇), PCB congeners 101 (□), and PCB 180 (△) in Roberts Bank (RB) sediment (British Columbia, Canada) after aging periods of 17 and 52 d. EVA = ethylene vinyl acetate.

The time required for 95% equilibration between sediment and thin films ranged from 23 h for tetrachlorobenzene to 600 h for PCB congener 194 and increased with increasing K_{OW} for both sediments and both aging periods (Fig. S1; <http://dx.doi.org/10.1897/08-081.S1>). The total analyte mass in the sediment sample that was transferred to the thin films at steady state ranged from 0.5 to 5.4% (Table S3).

Field sediment study

We detected 53 PCB congeners in thin-film extracts of field-collected SH sediments. Coeluting congeners (such as PCB 59 and PCB 42) were reported as the sum of concentrations. Method detection limits for individual PCB congeners ranged from 1.0 to 2.1 pg/sample, and recovery of ^{13}C -labeled standards averaged 90% (concentration data and method detection limits are presented in Table S4; <http://dx.doi.org/10.1897/08-081.S1>). Coefficients of variation for duplicate samples averaged 7.8%.

Uptake curves for PCB congeners 95, 149, and 180 are illustrated in Figure S2 (<http://dx.doi.org/10.1897/08-081.S1>). The two-compartment uptake model (i.e., Eqn. 4) fit the concentration–time data with an average r^2 of 0.97. With increasing K_{OW} of the chemical, the two-compartment model provided better fits of the data than did the one-compartment model (Fig. S3).

The majority of PCB congeners exhibited a rapid initial uptake, and estimates for k_{fast} were not possible. Estimates of k_{slow} ranged from 0.14 h^{-1} for PCB congener 201 to 0.44 h^{-1} for PCB congener 44, and $\log k_{slow}$ declined with increasing $\log K_{OW}$ (Fig. 2). As a consequence, the estimated time to reach 95% of equilibrium between sediment and thin film (t_{95}) increased from less than 10 h to approximately 200 h as $\log K_{OW}$ increased from 5.2 to 7.6. Estimated values for $C_{E(fast)}$, $C_{E(slow)}$, and k_{slow} are presented in Table S5 (<http://dx.doi.org/10.1897/08-081.S1>). Thin-film extraction depleted 0.05 to

0.4% of the total mass of each PCB congener from the sediment.

Bioaccumulation study

Survival of *M. balthica* in the 28-d bioaccumulation test exceeded 99%. The average tissue lipid content (kg/kg) was 1.8%. Congener-specific coefficients of variation averaged 9% for triplicate tissue analyses and 4.8% for duplicate thin-film extracts (all concentration data are presented in Table S6; <http://dx.doi.org/10.1897/08-081.S1>). Concentrations of some lower- K_{OW} PCBs declined between day 0 and day 28 in the bioaccumulation test sediment (Fig. S4), possibly due to volatilization. Concentrations in sediments were estimated as the average of measured values on day 0 and day 28. This decline may have acted to shorten the time required to reach steady state for these congeners. Sediment in the TF-SPE vials was not exposed to air, and PCB concentrations in these samples were not expected to decline over the course of the experiment.

Figure 3 illustrates the strong relationship between lipid-normalized PCB concentrations in *M. balthica* (C_L) and concentrations in the EVA thin film (C_E). $\log C_L$ followed a linear relationship with $\log C_E$ ($\log C_L = 0.97 \cdot \log C_E - 0.88$; $r^2 = 0.98$; $p < 0.0001$) with a slope near unity, indicating that the sorptive capacity of EVA is approximately proportional to that of lipid across the range of physicochemical properties represented by the measured PCB congeners. Biota–sediment accumulation factors declined slightly with increasing $\log K_{OW}$ (Fig. 4), suggesting that the concentrations in the clams had not reached steady state with concentrations in sediment for higher- K_{OW} PCB congeners. However, the decline of $\log K_{EVA-OC}$ with increasing $\log K_{OW}$ for chemicals with a $\log K_{OW} > 5.5$ was less than that for the lipid and organic carbon normalized biota–sediment accumulation factor (Fig. 4), indicating that the thin films approach equilibrium for higher- K_{OW} congeners more quickly than in clams. According to the

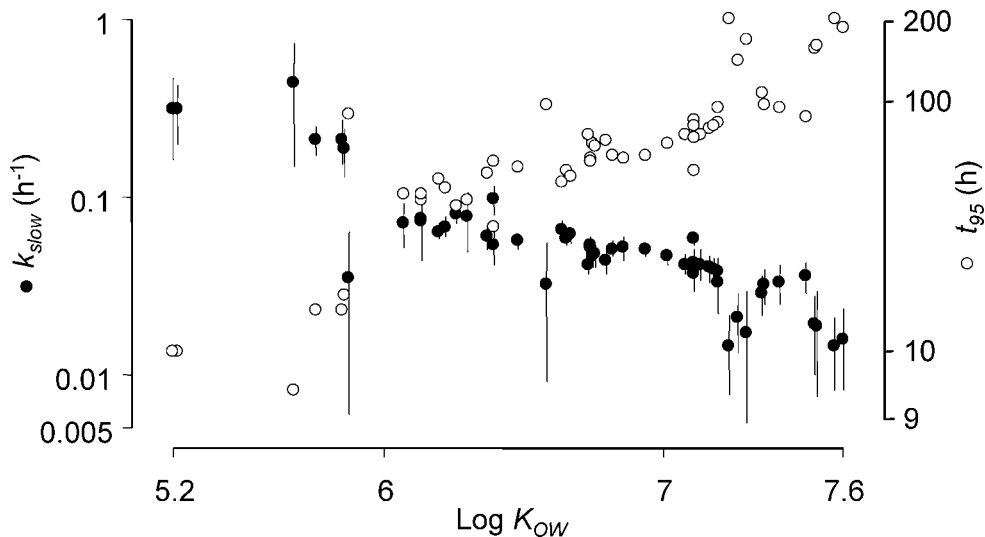


Fig. 2. The slow uptake rate constant (\bullet , k_{slow} ; mean \pm 1 standard error) and mean estimated time to achieve 95% of equilibrium (\circ , t_{95}) as a function of $\log K_{\text{OW}}$ for polychlorinated biphenyl congeners in Sydney Harbor (Nova Scotia, Canada) sediment.

C_L - C_E relationship described in the thin films earlier, the sorptive capacity of EVA is approximately 7.5 times (or the antilog of 0.88) greater than that of lipid in clams.

Combined data

Figure 5 shows equilibrium thin film-sediment concentration ratios for all test sediments, in terms of both bulk sediment concentrations (C_E/C_{Sed}) and organic carbon-normalized sediment concentrations (C_E/C_{OC}). This figure shows that the ratio C_E/C_{Sed} varied little among chemicals within a sediment but varied more than 1,000-fold among sediments, reflecting the large variability in sorptive capacity among the four test sediments. The ratio C_E/C_{OC} varied much less than this but still ranged over more than an order of magnitude, indicating that organic carbon content could account for much of the variability in sorptive capacity among sediments.

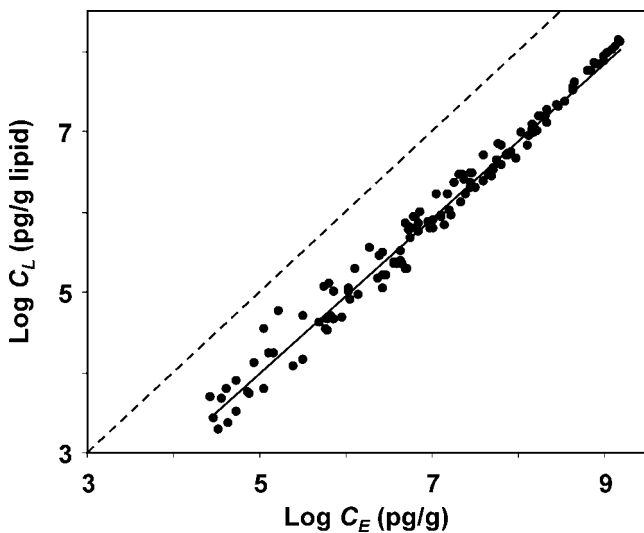


Fig. 3. Relationship between lipid-normalized polychlorinated biphenyl congener concentrations in *Macoma balthica* (C_L) and ethylene vinyl acetate thin films (C_E). Dashed line is 1:1. Solid line is linear best fit (see text for equation and statistics).

DISCUSSION

Our analysis showed that TF-SPE provided highly reproducible measurements that directly reflect chemical fugacity in sediment within a practical timeframe, with 95% equilibration times between 1 and 600 h. These relatively short equilibration times were achievable because of relatively high chemical exchange rates, with k_{slow} estimated to be on the order of 10^{-3} to 10^{-1} h^{-1} . These rates are greater than those reported in studies of desorption from slow sorption sites on sediment (typically 10^{-3} to 10^{-4} h^{-1} for PCBs; [16]) because the TF-SPE method approaches negligible depletion of sediment concentrations and is therefore not limited by the kinetics of chemical release from poorly accessible sorption sites. Assuming that the more rapidly exchanging pools of chemical (possibly pore water) are at internal equilibrium with the slow-exchanging pools, measuring the fugacity of the relatively rapidly ex-

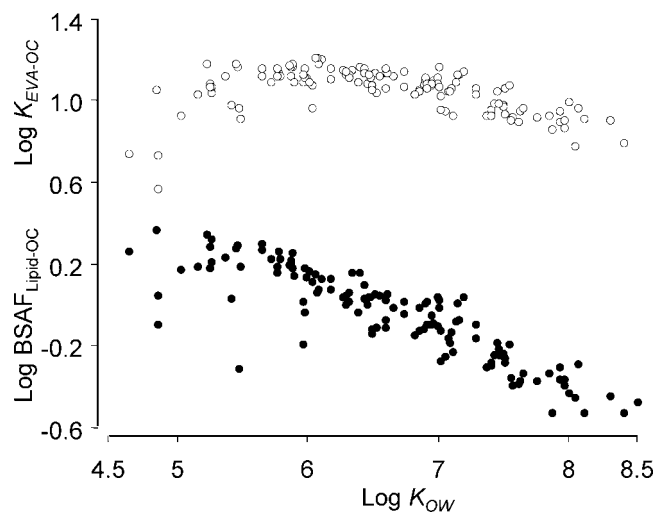


Fig. 4. Log biota-sediment accumulation factor (BSAF; lipid and organic carbon [OC] normalized) in *Macoma balthica* (closed symbols) and log ethylene vinyl acetate (EVA)-sediment partition coefficient (OC normalized, $\log K_{\text{EVA-OC}}$; open symbols) of polychlorinated biphenyl congeners after a 28-d exposure to spiked Boundary Bay (British Columbia, Canada) sediment.

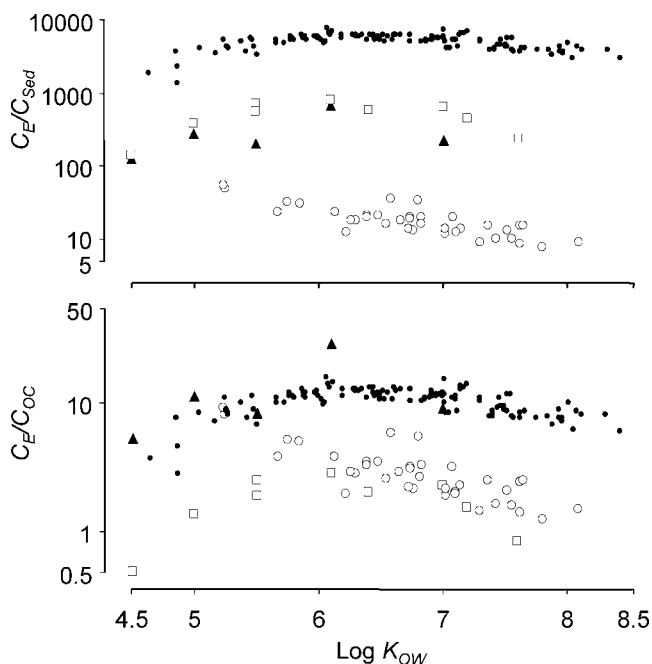


Fig. 5. Ratios of equilibrium thin-film concentrations to bulk dry weight sediment concentrations (C_E/C_{Sed}) and organic carbon-normalized sediment concentrations (C_E/C_{OC}) as a function of the octanol-water partition coefficient (K_{OW}) for chlorobenzenes and polychlorinated biphenyls in sediments from Port Moody, British Columbia, Canada (\blacktriangle); Roberts Bank, British Columbia, Canada (\square); Sydney Harbor, Nova Scotia, Canada (\circ); and Boundary Bay, British Columbia, Canada (\bullet).

changing chemical is sufficient to characterize exposure to the chemical in the sediment. Even if the pools are not at equilibrium, the fugacity of the rapidly exchanging chemical is likely a more ecologically relevant measure of the potential chemical exposure of sediment biota. Our comparison of TF-SPE to *M. balthica* bioaccumulation indicates that chemical accumulation in the EVA thin film is directly related to bioaccumulation in animal tissues. However, whereas *M. balthica* can take several weeks to approach steady state [21], we estimate that the EVA thin films reach 95% of equilibrium within a few days for most congeners and within little more than a week for even the highest- K_{OW} congeners [cf. 3]. Furthermore, the sorptive capacity of EVA was estimated to be 7.5-fold higher than that of lipid, a property that enhances the utility of EVA as a sensitive measure of low chemical fugacities in sediment.

In our study, depletion of sediment concentrations by uptake into the thin film was less than 1%, although local depletion at the thin film-sediment interface may have been greater than this if the rate of uptake into the thin film exceeded the rate at which chemical concentrations at the interface were replenished by diffusion from the bulk sediment or by mixing of sediments. Local depletion at the thin film-sediment interface is likely more important if desorption from sediment is an important rate-limiting step and less significant if chemical is predominantly obtained from pore water, as diffusion rates in water are greater than those in sediment solids. If local depletion occurs, our method is expected to underestimate f_s , k_{slow} , and k_{fast} and overestimate t_{95} . Gentle mixing by continuously rolling the vials may reduce the potential for depletion of chemical concentrations at the thin film-sediment interface.

Despite the small extracted quantities of analytes, method

detection limits were sufficiently low to apply the method to field-collected contaminated sediments. Method detection limits remained low because our method avoids the increase in analytical variability that can result from the multiple postextraction cleanup steps required following exhaustive extraction, and interference of analytes with sediment constituents was less because solid phase extraction is a more selective extraction than a typical solvent-based Soxhlet extraction. Furthermore, the hexane extract from a thin film can be injected directly into a chromatograph, avoiding potential losses of analyte with solvent exchange and blow-down steps.

The main advantage of using fugacities over concentrations in the assessment of sediment quality is that the large natural variation in sorptive capacities of sediment, and the effect of this variation on biological uptake, can be taken into account. Figure 5 illustrates that among sediments C_E/C_{Sed} ratios can vary by more than three orders of magnitude. This means that a particular concentration of PCB in the sediments can present a fugacity that can vary substantially as a function of the properties of the sediment and the history of contamination. Figure 5 illustrates that organic carbon content plays a key role in controlling the fugacity of organic chemicals, and accounting for this should be a key consideration in the assessment of sediment quality [6]. However, our analysis shows that organic carbon normalization is not sufficient to account for all variability in the apparent fugacities of PCBs.

Developing modeling tools that can incorporate and account for the remaining differences in chemical fugacity among sediments is likely to present a significant challenge for some time to come. We therefore propose that TF-SPE and similar solid phase extraction methods can play a useful role in empirically characterizing chemical fugacities in sediments [3,22]. It is straightforward to conduct sediment toxicity tests in which thin-film concentrations are measured alongside biological effects, such that toxicity can be related to thin-film concentrations or fugacities rather than to total sediment concentrations. Resulting relationships between toxicity and thin-film concentrations can then be applied to assess toxicological risk of contaminated sediments and to develop SQGs based on chemical fugacity. The findings of our study suggest that this approach has the potential to substantially improve sediment quality assessments for organic contaminants.

SUPPORTING INFORMATION

The supporting tables and figures show properties and nominal concentrations of test chemicals in spiked sediment; coefficients of determination for one- and two-compartment model fits; uptake curve parameters for spiked and natural contaminated sediments; concentrations and method detection limits for polychlorinated biphenyl (PCB) congeners in Sydney Harbor sediment; measured concentrations of PCB congeners in spiked Boundary Bay sediment, *M. balthica* and EVA thin films; *M. balthica* biota-sediment accumulation factors for PCB congeners; relationship between 95% equilibration time and $\log K_{OW}$ in spiked and natural contaminated sediments; representative thin-film uptake curves for PCBs in Sydney Harbor sediment; relationship between coefficients of determination for one- and two-compartment model fits and $\log K_{OW}$; and changes in concentrations of PCB congeners during bioaccumulation study.

Table S1. Logarithms of the octanol-water (K_{OW}) and octanol-air (K_{OA}) partition coefficients and the nominal chemical

concentrations (C_{sed}) in the Port Moody (PM) and Roberts Bank (RB) sediments.

Table S2. Coefficients of determination (r^2) for fitting one-compartment (1C) and two-compartment (2C) models to thin-film concentration–time data depicted in Figure 1.

Table S3. Fast and slow uptake rate constants (k_{fast} and k_{slow} , respectively), equilibrium thin-film concentrations ($C_{\text{E(fast)}}$ and $C_{\text{E(slow)}}$), 95% equilibration time (t_{95}), and fraction of chemical extracted from spiked sediments by the ethylene vinyl acetate thin film (Φ). Values are means (± 1 standard error in parentheses).

Table S4. Total sediment concentrations and method detection limits (MDLs) of polychlorinated biphenyl (PCB) congeners in Sydney Harbor sediment.

Table S5. Uptake rate constants (k_{slow}), equilibrium thin-film concentrations ($C_{\text{E(fast)}}$ and $C_{\text{E(slow)}}$), and 95% equilibration time (t_{95}) for natural, unspiked Sydney Harbor (SH) sediments by the ethylene vinyl acetate thin film (Φ). Values are means (± 1 standard error in parentheses).

Table S6. Results from the 28-d *Macoma balthica* bioaccumulation test: concentrations of Polychlorinated biphenyl (PCB) congeners in spiked Boundary Bay sediments (C_{sed}) on day 0 and day 28, wet weight PCB concentrations in *M. balthica* tissue (C_{tissue}), ethylene vinyl acetate (EVA) thin-film concentrations (C_{E}) after a 28-d exposure, and fraction of chemicals (by mass, Φ), extracted from the sediment into the EVA film.

Table S7. Biota–sediment accumulation factors on a wet weight/dry weight basis (BSAF) and on a lipid and organic carbon-normalized basis (BSAFL/OC) for *Macoma balthica* exposed for 28 d to sediments spiked with Aroclor 1254.

Figure S1. Time to reach 95% of equilibrium concentration (t_{95}) with ethylene vinyl acetate (EVA) thin films for chlorobenzenes and polychlorinated biphenyls (PCB) extracted from Port Moody sediment after 21 d (Δ) and 102 d aging (\blacktriangle), Roberts Bank sediment after 17 d (\circ) and 52 d aging (\bullet), and natural, unspiked Sydney Harbor sediment (\times).

Figure S2. Uptake curves for polychlorinated biphenyl (PCB) congeners 95 (\circ), 149 (\blacktriangle), and 180 (\blacklozenge) in field-collected (unspiked) Sydney Harbor sediment.

Figure S3. Coefficients of determination (r^2) for fitting one- and two-compartment models to thin-film concentration–time data for natural, unspiked Sydney Harbor sediments.

Figure S4. Observed reduction (%) over the 28-d *Macoma balthica* bioaccumulation test in the concentrations of individual polychlorinated biphenyl (PCB) congeners in Boundary Bay sediments spiked with Aroclor 1254.

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