

Critical Review

REVIEW OF POLYOXYMETHYLENE PASSIVE SAMPLING METHODS FOR QUANTIFYING FREELY DISSOLVED POREWATER CONCENTRATIONS OF HYDROPHOBIC ORGANIC CONTAMINANTS

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Abstract: Methods involving polyoxymethylene (POM) as a passive sampler are increasing in popularity to assess contaminant freely dissolved porewater concentrations in soils and sediments. These methods require contaminant-specific POM–water partition coefficients, K_{POM} . Certain methods for determining K_{POM} perform reproducibly (within 0.2 log units). However, other methods can give highly varying K_{POM} values (up to 2 log units), especially for polycyclic aromatic hydrocarbons (PAHs). To account for this variation, the authors tested the influence of key methodological components in K_{POM} determinations, including POM thickness, extraction procedures, and environmental temperature and salinity, as well as uptake kinetics in mixed and static systems. All inconsistencies in the peer-reviewed literature can be accounted for by the likelihood that thick POM materials (500 μm or thicker) do not achieve equilibrium (causing negative biases up to 1 log unit), or that certain POM extraction procedures do not ensure quantitative extraction (causing negative biases up to 2 log units). Temperature can also influence K_{POM} , although all previous literature studies were carried out at room temperature. The present study found that K_{POM} values at room temperature are independent (within 0.2 log units) of POM manufacture method, of thickness between 17 μm and 80 μm , and of salinity between 0% and 10%. Regarding kinetics, monochloro- to hexachloro-polychlorinated biphenyls (PCBs) were within 0.2 log units of equilibrium after 28 d in the mixed system, but only dichloro-PCBs achieved near equilibrium after 126 d in the static system. Based on these insights, recommended methods and K_{POM} values to facilitate interlaboratory reproducibility are presented. *Environ Toxicol Chem* 2015;34:710–720. © 2015 SETAC

Keywords: Bioavailability Passive sampling Polymer uptake Partitioning Kinetics

INTRODUCTION

Regulators are increasingly recognizing that risk assessments of soil and sediments should account for bioavailability [1–3]. For hydrophobic organic contaminants, bioavailability in soils and sediments is typically defined as the concentration currently available for partitioning with organisms, quantifiable as the *equilibrium* freely dissolved porewater concentration, C_{pw} (i.e., the contaminant fraction at equilibrium completely solvated by porewater and not associated with interstitial colloids or dissolved organic carbon) [4,5]. This definition, common in the passive sampling community, differentiates bioavailability from the concept of bioaccessibility, which is the fraction of chemicals available to organisms over some extended period [4,5]. Methods to quantify hydrophobic organic contaminant C_{pw} include placing equilibrium passive samplers such as polyoxymethylene (POM) [6–11], low-density polyethylene (LDPE) [8,12], or polydimethylsiloxane (PDMS) [8,13,14] in soil or sediment slurries, or placing solid-phase-microextraction fibers in flocculated (colloid-free) porewater samples [15–18]. An increasing number of soil and sediment bioassays show that bioaccumulation and toxicity correlates with C_{pw} more than with other measurements, including total

soil and sediment concentrations, Tenax extractions, cyclodextrin extractions, and supercritical fluid extractions [5,7,16]. Species investigated in such studies include the benthic amphipods *Hyaella azteca* and *Leptocheirus plumulosus* [14–16,18], the midge *Chironomus dilutus* [13], the earthworms *Eisenia fetida* [7,17] and *Enchytraeus crypticus* [19], the sediment worm *Lumbriculus variegatus* [6,9,11], and the polychaete *Neanthes arenaceodentata* [8,10]. Bioaccumulation in plants, however, has not correlated as well with C_{pw} as the aforementioned species [5], likely because plants have more complex uptake and metabolization pathways for hydrophobic organic contaminants.

In a batch system containing biota, environmental solid media, and the passive sampler POM, C_{pw} can be related to the concentration in any of these media (Equation 1):

$$C_{\text{pw}} = \frac{C_{\text{biota}}}{K_{\text{biota}}} = \frac{C_{\text{solid}}}{K_{\text{D}}} = \frac{C_{\text{POM}}}{K_{\text{POM}}} \quad (1)$$

In Equation 1, C_{biota} , C_{solid} , and C_{POM} are the equilibrium concentrations in biota, environmental solid media, and POM, respectively, and K_{biota} , K_{D} , and K_{POM} are the respective equilibrium partitioning coefficients. Thus, passive sampler measurements can also be used to derive partitioning coefficients to biota and environmental solids. A further advantage of using passive samplers like POM, as well as LDPE or PDMS, is that they can be used to determine C_{pw} at levels as low as pg L^{-1} to fg L^{-1} [8,20–22]. Critical reviews for

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LDPE [12] and PDMS [23] partitioning coefficients have been presented elsewhere; this is the first review of a broad dataset of K_{POM} .

REVIEW OF K_{POM} DATA AND METHODS

The most typical way of using POM to determine C_{pw} is the batch-mix test. In this test, a vial containing the POM, solid media, and water are mixed (rotated or tumbled) together until equilibrium is reached, considered to be at 28 d for most hydrophobic organic contaminants [20,21,24] but sometimes longer for polychlorinated biphenyls (PCBs) and dioxins [22,25]. Afterward, the POM strips are removed, C_{POM} is quantified (by extraction followed by quantification), and C_{pw} is determined using a compound-specific K_{POM} value (Equation 1). Generally K_{POM} values are also determined with the batch-mix test, with just the extra step that the C_{pw} must be independently quantified. K_{POM} values have been measured for polycyclic aromatic hydrocarbons (PAHs) and alkyl-PAHs [20,24,26–31], PCBs [20,21,24,25,27,32–34], oxy-PAHs [31], polychlorinated dibenzo-*p*-dioxins and -furans [35,36], polybrominated diphenyl ethers, triclosan and methyl triclosan [37], organochlorine pesticides, and diverse polar compounds [38].

All known peer-reviewed K_{POM} data for PAHs and PCBs are plotted in Figure 1 relative to the octanol–water partitioning coefficient for each compound, K_{OW} (see the Supplemental Data for raw data). Also plotted in Figure 1 is the $\log K_{\text{POM}}-\log K_{\text{OW}}$ relationship derived by Endo et al. [38] for a diverse set of polar and nonpolar compounds (Equation 2).

$$\log K_{\text{POM}} = 1.01 \times \log K_{\text{OW}} - 0.60 \quad (2)$$

A striking feature about Figure 1 is the scatter of some K_{POM} data. For the PAHs plotted in Figure 1A, it is evident that much of the data is clustered parallel to the K_{OW} relationship but others deviate, most notably when the $\log K_{\text{OW}}$ becomes larger than 5. As a result, literature K_{POM} values for PAHs with large K_{OW} values can differ by as much as a factor of 100 (Figure 1A).

For PCBs, the scatter can be greater than a factor of 10 (Figure 1B), with some data slightly above the K_{OW} relationship and other data a factor of 10 below.

This inconsistency in literature K_{POM} values must originate from some methodological variation. Varying parameters in methods used to determine K_{POM} include POM thickness (from 17 μm [29] to more than 2 mm [28]), mixing time (from 28 d [24] to 180 d [25,36]), and POM extraction procedures (including rotation for 2 d or more in hexane [22,32,33,35,36] or heptane:acetone (4:1) [38], sonication in hexane:acetone (1:1) for 3 h [20,21], Soxhlet extraction for 3 h to 6 h in acetone:hexane (1:3) [11] or methanol [20,24,26], and light agitation in acetone followed by dichloromethane for 24 h each [27,37]). As seen in Figure 1A, the K_{POM} values for PAHs that deviate the most from Equation 2 are those derived from methods that used cold shaking in hexane (hex, in the figure), or light agitation in acetone followed by dichloromethane (ace:DCM, in the figure). Figure 1B shows that the K_{POM} values for the PCBs that deviated the most were determined with POM that was 500 μm thick, as indicated in the figure by POM-500. Collectively, these data indicate that the POM extraction method and the thickness could explain many of the deviations that produced low K_{POM} values.

In the present study, we present a systematic series of experiments in combination with a review of the literature to test the hypothesis that extraction method and POM thickness can account for the deviations in POM values observed in Figure 1. Alternative hypotheses explored are the roles of temperature, salinity, and exposure time (i.e., kinetics). The present study is considered a preliminary step for the future development of interlaboratory, standardized POM-based methods and models [1,39].

MATERIALS AND METHODS

Polyoxymethylene

As a thermoplastic, semicrystalline polymer (of repeating $-\text{CH}_2\text{O}-$ units), POM has been used in diverse applications since the early 1960s for replacing metal parts when corrosion is an

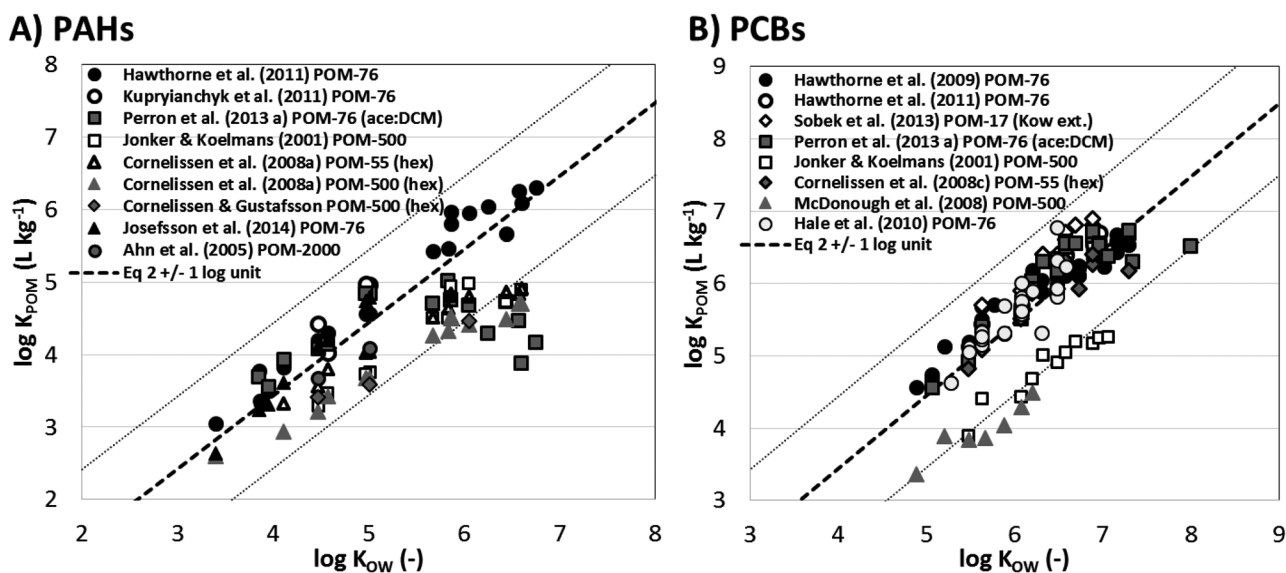


Figure 1. A compilation of peer-reviewed logarithms of polyoxymethylene (POM)–water partition coefficients, $\log K_{\text{POM}}$, plotted against the octanol–water partition coefficient, $\log K_{\text{OW}}$, for (A) polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs, and (B) polychlorinated biphenyls (PCBs), along with a $\log K_{\text{POM}}-\log K_{\text{OW}}$ linear free-energy relation (Equation 2; dashed black line) ± 1 log unit (gray lines). Citation references in the legend are Ahn et al. (2005) [28], Cornelissen and Gustafsson (2004) [30], Cornelissen et al. (2008) [29], Cornelissen et al. (2008) [33], Jonker and Koelmans (2001) [24], Josefsson et al. (2014) [31], Hale et al. (2010) [25], Hawthorne et al. (2009) [41], Hawthorne et al. (2011) [20], Kupryianchyk et al. (2011) [26], McDonough et al. (2008) [32], Perron et al. (2013) [27], and Sobek et al. (2013) [36]. hex = cold shaking in hexane; ace:DCM = light agitation in acetone followed by dichloromethane.

issue [40]. It is produced through the polymerization of formaldehyde, and is manufactured either as a homopolymer (POM-H) or a copolymer (POM-C). Polyoxymethylene-C has improved dimensional and chemical stability, is much cheaper, and sold in greater abundance than POM-H. Probably all POM materials used as a passive sampler thus far are POM-C. In the present study we tested 2 types of POM-C: POM-76, which uses ethylene oxide as a copolymer (Calcon, CS Hyde), and is manufactured as 76- μm -thick molded sheets. All other POM materials use trioxane as a copolymer (Astrup), and were purchased as a solid block that was lathe-cut into thicknesses of 17 μm , 40 μm , 55 μm , and 80 μm , respectively referred to as POM-17, POM-40, POM-55, and POM-80. Note that POM-17 was the thinnest that could be sliced and remain intact after exposure to sediment mixing.

Chemicals and sediments

The 2 uncontaminated sediments used for studying PAH uptake into POM are referred to as Lake sediment (3.1% organic carbon) and Coulee sediment (1.2% organic carbon; sediments D and E, respectively, in a previous study [41]). Per test vial (40-mL glass with Teflon-lined lids), approximately 10 g of dry, uncontaminated sediments were spiked with 200 μL of a 10-mg/mL mixed coal tar and petroleum standard (NIST SRM 1991) in pesticide-grade acetone, that is, a 200-mg/kg spike (see the Supplemental Data for PAH concentrations). Then 30 mL of water was added with 100 μL of 50 mg/mL sodium azide (as a biocide) and the samples were mixed by rotation for 72 h to homogenize them. For the PCB kinetic test, a noncontaminated sediment sampled near a gas plant site (2.8% organic carbon) was spiked to 5.3 $\mu\text{g/g}$ (dry wt) using a 3:2 mix of Aroclors 1242 and 1260, and then mixed as the coal tar-spiked sediments. Solvent extracts were spiked with either perdeuterated PAH internal standards [16] (Cambridge Isotopes) or PCB non-Aroclor internal standards (PCBs 14, 30, 65, 103, and 169, from Accustandard) [41].

Batch-mix method

Mixing batches of sediment, POM, and water for a period of 28 d to obtain equilibrium C_{POM} concentrations has been recommended throughout the POM literature since the first paper to present the technique [24]. Subsequent studies that looked at uptake kinetics in POM have consistently reported that 28 d of mixing is sufficient for achieving POM-water equilibrium partitioning for PAHs and PCBs, and thus reproducible K_{POM} values [20,24,31,41]. Therefore, to investigate the cause of the variations in the K_{POM} values reported in Figure 1, a generic 28-d batch-mix method was deemed representative of the majority of the literature and was used (along with appropriate modifications) to investigate systematically the influence of extraction method, POM thickness, temperature, salinity, and kinetics.

In the generic 28-d batch-mix method, approximately 50-mg POM pieces were cut and precleaned by sequential extraction for 2 h in *n*-hexane followed by methanol with the aid of sonication. (Hexane followed by methanol is a common choice for cleaning POM [20,38,41].) One or more POM pieces were placed in the glass vials containing the homogenized, spiked sediment and water. After end-over-end rotation at 6 rpm for 28 d, the POM was removed and the surface cleaned until it was visibly free from sediment particles. The POM was then extracted (see *Extraction methods* section below) and analyzed using an Agilent model 5973 gas chromatograph/mass spectrometer (GC/MS), equipped with a 60-m Agilent HP-5

MS column (0.25- μm film thickness, 250- μm internal diameter).

Polyoxymethylene thickness

The batch-mix test above was performed with 50 mg of POM-17, POM-55, POM-76, and POM-80 in each vial, thus ensuring that each POM thickness was exposed to identical PAH C_{pw} concentrations. Triplicate vials were prepared for both types of sediment (total 24 POM strips in 6 different vials), and mixed for 28 d at 6 rpm. The POM pieces were then removed and extracted using acetone:hexane (1:1) with 3 h of sonication [20,21], which was found to be a quantitative extraction procedure (see results of the *Extraction methods* experiments, below).

Extraction methods

To investigate the hypothesis that cold-shaking in hexane is not quantitative for PAHs (Figure 1), 3 strips of POM-17, POM-55, and POM-76 were exposed to 28 d of mixing with the spiked Lake Sediment in 9 separate vials (total 27 POM strips). Then the POMs were removed, cleaned, and placed in a vial (40-mL glass vial with Teflon-lined lid) and extracted using 20 mL of deuterated-PAH internal standard spiked solvent and 1 of the following 3 techniques: 1) 48-h rotation (6 rpm) in hexane (as described in Cornelissen et al. [29]); 2) 48-h rotation in hexane:acetone (1:1) at (6 rpm; as described in Endo et al. [38]); or 3) sonication for 3 h in hexane:acetone (1:1; as described in Hawthorn et al. [20]). The POM was removed and solvents were evaporated under a gentle stream of nitrogen to approximately 2 mL and transferred into an autosampler vial.

Temperature and salinity

The batch-mix method described above (10 g sediment, 0.05 g POM-76) was conducted in quadruplicate batches for 28 d with the Coulee sediment at 3 temperatures (4 $^{\circ}\text{C}$, room temperature; $\sim 22^{\circ}\text{C}$, and 40 $^{\circ}\text{C}$), with no salt added. To test the influence of salinity at room temperature, the batch-mix test was done 3.42% salt (corresponding to ocean water) and 10% salt, prepared with food grade sea salt. In addition, for the temperature experiments, C_{pw} was also independently measured after the POMs were removed, so that K_{POM} could be determined (Equation 1). The C_{pw} measurements were done by isolating a few mL of water immediately after incubation into a 40-mL glass vial, flocculating and centrifuging (twice) at room temperature, and then placing a solid-phase-microextraction fiber to extract PAHs for GC/MS analysis following ASTM D7363-7 [42]. The flocculation and centrifugation at room temperature was done as quickly as possible, to avoid artifacts from the system reverting to room temperature equilibrium with suspended colloids and dissolved organic carbon.

Mixed versus static exposure

Kinetic uptake rates were determined for PCBs in static and mixed systems. The static experiments are conducted in the present study for the first time. The mixed experiment is a near-repeat of that in Hawthorne et al. [21]. For PCBs, 42 sample vials were prepared as described above (*Batch-mix method*) except that a 300-mg POM-76 coupon was used. After introduction of POM, 24 of these vials were mixed at 6 rpm, and the remaining 18 were kept stationary. On days 3, 7, 14, 28, 42, 70, 98, and 126, triplicate vials from the mixed system were removed, and on days 3, 7, 14, 28, 56, and 126, triplicate vials for the static system were removed. The POM was then

extracted using 3-h sonication in internal standard spiked acetone:hexane as described in the *Extraction methods* section.

The C_{POM} data obtained were fitted to first-order (Equation 3) and second-order (Equation 4) [43] rate equations.

$$C_{\text{POM}} = C_{\text{POM,eq}} \times \left(1 - e^{-(k1)t}\right) \quad (3)$$

where $C_{\text{POM,eq}}$ is the POM concentration at equilibrium, t is time, and $k1$ is the first-order rate constant (determined by the slope of a linear regression of $\ln(C_{\text{POM,eq}} - C_{\text{POM}t}) = \ln C_{\text{POM,eq}} - (k1)t$, where the intercept is forced at $\ln C_{\text{POM,eq}}$). The second-order rate equation [43] used is presented in Equation 4.

$$\frac{1}{(C_{\text{POM,eq}} - C_{\text{POM}})} = \left(\frac{1}{C_{\text{POM,eq}}}\right) + (k2)t \quad (4)$$

where $k2$ is the second-order rate constant, and is determined using a linear regression. For both Equations 3 and 4, $C_{\text{POM,eq}}$ is assumed as the C_{POM} after 128 d of shaking. Note that Equations 3 and 4 should be referred to as pseudo-first-order and pseudo-second-order rate equations, where the term *pseudo* is used to imply that the k values are not dependent on concentration but more on the presence of sorption sites in the sorbing medium (i.e., POM) [43].

Quantification

Quantification with GC/MS was done in selected ion monitoring, using the molecular ion m/z for PAHs [20], and the most intense ion at the molecular ion range for PCBs [21]. Four point calibrations were done initially, followed by daily duplicate continuing calibrations with each sample set. Daily calibrations had to meet the mean response of the 4-point calibrations within 10% to 15% depending on the species. All samples had the internal standards described above. Signal to noise had to be $>5:1$, and all peaks were integrated manually. Note that all experiments were done at a single laboratory (the Energy and Environmental Research Center, University of North Dakota, Grand Forks, North Dakota, USA) to ensure that all steps were identical, and to eliminate any chance of

different procedures in different laboratories causing apparent laboratory-biases in POM results (e.g., GC/MS calibration).

RESULTS AND DISCUSSION

Polyoxymethylene thickness

To present the data relating to PAH uptake into various thicknesses of POM, POM-76 is used as the reference material, as it is the most readily available and the only POM material that was molded and not lathe-cut. Figure 2 presents the C_{POM} for POM-17, POM-55, and POM-80 relative to POM-76 (i.e., $C_{\text{POM}}/C_{\text{POM-76}}$) after the standard 28-d batch-mix test. Corresponding raw data are presented in the Supplemental Data, Section S1.

Polyoxymethylene-76 and POM-80 are the 2 POMs most similar in thickness; they differ, however, in their copolymer (ethylene oxide vs trioxane, respectively) as well as their manufacturing processes (molded vs lathe-cut, respectively). As is evident in Figure 2, these 2 types of POMs have nearly identical PAH concentrations, with an average $C_{\text{POM}}/C_{\text{POM-76}}$ for all compounds and sediments of 0.96 ± 0.13 (p value [unpaired, 1-tailed t test] > 0.05). Ratios for individual PAHs range from 0.7 ± 0.1 to 1.2 ± 0.1 , with the largest deviations being for the 6-ring PAHs. This implies that neither manufacturing process nor copolymer substance substantially influences the magnitude of K_{POM} for PAHs.

The average $C_{\text{POM}}/C_{\text{POM-76}}$ for POM-55 is 1.08 ± 0.14 , slightly but significantly above equivalence ($p = 0.01$), with slightly larger values for the 4,5-ring PAHs (1.25 ± 0.08 ; Figure 2).

Ratios of $C_{\text{POM}}/C_{\text{POM-76}}$ for POM-17 are presented for the Coulee sediment only, as the Lake sediment samples were difficult to clean free of colloids (raw data for both sediments are presented in the Supplemental Data, Table S1.1). The $C_{\text{POM}}/C_{\text{POM-76}}$ values for POM-17 are 1.10 ± 0.16 ($p = 0.01$), again with the largest differences for the 4,5-ring PAHs (1.26 ± 0.09).

The largest positive concentration deviation compared with $C_{\text{POM-76}}$ is observed for 4,5-ring PAHs and POM-17 (maximum 40% measured for chrysene, POM-17) and the largest negative deviation is for POM-80 (maximum 30% measured for

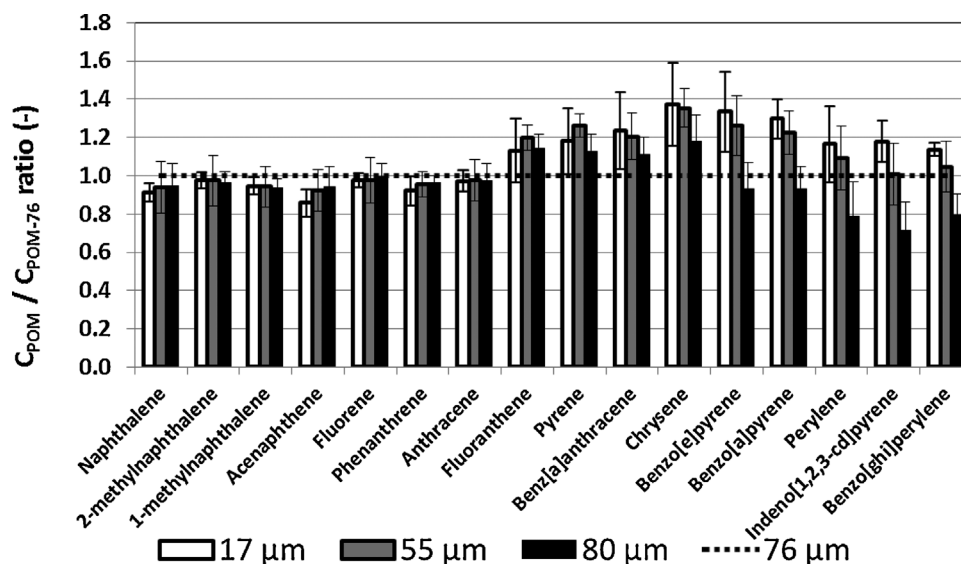


Figure 2. Average ratios of polycyclic aromatic hydrocarbon (PAH) concentrations in polyoxymethylene (POM) of varying thicknesses (17 μm , 55 μm , and 80 μm) relative to 76 μm POM ($C_{\text{POM}}/C_{\text{POM-76}}$), along with standard deviations (error bars), after placing all 4 thicknesses into jars of coal, tar/petroleum-spiked sediment and water and shaking for 28 d ($n = 6$, except for 17 μm POM, where $n = 3$).

indeno[1,2,3-cd]pyrene, POM-80). These differences are small for most practical purposes (i.e., within 0.2 log units), although they could indicate that the thicker POMs did not come into complete equilibration with PAHs larger than chrysene. We conclude that only slight differences in C_{POM} (and K_{POM}) result when POM thicknesses range from 17 μm to 80 μm , as well as when molded POM (with ethylene oxide copolymer) is used versus lathe-cut POM (with trioxane copolymer).

Extraction method

It is hypothesized that extracting POM by cold shaking in hexane will lead to lower K_{POM} values for PAHs than from other extraction methods. Thus experiments were designed to compare 48-h rotation in cold hexane with more aggressive techniques (48-h rotation in hexane:acetone, 3-h sonication in hexane:acetone), considering various PAHs and POM thicknesses (POM-17, POM-55, and POM-76). Note that 3 h of sonication was confirmed to be quantitative, as an additional 18 h of sonication in fresh solvent resulted in <1% additional removal of all PAHs for all thicknesses, confirming similar results from a previous study by an independent comparison with Soxhlet extraction [20]. The results are presented in Figure 3 as C_{POM} ratios, with the C_{POM} determined by the hexane:acetone sonication technique in the denominator (raw data are presented in the Supplemental Data).

As is evident from Figure 3A, for all thicknesses the 48-h rotation with cold hexane:acetone gives the same recoveries as 3 h of sonication with hexane:acetone, with an average of 0.99 ± 0.07 ($p > 0.05$). However, this is clearly not the case for the 48-h hexane rotations shown in Figure 3B, which exhibit increasingly smaller C_{POM} ratios with increasing POM thickness and PAH size, and an average of 0.55 ± 0.28 ($p < 0.0001$).

Evidently, extraction by shaking in cold hexane appears to be an insufficient method for the extraction of PAHs from POM. Therefore, PAH K_{POM} values in the literature derived with this technique [29,30] are consistently low compared with K_{POM} values determined using other extraction techniques. Note that studies that used shaking in cold hexane or heptane report <3%

additional PAHs being released [29,30], even after 10 d of subsequent shaking, indicating that the method is reproducible. It is likely that more aggressive extractions with hexane (e.g., Soxhlet) may be quantitative, but this was not tested in the present study. The only other extraction technique in the literature to give deviating K_{POM} results for POM-76 was sequential acetone–dichloromethane extraction on an orbital shaker with light agitation [27] for PAHs larger than pyrene (Figure 1). Insufficient information is available to account for this method's deviation.

Regarding PCBs, extractions with cold hexane [33] as well as acetone–dichloromethane [27] result in K_{POM} values that are similar to those from other extraction techniques in the literature for POMs of 17 μm to 76 μm thickness, indicating that PCBs are easier to extract from POM than PAHs. Because POM and PAHs have some polarity, albeit weak, apolar hexane may be insufficient for PAH extraction but not PCB extraction. Solvents and methods that are able to sufficiently wet (i.e., saturate) the POM are needed to displace PAHs. However, as PCBs are more apolar and have large chlorine substituents (and thus requiring large cavity formation energy), the POM does not have to be as wetted to displace PCBs. Dioxin K_{POM} values were also determined using shaking in cold hexane in 2 different studies [35,36]. As elaborated in the Supplemental Data, Section 2b, it appears that hexane is a poor solvent for extracting dioxins, unless POM-17 is used along with an extended extraction time (96 h).

Diffusion rates of hydrophobic organic contaminants like PAHs into POM are relatively slower than other passive samplers [28,44], indicating that relatively more aggressive extraction techniques are needed to remove the hydrophobic organic contaminants from POM than LDPE and PDMS. We conclude that shaking in cold hexane (and other alkanes) is not recommended to extract PAHs from POM, and that in general polar solvents (e.g., hexane:acetone, methanol, acetonitrile) and aggressive techniques are recommended (e.g., sonication or Soxhlet). Solvents not considered in the present study should be tested for extraction efficiency.

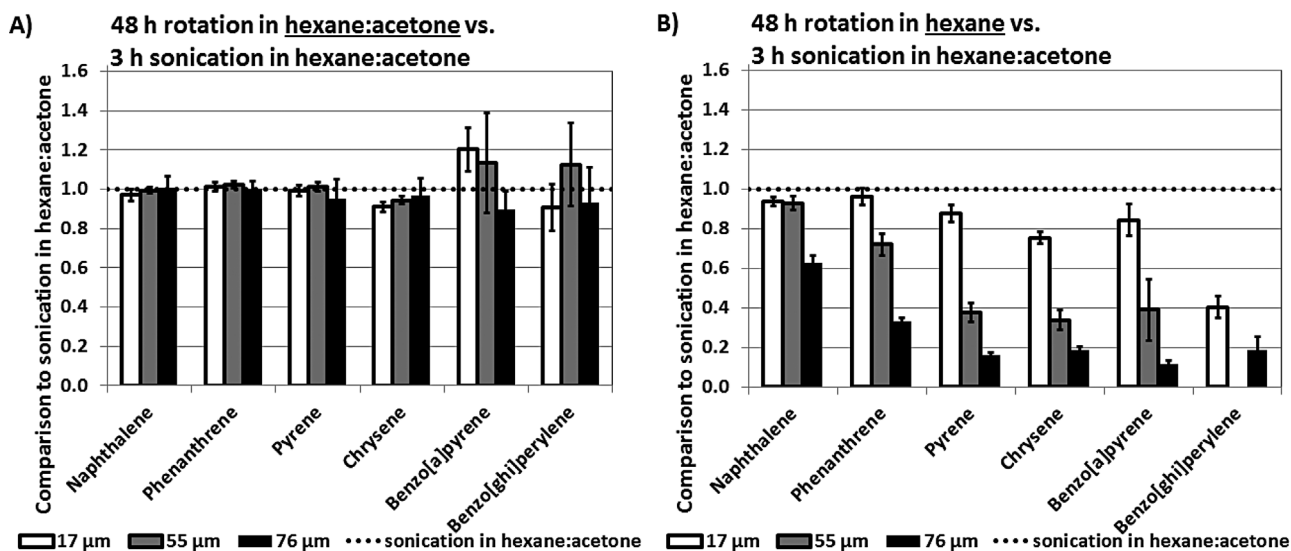


Figure 3. Ratios of polyoxymethylene (POM) concentrations, C_{POM} , for various polycyclic aromatic hydrocarbons (PAHs) and POM thicknesses (17 μm , 55 μm , and 76 μm) after preloading the POM with identical concentrations of PAHs and varying the extraction technique. (A) Extraction by 48-h rotation in cold hexane:acetone (1:1) is compared with 3 h of sonication in hexane:acetone. (B) Extraction by 48-h rotation in cold hexane is compared with 3 h of sonication in hexane:acetone (1:1).

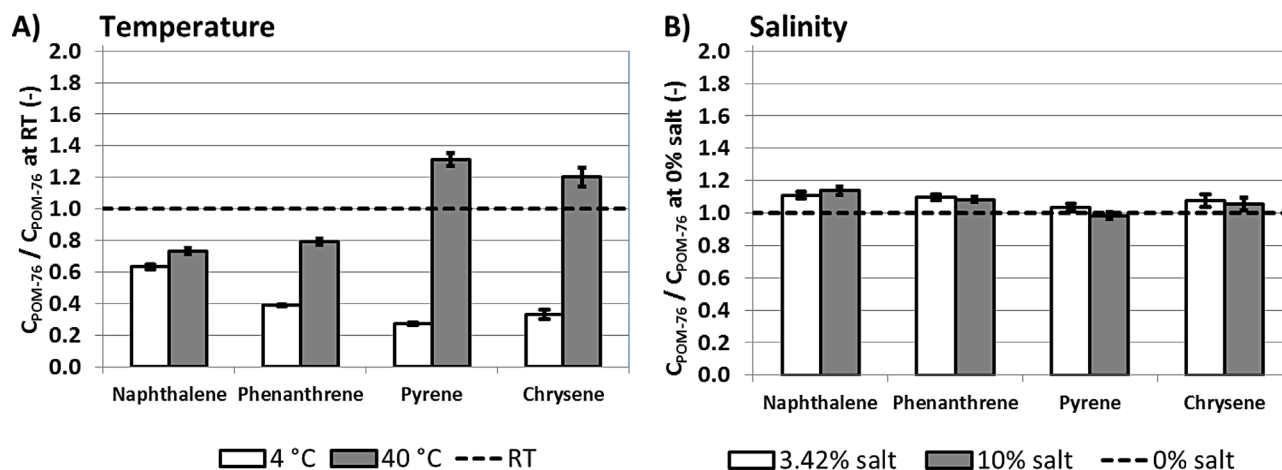


Figure 4. (A) Ratios of 76- μm thick polyoxymethylene (POM)–water partition coefficients, $C_{\text{POM-76}}$, measured at 4 °C and 40 °C compared with room temperature (RT) and 0% salt for selected polycyclic aromatic hydrocarbons (PAHs). (B) Ratios of 76- μm -thick POM concentrations at equilibrium, $C_{\text{POM-76}}$, measured at 3.42% and 10% compared with 0% salt (at room temperature).

Temperature and salinity

For the temperature study both $C_{\text{POM-76}}$ and C_{pw} were measured. Figure 4A presents measured C_{POM} at 4 °C and 40 °C relative to room temperature or PAHs that fulfilled the 5:1 signal to noise criteria. Temperature had a negligible influence on C_{pw} for quantifiable PAHs, with $C_{\text{pw}}(4\text{ °C})/C_{\text{pw}}(\text{room temperature}) = 1.09 \pm 0.15$ and $C_{\text{pw}}(40\text{ °C})/C_{\text{pw}}(\text{room temperature}) = 0.97 \pm 0.07$ (Supplemental Data, Table S3.1), which is expected because of the previously reported slight effect of temperature on sediment–water partitioning, generally within a factor 1.5 over a change of 20 °C [45,46]. Raw C_{pw} , C_{POM} , and derived K_{POM} data (Equation 1) are presented in the Supplemental Data, Section S3.

As is evident in Figure 4A, the influence of temperature on C_{POM} is substantial and depends on PAH size. At 4 °C, resulting $C_{\text{POM-76}}$ values are smaller than room temperature values by approximately a factor of 2 for the 2,3-ring PAHs, and a factor 3 for the 4-ring PAHs (C_{POM} values for larger PAHs were below detection limits). At 40 °C, $C_{\text{POM-76}}$ values ranged from a factor of 1.5 smaller than room temperature for the 2,3-ring PAHs to a factor of 1.5 larger for the 4-ring PAHs.

This observed temperature-dependent behavior is different from that generally observed for PAHs in liquid solvent–water partitioning systems. In such systems a negligible to slight increase in solvent concentrations (or K values) occurs as temperature decreases [47,48]. Two hypotheses to account for the deviating trend are observed in the present study. First, experimental kinetic artifacts originating from the 28-d shake test could be insufficient for equilibrium to be reached at 4 °C in the sediment–water–POM system and possibly at room temperature for the largest PAHs. An alternative hypothesis is that the solubility and diffusion in the POM or sediment material changes as amorphous subdomains crystallize with decreasing temperature. Isolating which of these hypotheses (or experimental artifacts) best accounts for the data in Figure 4A is not possible because of the limited amount of data. In the Supplemental Data, Section S3, we discuss these hypotheses in more detail, including implications for derived enthalpies of POM–water phase transfer, for the purposes of developing a follow-up study. Such a study may be relevant not only for passive sampling, but also for a better understanding of the fate

and transport of microplastics. It is worth noting that similar unexpected temperature effects for PAH sorption to the LDPE (another semicrystalline polymer) have occasionally been observed previously. Booij et al. [49] reported increasing K_{LDPE} with temperature for 5-ring PAHs and some PCBs from 13 °C to 30 °C. However, for most PAHs and PCBs, Booij et al. [49] reported the expected trend that partitioning into LDPE increases slightly with decreasing temperature [12].

Regardless of the mechanism, we can conclude that the influence of temperature is similar in magnitude to other passive samplers, being within a factor of 2 per 10 °C [12,23]. As all literature K_{POM} data were for room temperature, it is unlikely that minor temperature fluctuations, between a range of 15 °C to 30 °C, accounted for the deviations observed in Figure 1. The influence of temperature outside this temperature range should be investigated in more detail before experiments are conducted at such temperatures, as in field studies.

In contrast to temperature, salinity had little effect on C_{POM} values (Figure 4B and Supplemental Data, Section S4), with the PAH concentration data being significantly similar to 1.0 ± 0.1 ($p > 0.05$) regardless of salt concentration. Water solubility of PAHs is known to be marginally affected by salt concentration (e.g., in the order of 10% for naphthalene between pure water and seawater) [47,50]. Thus, any effect of differences in K_{POM} between freshwater and seawater would be similar to that observed for water solubility (<0.2 log units), and thus negligible and within the current limit of analytical precision for hydrophobic organic contaminants; accounting for these minor differences could be done by use of Setschenow (or salting-out) coefficients [50]. A similar finding was reported for the influence of salinity on LDPE–water partitioning [12].

Kinetics

Kinetic uptake data are presented in the Supplemental Data, Section S5, with an overview for 3 of the PCBs (out of 54 measured) presented in Figure 5. When the data below are interpreted, it is important to note beforehand that uptake kinetics are dependent on the sampler:sediment weight ratio, in that an increasing weight ratio will lead to an increase in uptake kinetics [51]. Thus, the observations apply mainly to the weight

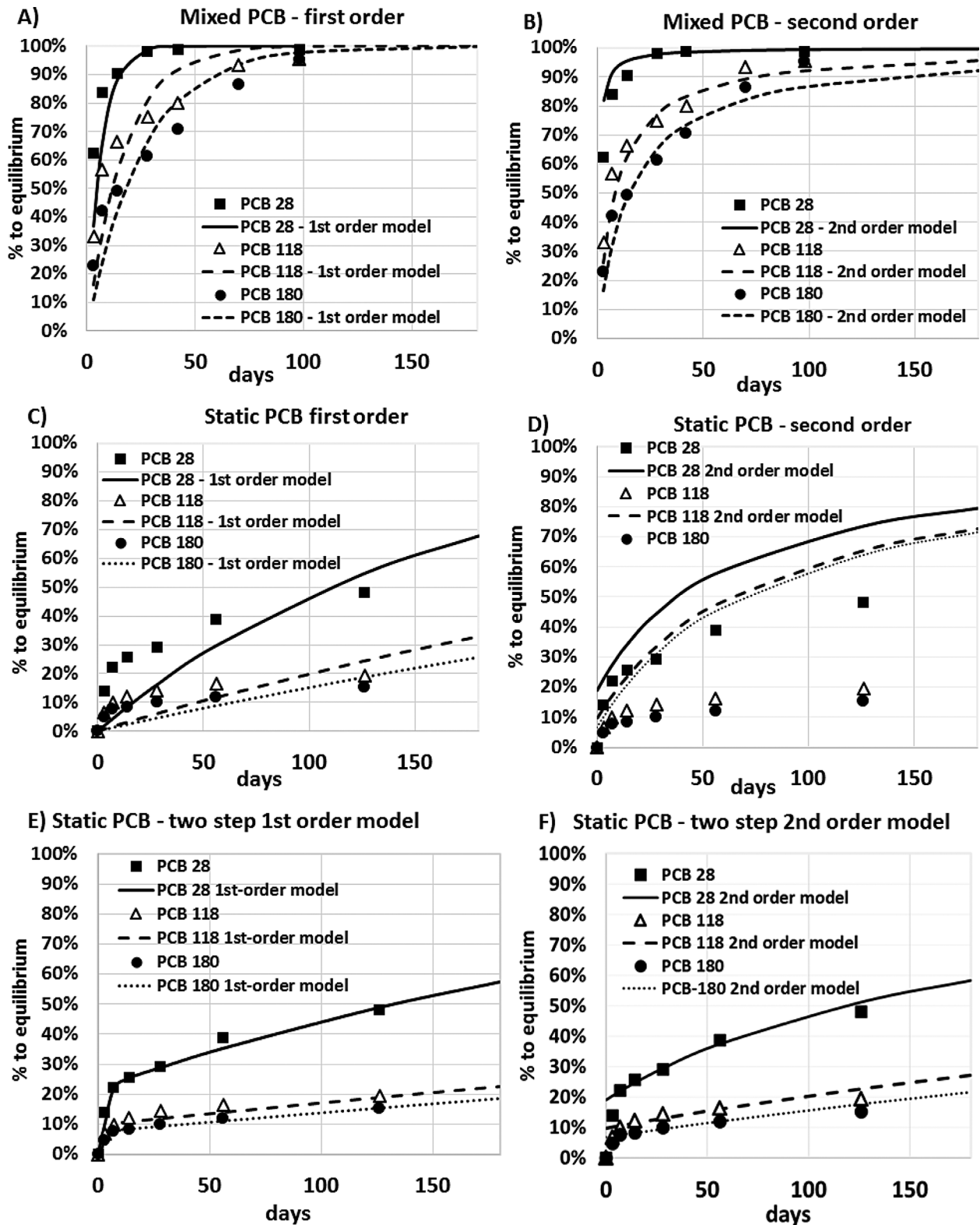


Figure 5. Degree of equilibrium of selected polychlorinated biphenyls (PCBs) from contaminated sediments into POM-76 at various time intervals under mixed (A and B) and static (C–F) conditions. (A and B) Measurements in a continuously mixed system compared with a first-order kinetic model (A; Equation 3) and second-order kinetic model (B; Equation 4). (C and D) Measurements from a static system compared with a first-order kinetic model and (C; Equation 3) and a second-order model (D; Equation 4). (E and F) Also measurements from the static system, but fit kinetic models from days 7 to 126 for the first-order model (E) and days 3 to 126 for the second-order model (F).

ratio used in the present study (300 mg POM to 10 g of 2.8% organic carbon sediment).

Mixed system

The observed uptakes of the mono-tetrachloro-PCBs, pentachloro-PCBs, hexachloro-PCBs, heptachloro-PCBs, and octachloro-PCBs into POM after 28 d of mixing are greater than 80%, 75%, 67%, 61%, and 55% of equilibrium, respectively (Supplemental Data, Table S5.1). This indicates slower uptake than observed in Hawthorne et al. [21] using a similar sampler: sediment weight ratio (although a different sediment), in which all PCBs (including the octachloros) were within 80% of equilibrium after 28 d. The reason for the slower uptake observed in the present study could be slower desorption from the less available subdomains of the sediment. Nevertheless, these differences are considered minor as they are well within 0.2 log units (66% equilibrium, which we consider an acceptable margin of error), except for the hepta- and octachloro-PCBs. However, large PCBs are generally minor contributors to total C_{pw} from Aroclor-PCB mixtures [21]. The fact that hydrophobic organic contaminants with large K_{OW} values did not come to equilibrium may contribute to the flattening of $\log K_{POM} - \log K_{OW}$ relationships for large PBDEs in POM-76 [37] and to a minor extent for octachloro-PCBs in POM-76 [21] (Figure 2). When POM-76 is used for compounds with a $K_{OW} > 7$, this may cause some discrepancies between POM-76 and thinner POM materials. For very large hydrophobic organic contaminants, longer equilibration times or thinner materials may assist in promoting equilibrium. Greater sampler: sediment weight ratios are not recommended to speed up kinetics, because of the possibility that this will cause enough depletion to disturb the equilibrium regime. More rapid mixing speeds may also help, but as the uptake is probably membrane controlled, effects are likely to be minor. Identifying the influence of mixing speeds on sorption kinetics is recommended for future work.

The uptake of 54 PCBs into POM-76 could be described with similar success using the first-order or second-order uptake model (Supplemental Data, Table S5.2). For the first-order model, R^2 varied from 0.82 to 0.98 (average 0.89, $n = 54$); for the second-order model, R^2 varied from 0.79 to 0.99 (average 0.91, $n = 54$). Diffusion coefficients into POM could not be estimated in the present study, as most equations for deriving diffusion coefficients require constant external (porewater) concentrations, which was not the case in the present study. Ahn et al. [28] reported a POM diffusion coefficient for pyrene ($1.5 \text{ E-11 cm}^2 \text{ s}^{-1}$). Rusina et al. [44] measured hydrophobic organic contaminant uptake for POM using 1-d exposure times, and found slower uptake in POM than in polyethylene or silicon samplers, but could not quantify the POM uptake. Thus, future work is needed to measure POM diffusion coefficients.

We did not include POM-500 (500 μm thick) in the present study. However, based on the PCB K_{POM} values for POM-500 (Figure 1B) that are consistently smaller than for 17 μm to 76 μm POM, and considering that extraction methods used in the literature for POM-500 were aggressive (including Soxhlet with methanol), it is likely POM-500 does not reach true equilibrium after 28 d of mixing. The reported appearance of equilibrium after 28 d [24] may be a consistently occurring pseudo-equilibrium (e.g., equilibrium occurring within the outer subdomain), within analytical reproducibility limits, which would allow for reproducible $K_{POM-500}$ values, but for values that are smaller than the K_{POM} of thinner materials (Figure 1B).

Static system

For the static system (Figure 5C and D), uptake was, as expected, much slower than for the mixed system [52,53]. After 28 d, 10% to 48% equilibrium was achieved for the different congeners, with the percentage uptake decreasing with increasing chlorination. After 126 d, the percentage uptake was from 72% to 84% for the dichloro-PCBs, from 41% to 58% for the trichloro-PCBs, from 29% to 45% for the tetrachloro-PCBs, from 19% to 30% for the pentachloro-PCBs, from 17% to 26% for the hexachloro-PCBs, and from 15% to 21% for the heptachloro- and octachloro-PCBs.

Neither the first-order rate equation (Equation 3 and Figure 5C; $R^2 = 0.55\text{--}0.89$, average 0.74) nor the second-order rate equation (Equation 4, Figure 5D; $R^2 = 0.68\text{--}0.98$, average 0.82) described uptake in the static system for the 54 PCBs as well as the mixed system. In addition to uptake into the sampler, the diffusion of PCBs from the sediment must be considered, especially increasing travel distances and travel times as the PCBs near the sampler become more depleted [52–54]. Closer inspection of the data indicated that static uptake rates slowed down rapidly 3 d to 7 d after initial exposure. Thus, the first-order model fit the data much better when only the data from day 7 to day 126 were considered ($R^2 = 0.89\text{--}0.99$, average 0.96), and the second-order model fit better with data from day 3 to day 126 ($R^2 = 0.83\text{--}0.98$, average 0.92). Considering previous research on static systems [52–54], it is likely that in the initial time step, rapidly available PCBs in the porewater are taken up by the POM, and following this, slow desorption from the sediments takes place.

A better understanding of POM uptake in the static system, similar to previous research for LDPE [52–54], would be useful for developing POM for field applications, which is outside the goal of the present study, although this issue has been investigated elsewhere. More studies on the use of performance reference compounds to measure uptake and desorption kinetics would be useful. Oen et al. [55] spiked POM-17 with PCBs, and then placed them in a tidal flat sediment; depletion of spiked PCBs generally stopped after 100 d, even though only 20% to 70% of the spike remained in the POM, giving the appearance of a pseudo-steady state. Kinetic uptake rates reported by Oen et al. [55], as well as those measured in open harbor waters [29], appear to be closer to the mixed data than to the static data, owing to mixing of water surrounding the POM and direct contact with contaminated particles.

A more thorough analysis of uptake kinetics in POM and other passive samplers in static or field settings is recommended for future research, particularly the occurrence of faster kinetics during the initial time steps, which may be important, for instance, when results from performance reference compounds are interpreted [55,56]. We anticipate that based on work available thus far on the diffusion of PAHs into diverse passive sampling materials [44], equilibrium will occur most rapidly for PDMS, then for LDPE, and then for POM.

Consistent K_{POM}

All inconsistencies regarding K_{POM} values in the literature, as summarized in Figure 1, can be accounted for by removing values obtained with POM-500 as well as values in which the POM was not extracted completely (e.g., when the extract method was cold shaking in hexane, heptanes, or alternatively, acetone:dichloromethane with light agitation). When these data are removed, $\log K_{POM}$ values for PAHs and PCBs are consistent across the literature on average by 0.15 log units for a given compound.

It should be emphasized that this does not imply that the methods leading to deviating K_{POM} are not reproducible, nor does it imply that the derived C_{pw} and bioavailability assessments made with these methods are incorrect. Provided that C_{POM} and the relevant K_{POM} values were determined following the exact same experimental protocols, following Equation 1, all experimental biases in the C_{POM} and K_{POM} measurements would cancel out. Problems arise when C_{POM} and K_{POM} are determined by inconsistently performing methods. Until the establishment of good laboratory practice protocols for POM, to ensure consistency in all steps across laboratories and to prevent inappropriate K_{POM} values from being used, we recommend the following methods for consistency.

Material and sediment mixing time

All POM-C materials (with ethylene oxide or trioxane as a copolymer) from 17 μm to 80 μm in thickness are suitable, regardless of whether they are commercially produced or lathe-cut. Practical issues are that POM-17 is more difficult to clean

when used with colloid rich-sediments, and thus artifacts from fouling cannot be ruled out (as is sometimes observed with PDMS [57]). Also, POM of 55 μm and thicker may not come into equilibrium for hydrophobic organic contaminants with $\log K_{\text{OW}} > 7$ in the typical 28-d mixed exposure.

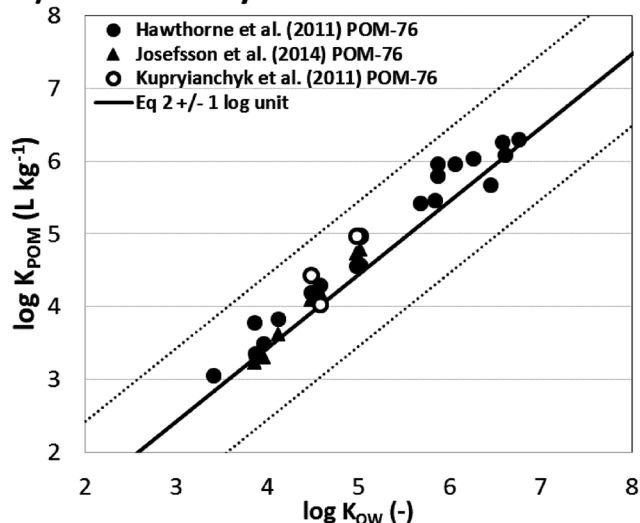
Extraction method

Solvents capable of wetting POM, such as mixed acetone:hexane, appear sufficient to recover hydrophobic organic contaminants quantitatively, whether using a 48-h rotation, 3 h of sonication, or Soxhlet. Other polar solvents (e.g., methanol) are likely also suitable provided the extraction technique is aggressive enough. New methods should be validated.

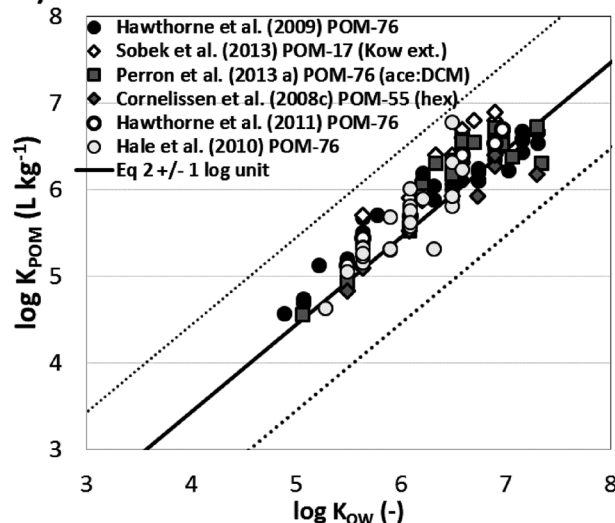
Temperature and salinity

Published K_{POM} values apply to a temperature range of 15 $^{\circ}\text{C}$ to 30 $^{\circ}\text{C}$ (i.e., regular fluctuations of laboratory temperature). Field sampling at lower and higher temperatures may

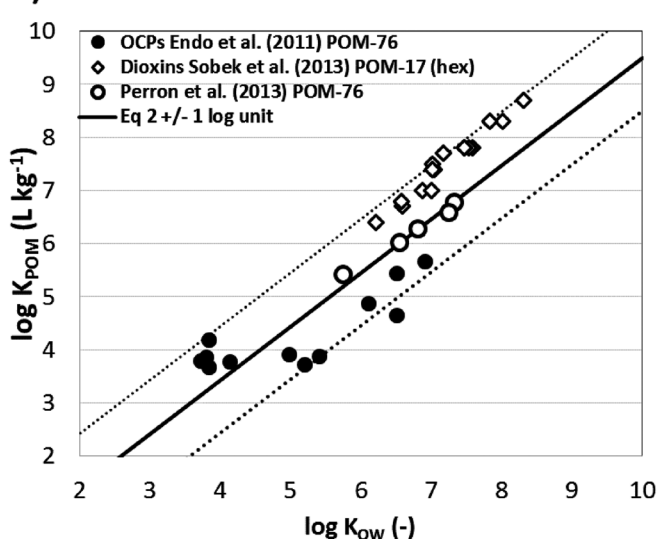
A) PAHs and alkyl PAHs



B) PCBs



C) Other HOCs



D) Polar compounds and VOCs

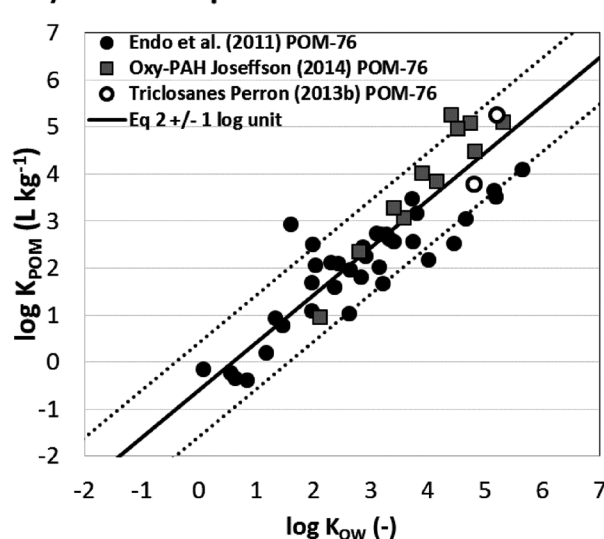


Figure 6. A compilation of literature polyoxymethylene (POM)–water partition coefficients, K_{POM} , measured with the recommended methodological procedures mentioned in the present study, along with the generic $\log K_{\text{POM}}\text{--}\log K_{\text{OW}}$ relationship (Equation 2) [38] for (A) polycyclic aromatic hydrocarbons (PAHs) and alkyl-PAHs, (B) polychlorinated biphenyls (PCBs), (C) other hydrophobic organic compounds (HOCs), and (D) polar compounds and volatile organic compounds (VOCs). Citation references include Cornelissen et al. (2008) [33], Endo et al. (2011) [38], Josefsson et al. (2014) [31], Hawthorne et al. (2009) [41], Hawthorne et al. (2011) [20], Kupryianchyk et al. (2011) [26], Perron et al. (2013) [27], Perron et al. (2013b) [37], and Sobek et al. (2013) [36].

require temperature-specific K_{POM} values currently not available. Salinity effects are negligible in most natural waters, although if desired can be accounted for with a salting-out correction [50].

Best available K_{POM}

Literature K_{POM} for hydrophobic organic contaminants, including PAHs, PCBs, dioxins, PBDEs and organochlorine pesticides, triclosanes, and diverse polar and volatile organic compounds that fulfill these recommendations are plotted in Figure 6 and presented in the Supplemental Data, Section S5. Some of the scatter that remains in this figure is because of the limitations of the $\log K_{POM}$ – $\log K_{OW}$ relationship (Equation 2), and alternative models should be considered for estimating K_{POM} values [38].

SUPPLEMENTAL DATA

Tables S1–S18.

Figure S1. (838 KB PDF).

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Disclosure—The authors' collective research institutes analyze passive samplers such as polyoxymethylene on both commercial (consulting) and research basis. There are no further conflicts of interest.

Data availability—All raw data presented are provided online in the Supplemental Data. Further data (e.g., underlying calculations) are available on request through the corresponding author (hpa@ngi.no).

REFERENCES

- Brand E, Lijzen J, Peijnenburg W, Swartjes F. 2013. Possibilities of implementation of bioavailability methods for organic contaminants in the Dutch Soil Quality Assessment Framework. *J Hazard Mater* 261:833–839.
- Harmsen J, Naidu R. 2013. Bioavailability as a tool in site management. *J Hazard Mater* 261:840–846.
- Greenberg MS, Chapman PM, Allan IJ, Anderson KA, Apitz SE, Beegan C, Bridges TS, Brown SS, Cargill JG, McCulloch MC, Menzie CA, Shine JP, Parkerton TF. 2014. Passive sampling methods for contaminated sediments: Risk assessment and management. *Integr Environ Assess Manag* 10:224–236.
- Reichenberg F, Mayer P. 2006. Two complementary sides of bioavailability: Accessibility and chemical activity of organic contaminants in sediments and soils. *Environ Toxicol Chem* 25:1239–1245.
- Cachada A, Pereira R, da Silva EF, Duarte AC. 2014. The prediction of PAHs bioavailability in soils using chemical methods: State of the art and future challenges. *Sci Total Environ* 472:463–480.
- Burkhard LP, Mount DR, Highland TL, Hockett JR, Norberg-King T, Billa N, Hawthorne SB, Miller DJ, Grabanski CB. 2013. Evaluation of PCB bioaccumulation by *Lumbriculus variegatus* in field-collected sediments. *Environ Toxicol Chem* 32:1495–1503.
- Gomez-Eyles JL, Jonker MTO, Hodson ME, Collins CD. 2012. Passive samplers provide a better prediction of PAH bioaccumulation in earthworms and plant roots than exhaustive, mild solvent, and cyclodextrin extractions. *Environ Sci Technol* 46:962–969.
- Gschwend PM, MacFarlane JK, Reible DD, Lu X, Hawthorne SB, Nakles DV, Thompson T. 2011. Comparison of polymeric samplers for accurately assessing PCBs in pore waters. *Environ Toxicol Chem* 30:1288–1296.
- Sormunen A, Tuikka A, Akkanen J, Leppänen M, Kukkonen JK. 2010. Predicting the bioavailability of sediment-associated spiked compounds by using the polyoxymethylene passive sampling and Tenax[®] extraction methods in sediments from three river basins in Europe. *Arch Environ Contam Toxicol* 59:80–90.
- Janssen EML, Oen AMP, Luoma SN, Luthy RG. 2011. Assessment of field-related influences on polychlorinated biphenyl exposures and sorbent amendment using polychaete bioassays and passive sampler measurements. *Environ Toxicol Chem* 30:173–180.
- Muijs B, Jonker MTO. 2011. Does equilibrium passive sampling reflect actual in situ bioaccumulation of PAHs and petroleum hydrocarbon mixtures in aquatic worms. *Environ Sci Technol* 46:937–944.
- Lohmann R. 2012. Critical review of low-density polyethylene's partitioning and diffusion coefficients for trace organic contaminants and implications for its use as a passive sampler. *Environ Sci Technol* 46:606–618.
- Ding Y, Landrum PF, You J, Harwood AD, Lydy MJ. 2012. Use of solid phase microextraction to estimate toxicity: Relating fiber concentrations to toxicity—part I. *Environ Toxicol Chem* 31:2159–2167.
- Li H, Sun B, Chen X, Lydy MJ, You J. 2013. Addition of contaminant bioavailability and species susceptibility to a sediment toxicity assessment: Application in an urban stream in China. *Environ Pollut* 178:135–141.
- Arp HPH, Azzolina NA, Cornelissen G, Hawthorne SB. 2011. Predicting pore water EPA-34 PAH concentrations and toxicity in pyrogenic-impacted sediments using pyrene content. *Environ Sci Technol* 45:5139–5146.
- Hawthorne SB, Azzolina NA, Neuhauser EF, Kreitinger JP. 2007. Predicting bioavailability of sediment polycyclic aromatic hydrocarbons to *Hyalella azteca* using equilibrium partitioning, supercritical fluid extraction, and pore water concentrations. *Environ Sci Technol* 41:6297–6304.
- Jonker MTO, van der Heijden SA, Kreitinger JP, Hawthorne SB. 2007. Predicting PAH bioaccumulation and toxicity in earthworms exposed to manufactured gas plant soils with solid-phase microextraction. *Environ Sci Technol* 41:7472–7478.
- McDonough KM, Azzolina NA, Hawthorne SB, Nakles DV, Neuhauser EF. 2010. An evaluation of the ability of chemical measurements to predict polycyclic aromatic hydrocarbon-contaminated sediment toxicity to *Hyalella azteca*. *Environ Toxicol Chem* 29:1545–1550.
- Arp HPH, Lundstedt S, Josefsson S, Cornelissen G, Enell A, Allard A-S, Kleja DB. 2014. Native oxy-PAHs, N-PACs, and PAHs in historically contaminated soils from Sweden, Belgium, and France: Their soil-porewater partitioning behavior, bioaccumulation in *Enchytraeus crypticus*, and bioavailability. *Environ Sci Technol* 48:11187–11195.
- Hawthorne SB, Jonker MTO, van der Heijden SA, Grabanski CB, Azzolina NA, Miller DJ. 2011. Measuring picogram per liter concentrations of freely dissolved parent and alkyl PAHs (PAH-34), using passive sampling with polyoxymethylene. *Anal Chem* 83:6754–6761.
- Hawthorne SB, Miller DJ, Grabanski CB. 2009. Measuring low picogram per liter concentrations of freely dissolved polychlorinated biphenyls in sediment pore water using passive sampling with polyoxymethylene. *Anal Chem* 81:9472–9480.
- Cornelissen G, Wiberg K, Broman D, Arp HPH, Persson Y, Sundqvist K, Jonsson P. 2008. Freely dissolved concentrations and sediment-water activity ratios of PCDD/Fs and PCBs in the open Baltic Sea. *Environ Sci Technol* 42:8733–8739.
- DiFilippo EL, Eganhouse RP. 2010. Assessment of PDMS-water partition coefficients: Implications for passive environmental sampling of hydrophobic organic compounds. *Environ Sci Technol* 44:6917–6925.
- Jonker MTO, Koelmans AA. 2001. Polyoxymethylene solid phase extraction as a partitioning method for hydrophobic organic chemicals in sediment and soot. *Environ Sci Technol* 35:3742–3748.
- Hale SE, Kwon S, Ghosh U, Werner D. 2010. Polychlorinated biphenyl sorption to activated carbon and the attenuation caused by sediment. *Glob Nest J* 12:318–326.
- Kupryianchyk D, Reichman EP, Rakowska MI, Peeters ETHM, Grotenhuis JTC, Koelmans AA. 2011. Ecotoxicological effects of activated carbon amendments on macroinvertebrates in nonpolluted and polluted sediments. *Environ Sci Technol* 45:8567–8574.
- Perron MM, Burgess RM, Suuberg EM, Cantwell MG, Pennell KG. 2013. Performance of passive samplers for monitoring estuarine water column concentrations: 1. Contaminants of concern. *Environ Toxicol Chem* 32:2182–2189.
- Ahn S, Werner D, Karapanagioti HK, Mc Glothlin DR, Zare RN, Luthy RG. 2005. Phenanthrene and pyrene sorption and intraparticle diffusion in polyoxymethylene, coke, and activated carbon. *Environ Sci Technol* 39:6516–6526.

29. Cornelissen G, Pettersen A, Broman D, Mayer P, Breedveld GD. 2008. Field testing of equilibrium passive samplers to determine freely dissolved native polycyclic aromatic hydrocarbon concentrations. *Environ Toxicol Chem* 27:499–508.
30. Cornelissen G, Gustafsson O. 2004. Sorption of phenanthrene to environmental black carbon in sediment with and without organic matter and native sorbates. *Environ Sci Technol* 38:148–155.
31. Josefsson S, Arp HPH, Berggren-Kleja D, Enell A, Lundstedt S. 2014. Determination of POM-water partition coefficients for oxy-PAHs and PAHs. *Chemosphere* 119:1268–1274.
32. McDonough KM, Fairey JL, Lowry GV. 2008. Adsorption of polychlorinated biphenyls to activated carbon: Equilibrium isotherms and a preliminary assessment of the effect of dissolved organic matter and biofilm loadings. *Water Res* 42:575–584.
33. Cornelissen G, Arp HPH, Pettersen A, Hauge A, Breedveld GD. 2008. Assessing PAH and PCB emissions from the relocation of harbour sediments using equilibrium passive samplers. *Chemosphere* 72:1581–1587.
34. Beckingham B, Ghosh U. 2013. Polyoxymethylene passive samplers to monitor changes in bioavailability and flux of PCBs after activated carbon amendment to sediment in the field. *Chemosphere* 91:1401–1407.
35. Cornelissen G, Cousins IT, Wiberg K, Tysklind M, Holmstrom H, Broman D. 2008. Black carbon-dominated PCDD/Fs sorption to soils at a former wood impregnation site. *Chemosphere* 72:1455–1461.
36. Sobek A, Arp HPH, Wiberg K, Hedman J, Cornelissen G. 2013. Aerosol-water distribution of PCDD/Fs and PCBs in the Baltic Sea region. *Environ Sci Technol* 47:781–789.
37. Perron MM, Burgess RM, Suuberg EM, Cantwell MG, Pennell KG. 2013. Performance of passive samplers for monitoring estuarine water column concentrations: 2. Emerging contaminants. *Environ Toxicol Chem* 32:2190–2196.
38. Endo S, Hale SE, Goss K-U, Arp HPH. 2011. Equilibrium partition coefficients of diverse polar and nonpolar organic compounds to polyoxymethylene (POM) passive sampling devices. *Environ Sci Technol* 45:10124–10132.
39. Ghosh U, Kane Driscoll, Burgess S, Jonker RM, Reible MTO, Gobas D, Choi F, Apitz Y, Maruya SE, Gala KA, Mortimer WR, Beegan M. 2014. Passive sampling methods for contaminated sediments: Practical guidance for selection, calibration, and implementation. *Integr Environ Assess Manag* 10:210–223.
40. Lorthioir C, Lauprêtre F, Sharavanan K, Lange RFM, Desbois P, Moreau M, Vairon J-P. 2007. Solid-state organization and morphological partitioning in polyoxymethylene-based copolymers: A solid-state NMR and WAXS study. *Macromolecules* 40:5001–5013.
41. Hawthorne SB, Grabanski CB, Miller DJ. 2009. Solid-phase-microextraction measurement of 62 polychlorinated biphenyl congeners in milliliter sediment pore water samples and determination of K-DOC values. *Anal Chem* 81:6936–6943.
42. Hawthorne SB, Grabanski CB, Miller DJ, Kreitinger JP. 2005. Solid-phase microextraction measurement of parent and alkyl polycyclic aromatic hydrocarbons in milliliter sediment pore water samples and determination of K-DOC values. *Environ Sci Technol* 39:2795–2803.
43. Ho YS, McKay G. 1999. Pseudo-second order model for sorption processes. *Process Biochem* 34:451–465.
44. Rusina TP, Smedes F, Klanova J, Booij K, Holoubek I. 2007. Polymer selection for passive sampling: A comparison of critical properties. *Chemosphere* 68:1344–1351.
45. Haftka JH, Govers HJ, Parsons J. 2010. Influence of temperature and origin of dissolved organic matter on the partitioning behavior of polycyclic aromatic hydrocarbons. *Environ Sci Pollut Res* 17:1070–1079.
46. Tremblay L, Kohl SD, Rice JA, Gagné J-P. 2005. Effects of temperature, salinity, and dissolved humic substances on the sorption of polycyclic aromatic hydrocarbons to estuarine particles. *Mar Chem* 96:21–34.
47. Schwarzenbach RP, Gschwend PM, Imboden DM. 2003. *Environmental Organic Chemistry*, 2nd ed. John Wiley & Sons, Hoboken, NJ, USA.
48. Lei YD, Wania F, Shiu WY, Boocock DGB. 2000. HPLC-based method for estimating the temperature dependence of n-octanol – water partition coefficients. *J Chem Eng Data* 45:738–742.
49. Booij K, Hofmans HE, Fischer CV, Van Weerlee EM. 2003. Temperature-dependent uptake rates of nonpolar organic compounds by semipermeable membrane devices and low-density polyethylene membranes. *Environ Sci Technol* 37:361–366.
50. Endo S, Pfennigsdorff A, Goss K-U. 2012. Salting-out effect in aqueous NaCl solutions: Trends with size and polarity of solute molecules. *Environ Sci Technol* 46:1496–1503.
51. Smedes F, van Vliet LA, Booij K. 2012. Multi-ratio equilibrium passive sampling method to estimate accessible and pore water concentrations of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in sediment. *Environ Sci Technol* 47:510–517.
52. Booij K, Hoedemaker JR, Bakker JF. 2003. Dissolved PCBs, PAHs, and HCB in pore waters and overlying waters of contaminated harbor sediments. *Environ Sci Technol* 37:4213–4220.
53. Fernandez LA, Harvey CF, Gschwend PM. 2009. Using performance reference compounds in polyethylene passive samplers to deduce sediment porewater concentrations for numerous target chemicals. *Environ Sci Technol* 43:8888–8894.
54. Fernandez LA, MacFarlane JK, Tcaciuc AP, Gschwend PM. 2009. Measurement of freely dissolved PAH concentrations in sediment beds using passive sampling with low-density polyethylene strips. *Environ Sci Technol* 43:1430–1436.
55. Oen AMP, Janssen EML, Cornelissen G, Breedveld GD, Eek E, Luthy RG. 2011. In situ measurement of PCB pore water concentration profiles in activated carbon-amended sediment using passive samplers. *Environ Sci Technol* 45:4053–4059.
56. Fernandez LA, Lao W, Maruya KA, Burgess RM. 2014. Calculating the diffusive flux of persistent organic pollutants between sediments and the water column on the Palos Verdes Shelf superfund site using polymeric passive samplers. *Environ Sci Technol* 48:3925–3934.
57. Heringa MB, Hermens JLM. 2003. Measurement of free concentrations using negligible depletion-solid phase microextraction (nd-SPME). *TrAC-Trend Anal Chem* 22:575–587.