EPA Public Access

Author manuscript

Environ Toxicol Chem. Author manuscript; available in PMC 2019 August 01.

About author manuscripts

Submit a manuscript

Published in final edited form as:

Environ Toxicol Chem. 2018 August ; 37(8): 2089–2097. doi:10.1002/etc.4167.

Using performance reference compounds to compare mass transfer calibration methodologies in passive samplers deployed in the water column

Abigail S Joyce^{*,a} and Robert M Burgess^b

^aNational Research Council Post-Doctoral Research Associate, U.S. Environmental Protection Agency, ORD, NHEERL, AED, 27 Tarzwell Dr., Narragansett, RI, USA

^bU.S. Environmental Protection Agency, ORD, NHEERL, AED, 27 Tarzwell Dr., Narragansett, RI, USA

Abstract

Performance reference compounds (PRCs) are often added to passive samplers prior to field deployments to provide information about mass transfer kinetics between the sampled environment and the passive sampler. Their popularity has resulted in different methods of varying complexity to estimate mass transfer and better estimate freely dissolved concentrations (C_{free}) of targeted compounds. Three methods for describing a mass transfer model are commonly used: a first order (FO) kinetic method, a non-linear least squares (NLS) fitting of sampling rate, and a diffusion (DIF) method. PRC-loaded, low-density polyethylene (PE) strips of four different thicknesses were used as passive samplers to create an array of PRC results to assess the comparability and reproducibility of each of the methods. Samplers were deployed in the water column at three stations in New Bedford Harbor (MA, USA). Collected data allowed C_{free} comparisons to be performed in two ways: (1) comparing C_{free} derived from one thickness using different methods and (2) comparing C_{free} derived by the same method using different thicknesses of PE. Overall, the NLS and DIF methods demonstrated the most precise results for all of the PCBs measured and generated C_{free} values that were often statistically indistinguishable. Relative standard deviations (RSDs) for total PCB measurements using the same thickness and varying model types range from 0.04–12% and increased with sampler thickness and RSDs for estimates using the same method and varying thickness ranged from 8 – 18%. Environmental scientists and managers are encouraged to use these methods when estimating C_{free} from passive sampling and PRC data.

Graphical Abstract

^{*}To whom correspondence may be addressed: joyce.abbey@epa.gov.

DATA AVAILABILITY STATEMENT

Readers can access much of the data in the Supporting Information. Additional data and supporting calculation tools are available upon request.

This is NHEERL Contribution ORD-021785.

Mention of trade names or commercial products does not constitute endorsement or recommendation for use. The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

Mean freely dissolved water concentration (C_{free}) per PCB congener as measured without PRC correction and by each examined PRC modeling approach for a 76 ¼m thick LDPE passive sampler deployed in the water column of New Bedford Harbor.

Keywords

passive sampling; polychlorinated biphenyls (PCBs); persistent organic pollutants (POPs); performance reference compounds (PRCs)

INTRODUCTION

Passive sampling in environmental applications has evolved from a scientific concept to a tool being promoted for use in regulatory decision making (Greenberg et al., 2014, Booij et al., 2016, Mayer et al., 2003). During this evolution, several review articles have summarized the scientific foundations and approaches for passive sampling including its ability to estimate a chemical's freely dissolved concentration (C_{free}) (Lohmann, 2012, Lydy et al., 2014, Mayer et al., 2014, Ghosh et al., 2014). The importance of C_{free} as a surrogate for a chemical's actual bioavailable concentrations was described by (Di Toro et al., 1991) but measuring or estimating C_{free} in the water column or sediment interstitial waters can be challenging because of experimental artifacts (e.g., presence of colloids and dissolved organic carbon) and modeling uncertainties. Several studies have demonstrated the advantages of using passive sampling compared to traditional sampling and modelling approaches for measuring C_{free} (Gschwend et al., 2011, Burgess et al., 2015, Maruya et al., 2009). Using passive sampling to estimate C_{free} , environmental managers can make better informed decisions with greater certainty about the magnitude of risk associated with target contaminants at contaminated sites.

Ideally, when using passive sampling to measure C_{free} in the water column or sediment interstitial waters a thermodynamic equilibrium between the sampling environment and passive sampler is attained for all targeted contaminants. This equilibrium allows for the use of Equation 1 for calculating C_{free} (ng/L):

$$C_{\text{free}} = \frac{C_{\text{PS}}^{\infty}}{K_{\text{PW}}} \quad (1)$$

where, C_{PS}^{∞} (ng/kg_{polymer}) is the concentration of a target contaminant in the passive sampler at equilibrium and K_{PW} (L_{water}/kg_{polymer}) is its polymer-water partition coefficient. In some instances, the application of the passive samplers requires 'real world' scenarios to be assessed and exposures must be performed in the field where environmental conditions may control the rate at which equilibrium is attained (Fernandez et al., 2014). In this respect, highly hydrophobic organic contaminants (HOCs) of interest may require months or even years to reach equilibrium. Assuming equilibrium has been attained and using Equation 1 to calculate C_{free} may result in under-estimating C_{free} and ultimately under-estimating exposure and risk for many hydrophobic compounds that have not reached equilibrium. In these cases, the use of performance reference compounds (PRCs) allows C_{free} to be estimated from the measured passive sampler concentration at a given time, C_{PS}^t (ng/kg_{polymer}), even when a compound has not attained equilibrium (Huckins et al., 2002). PRCs are dosed into a passive sampler prior to deployment and their release from the sampler can then be used to determine mass transfer kinetics to more accurately estimate C_{free} . Several methods, of varying complexity, describing this mass transfer have been developed to generate practical information about equilibrium conditions using PRC data.

The availability of multiple methods for estimating C_{free} using PRC data allows environmental scientists and managers options for assessing risk. The objective of this investigation was to generate a data set of target contaminant concentrations, estimate C_{free} using three different methods to model mass transfer, and compare the results. Low-density polyethylene (PE) in four thicknesses was used as a passive sampler and the target contaminants were 27 polychlorinated biphenyl (PCB) congeners. The deployment was performed in the water column of three stations at the New Bedford Harbor Superfund site in New Bedford, Massachusetts (USA).

From an environmental management perspective, the goal of this research is to provide guidance to environmental managers and scientists at contaminated sediment sites for selecting which method(s) to use when analyzing PRC data from passive sampling deployments.

Theory

The dominating environmental factor controlling sampling kinetics in the water column is the water boundary layer (WBL). The WBL is the region separating the passive sampler from the bulk water where molecular diffusion dictates mass transfer and resistance to mass transfer. HOCs are often rate limited by diffusion through the WBL when using PE as a sampling medium (Tomaszewski and Luthy, 2008, Belles et al., 2016, Vrana and Schüürmann, 2002). When kinetics are WBL-controlled there are several methods to estimate C_{free} using PRCs pre-loaded into a passive sampler. The simplest method for estimating C_{free} is using the release rate of PRCs based on first order kinetics which assumes that uptake into the passive sampler follows a first order (FO) kinetic regime as described by:

$$C_{free} = \frac{C_{PS}^t}{K_{PW} \cdot (1 - e^{-k_e t})} \quad (2)$$

where, t (days) is the deployment time and k_e (days⁻¹) is the overall exchange rate constant. The value for is determined from the fraction of PRC retained by the sampler, f_{ret} , over the course of the deployment:

$$k_e = - \left(\frac{\ln \left(\frac{C_{PRC}^t}{C_{PRC}^0} \right)}{t} \right) \quad (3)$$

where, C_{PRC}^0 and C_{PRC}^t (ng/kg_{polymer}) are the PRC concentrations in the PE prior to deployment and after deployment, respectively, this ratio defines f_{ret} . Often there is a specific PRC for each targeted HOC in the study (Joyce et al., 2015), though has been interpolated for target HOCs by correlation with K_{OW} , molecular volume, or molecular weight when a dedicated PRC was not used (Friedman et al., 2012, Perron et al., 2013a, Perron et al., 2013b). Because of analytical issues associated with low f_{ret} (i.e., quantification limit issues for low K_{OW} PRCs) and high f_{ret} (i.e., difficulty differentiating C_{PRC}^0 and C_{PRC}^t of high K_{OW} PRCs), the literature suggests limiting the use of the f_{ret} to $0.2 < f_{ret} < 0.8$, sometimes referred to as the 80/20 method (Smedes, 2007, Booij and Smedes, 2010).

Taking the mass transfer model one step further and calculating a sampling rate, R_S (L/day), introduces physiochemical characteristics of the PRCs and target compounds such that predictive relationships between all PRC data can be used to estimate compound specific sampling rates for targeted compounds. (Booij and Smedes, 2010) reported a method for better estimating R_S using a non-linear least squares (NLS) fit:

$$f_{ret} = e^{-R_S \cdot t / m_p \cdot K_{PW}} \quad (4)$$

where m_p is the mass (kg) of the passive sampler and R_S is the product of m_p , K_{PW} , and k_e . It allows for using all acquired PRC data – even data for which the fraction of PRC retained by the passive sampler is less than 0.20 or greater than 0.8. This formula gives a site-specific R_S , guidance in calculating compound specific can be found in the literature (Booij and Smedes, 2010, Rusina et al., 2010). Once a compound specific R_S has been determined, C_{free} can be estimated from:

$$C_{free} = C_{PS}^t \cdot m_p / R_s \cdot t \quad (5)$$

A third method for modelling mass transfer has also been developed for both the sediments and the water column and accounts for compound-specific diffusivities within both the sampler and the WBL or interstitial water (Fernandez et al., 2009, Fernandez et al., 2012, Apell and Gschwend, 2014, Thompson et al., 2015). The diffusion method (DIF) is useful when uptake is controlled or partially controlled by the polymer, or if it is unclear how a compound's diffusion through the polymer will affect transfer kinetics. The model, derivation, and code used in this study were originally reported by (Thompson et al., 2015). It is based on Fickian diffusion in a symmetrical system with PE thickness (cm) of $2l$ and WBL of thickness b where $x = 0$ is the center of the PE film. Diffusion is assumed to be unidirectional through half the sheet thickness. The resulting governing equations for the system become:

$$\frac{\partial C_{PS}}{\partial t} = D_{PE} \frac{\partial^2 C_{PS}}{\partial x^2} \text{ for } 0 < x < l \quad (6)$$

$$\frac{\partial C_{WBL}}{\partial t} = D_W \frac{\partial^2 C_{WBL}}{\partial x^2} \text{ for } l < x < l + b \quad (7)$$

where, D_{PE} and D_W are the diffusivities (cm^2/s) of each HOC through the PE and water, respectively, x is the distance from the center of the PE, l is half the thickness of the PE (cm), and b is the thickness of the WBL (cm). Solving this system of partial differential equations allows for a calculation of the WBL thickness using PRC results. Assuming that compounds with varying physio-chemical properties experience the same WBL, data from several PRCs can be used to estimate an average WBL thickness though similar f_{ret} restrictions to the FO method must be implemented into the input. Once WBL thickness is known, fractional equilibria (f_{eq}), can be estimated for target HOCs. For clarification, the f_{eq} refers to the fraction of equilibrium that had been attained by a target contaminant over the deployment period. It is related to the f_{ret} in that the sum of f_{eq} and f_{ret} should be one for a target contaminant and its corresponding PRC. Once f_{eq} are calculated for the target compounds, C_{free} can then be calculated as:

$$C_{free} = \left(\frac{C_{PS}^t}{f_{eq}} \right) / K_{PW} \quad (8)$$

The error associated with C_{free} can be attributed to different factors depending on the method used to estimate equilibrium conditions. In general, the error is mainly dependent on

K_{PW} . Log K_{PW} values usually have an error of ± 0.2 which can affect the calculated C_{free} by a factor of two. This work used an estimated set of log K_{PW} based on a log K_{OW} values (Ghosh et al., 2014, Hawker and Connell, 1988), as such K_{PW} would contribute to the systematic error of C_{free} estimates. For compounds near equilibrium, K_{PW} will be the dominant contributor to error and as the C_{PRC}^t/C_{PRC}^0 ratio gets smaller, analytical errors in these measurements will have a larger contribution to total error. When compounds are not at equilibrium, the K_{PW} and analytical error can amplify the error in C_{free} . For instance, error is introduced to the FO method because this method only uses one PRC for each targeted compound, whereas the NLS and DIF methods use data from all PRCs which should average-out analytical errors introduced by calculating $\frac{C_{PRC}^t}{C_{PRC}^0}$. In this way, errors

introduced by K_{PW} , C_{PRC}^t , and C_{PRC}^0 contribute to total error differently depending on how close to equilibrium a compound is. As such, errors contributed by K_{PW} in C_{free} for Equations 1, 2, and 8 would only contribute a bias between the C_{free} values from the different thicknesses tested. However, because K_{PW} is used to determine R_S , errors in K_{PW} will contribute to the final C_{free} generated by the NLS method, similar errors associated with D_W and D_{PS} will contribute to C_{free} error using the DIF method. These factors will likely contribute more toward bias and not variability. Much of the variability from the equilibrium corrections will be introduced through analytical error associated with C_{PRC}^t and C_{PRC}^0 .

MATERIALS AND METHODS

Materials

Four different thicknesses of low-density PE sheeting (Ace Hardware, Oak Brook, IL, USA; 12.5 μ m, 25.4 μ m, 50.8 μ m, and 76.2 μ m thick) were cut into strips (8cm x 50cm, ~ 0.5 to 3 g) and pre-cleaned in dichloromethane (DCM; 1 day), methanol (MeOH; 2 days), and stored in ultrapure water (18.3 M Ω) prior to loading PRCs. Passive samplers were separated according to thickness. PRCs were loaded into cleaned PE in 2 L of a 4:1 MeOH:water spiking solution containing ^{13}C -labeled PCB congeners: 8, 28, 52, 101, 138, and 180 (99%, Cambridge Isotope Laboratories, Inc., Andover, MA, USA) for 36 days while gently shaking on an orbital shaker. The nominal concentration of each PRC in the spiking solution is given in Table S1. PRC-loaded PE strips were then dried and woven on stainless steel wire (Malin Co., Brookpark, OH, USA; 20 gauge) which was then shaped into a ring. Prior to weaving on the wire, a piece of PE (~5 cm) was cut from each sampler to determine C_{PE}^0 . Samplers were stored at $-20^\circ C$ or on ice in the dark until deployment.

The target compounds of interest included 27 chlorinated biphenyls (CBs): 8, 18, 28, 44, 52, 66, 70, 77, 81, 99, 101, 105, 110, 114, 118, 123, 126, 138, 153, 156, 157, 167, 169, 170, 180, 189, and 206. Standards for non-labeled target PCBs (Ultra Scientific, North Kingstown, RI, USA) were purchased individually, combined, and diluted in hexane to make a 3000 ng/mL stock standard solution. Internal standard, CB198, was also purchased from Ultra Scientific and recovery standards, ^{13}C -PCB: 9, 118, and 188, were acquired from Cambridge Isotope Laboratories, Inc. ACS/Pesticide grade DCM and MeOH, were purchased from

Honeywell (Muskegon, MI, USA) and used without further purification. Ultra-resi analysed grade hexane (95% n-hexane) was purchased from J.T. Baker (Center Valley, PA, USA). Concentrated sulfuric acid (Fisher Scientific, Hampton, NH, USA) was used to clean-up extracts when necessary.

Field studies

In September of 2014, all thicknesses of PE were deployed for 30 days, in triplicate, at two stations in New Bedford Harbor (NBH 2 and NBH4) and one station in Buzzards Bay (NBH5) (Figure S1). One non-PRC-loaded PE of each thickness was exposed to air during deployment and retrieval operations at each station to serve as a station-specific travel/field blank. One PRC-loaded PE blank of each thickness was also exposed but not deployed at all three stations and served as a travel/field blank. Upon retrieval, PE samplers were placed in aluminum foil and stored on ice during transit. Once at the laboratory, samplers were wiped clean of visible residue/biological growth using a lab tissue and rinsed with de-ionized water. Samplers were then dried and individually stored in pre-cleaned glass vials at -20°C in the dark until extraction.

Sample processing and analysis

PE samplers and blanks were spiked with recovery standards: ^{13}C -labeled PCB 9, 118, and 188 ($12.5\ \frac{1}{4}\text{L}$; $20\ \frac{1}{4}\text{g/mL}$) and extracted three times by gently mixing on an orbital shaker in DCM ($\sim 90\text{mL}$, overnight). The combined DCM extract was concentrated using a TurboVap (Zymark, Hopkinton, MA, USA; 5–10 psi, 35°C), exchanged to hexane, and further concentrated to $0.5\ \text{mL}$. The TurboVap vial was then rinsed with an additional $0.5\ \text{mL}$ of hexane and combined with the concentrated extract for $1\ \text{mL}$ total volume. Internal standard, CB198 ($12.5\ \frac{1}{4}\text{L}$; $20\ \frac{1}{4}\text{g/mL}$), was then added to the extract. Concentrated extracts from Stations NBH4 and NBH5 were dark green and therefore were acid washed with concentrated H_2SO_4 ($200\ \frac{1}{4}\text{L}$) and allowed to separate overnight. The organic solvent layer was then pipetted off and stored. All sampler extracts were stored in amber glass, crimp cap vials at -20°C in the dark until analysis by GC-MS (details in Supporting Information).

Data analysis and quality control

Chromatograms were integrated using MSD ChemStation (E.02.00.493; Santa Clara, CA, USA) and quantified by the internal standard method using a seven-point calibration curve. Analysis of pre-cleaned, virgin PE showed that no target contaminants were detectable prior to deployment. Six of the 5-cm, pre-cut pieces per thickness were extracted to determine C_{PRC}^0 for all PRCs, C_{PRC}^0 values for each PRC agreed within 15%. One $76\ \frac{1}{4}\text{m}$ thick PE replicate was lost during analysis, thus only duplicates were available. Throughout this paper, data are presented as the mean $\pm$ one standard deviation, unless otherwise stated. Recoveries of ^{13}C -PCB 9, 118, and 188 were 51 ± 9 , 83 ± 7 , and 76 ± 6 , respectively, for all PE at all three stations. All target contaminants were corrected for surrogate recovery according to Table S2. C_{free} was calculated using a compound specific K_{PW} (Table S2) and corrected for nonequilibrium conditions using the correction methods described in the **Theory** section. To compare PCB congener and total PCB C_{free} values generated by different thicknesses and method, analysis of variance (ANOVA) was performed followed by a protected Fisher's test

to identify any statistically-significant differences between method estimates of C_{free} . An $\alpha = 0.05$ was used to indicate significant differences between mean C_{free} values. Analyses were performed using SAS 9.4 (Cary, NC, USA).

RESULTS AND DISCUSSION

Comparisons of the C_{free} generated by the different methods were performed in two ways: comparing C_{free} from different thicknesses of PE using the same correction method and comparing C_{free} from the same thickness using a different correction method. Similar concentration trends were observed at each sampling station. Comparisons from NBH2 will be shown in the main text and corresponding tables and figures for NBH4 and NBH5 are provided in the Supporting Information. All C_{free} values are given in Supporting Information (Tables S3 - S5). C_{free} results using equation 1 are reported, and compared, labeled as “no model” to illustrate the differences when equilibrium is assumed to be achieved.

PRC results

As expected, f_{ret} increased with increasing PRC log K_{OW} as well as with increasing PE thickness (Figure 1). PRC fraction retained was lowest at NBH5, followed by NBH2 and highest at NBH4 (Table S6). In most cases, small variations were observed between a station's triplicates. However, in some instances, substantial variability was observed, so calculations of k_e , R_s , and WBL thickness (Table S7) were performed for each replicate as opposed to taking a mean for each station. The retention of the PRCs, ^{13}C -PCB 8 and ^{13}C -PCB 28, on the 25.4 μm thick PE was higher than expected at all stations and on all replicates. The ^{13}C -PCB 8 results had a small influence on the resulting C_{free} calculations which can be observed in the elevated C_{free} concentration of CB8 using the FO method. The ^{13}C -PCB 28 results had more variation as evidenced in both the FO and DIF model. The origins of this behavior are unclear but this behavior was consistent for all deployed PE. There was no indication of contamination in either the laboratory blanks or non-PRC loaded field blanks, and full scan data was not available due to their low concentrations. There was no evidence that these results were incorrect and they were used when applicable. All estimated f_{eq} values are given in Supporting Information Table S8.

Intra-method comparison of congener C_{free}

PRCs suggested that CB8 had reached equilibrium for all PE deployed. Calculating C_{free} using Equation 1 for all PE yielded approximately 20% relative standard deviation (RSD; Figure 2). This RSD was also observed at the NBH4 station for CB8 (Figure S4) suggesting that a 20% RSD would be representative of the precision for passive sampling in this investigation and served as a standard for good agreement for congeners where an equilibrium correction was appropriate. (Apell and Gschwend, 2016) came to a similar conclusion finding an estimated PE sampler RSD precision of 27%.

The RSDs increased (Figure 2) as the congeners became more hydrophobic suggesting that equilibrium had not been attained on all samplers during deployment. Referencing a congener from each chlorination level, specifically, CB28, CB52, CB101, CB138, CB180, and CB206, the corresponding RSDs were: 20%, 15%, 34%, 46%, 50%, and 53%,

respectively, suggesting that CB28 and CB52 had reached equilibrium based on the previously defined 20% RSD standard. Both the NLS and DIF methods suggested that CB8 and CB28 had a f_{eq} of 0.9 or greater for most of the PE deployed, CB52 predicted f_{eq} 0.9 in half of the PE deployed.

Estimating C_{free} using the FO method required set stipulations due to instances where the f_{ret} was greater than one resulting in a negative k_e . In these cases, a k_e correlating to a f_{ret} of 0.99 was used. The 80/20 rule was not used because these correction restrictions were not applied for the other methods. A minimum f_{eq} of 0.01 equivalent was used while no upper bound for f_{eq} was implemented. Applying the FO method decreased C_{free} RSD values for several of the congeners measured through the pentachlorinated homolog (Figures 2, S4 and S5). Of these, less than a quarter of the congeners had RSDs greater than 20% at NBH2. Hexachlorinated congeners had RSD values greater than 100%. These large RSDs were due to the 76 μ m measurements. PRC, ^{13}C -PCB138, had a measured f_{ret} greater than one, so a f_{eq} equivalent of 0.01 was used (NLS and DIF methods predicted f_{eq} s 0.06), resulting in an estimated C_{free} that was about five times larger than the other thicknesses measured. This example illustrates the risk of over-correction using the FO method when C_{PE}^t and C_{PE}^0 do not show a significant difference.

The NLS method allowed for an individual f_{eq} value to be estimated for each target PCB. C_{free} values calculated using this model resulted in a decrease in measured RSDs throughout the suite of PCBs investigated (Figures 2, S4, S5), relative to other models or no correction at all. Only congener CB126 had a RSD value above 20%. Calculated RSD values ranged from 10 to 23% with a mean of 15% for the suite of PCBs. The 76.2 μ m PE generally demonstrated the highest C_{free} estimates followed by the 25.4 μ m sampler. The C_{free} s for the 12.7 μ m and 50.8 μ m samplers often agreed within one standard deviation of each other (Tables S3a,b).

WBL measurements for the passive samplers ranged from 66 to 268 μ m (Table S7) and were in agreement with those reported or estimated (Fernandez et al., 2012, Lohmann, 2012, Apell et al., 2016). Only f_{ret} values between 0.15 and 0.85 were used in the calculation of the WBL for each sampler. Using fraction retained values where an equilibrium may have been achieved (e.g., $f_{ret} < 0.15$) resulted in very large WBL thickness estimates. Anomalous WBL values were also observed (both large and very small ranging from 0.6 μ m to 660 μ m) when f_{ret} values were larger than 0.85. Due to analytical uncertainties associated with these endmember f_{ret} s, they were not used, which reduced the estimated WBL RSD by about 30% and, at least, two values were used for each WBL estimation. The triplicate f_{eq} variability is most notable with the 25.4 μ m polymer thicknesses measurements. Closer inspection of this dataset from NBH2 revealed the f_{ret} for ^{13}C PCB 28 was acceptable for only two of the replicates. The average WBL for the two replicates that used ^{13}C -PCB 28 data are nearly identical and almost double that of the ^{13}C -PCB 28 replicate that was not included ($f_{ret} = 0.11$). However, the C_{free} results from the replicate that did not use ^{13}C PCB 28 data were closer to the results generated from the other thicknesses. This range in WBL values likely contributed to f_{eq} variability and ultimately increased C_{free} RSDs for this method.

Variations observed in the DIF-estimated f_{eq} resulted in larger C_{free} RSDs for the four thicknesses tested (Figures 2, S4, S5) than the NLS method. An RSD of greater than 20% was observed for many congeners with a $\log K_{OW} > 6.2$, though the RSDs did decrease compared to the non-corrected RSD values. Only two congeners, CB126 (35%) and CB189 (30%) had RSDs above 30%, whereas the majority of C_{free} measurements demonstrated relatively favorable agreement it was not as good as measurements where equilibrium had been attained and over 70% of the PCBs measured had a RSD of 27% or less. Similar to the NLS method, the 25.4 and 76.2 μ m PE thicknesses estimated the highest C_{free} concentrations and in the majority of cases were not significantly different. (Tables S3a and b).

When statistically comparing the C_{free} by thickness, congeners CB8, CB18 and CB28 demonstrated no significant differences between thicknesses for any of the equilibrium correction methods (Table S9). The occurrence of significantly different C_{free} estimates between the thicknesses increased starting with the tetrachlorinated PCBs and continued for higher chlorinated congeners. C_{free} values determined for each thickness using the DIF method were not statistically different 70% of the time. These results may be due, in part, to the relatively large standard deviations between replicates for each thickness resulting in the different thicknesses being difficult to distinguish statistically. Results of similar statistical analyses for NBH4 and NBH5 are provided in Tables S11 and S13. Overall, this data suggests in the cases of the DIF and NLS method using multiple PRCs to deduce WBL or R_S , resulted in similar C_{free} results between data sets and reduced variation in the results.

Inter-method comparison of congener C_{free}

Estimates of C_{free} were also compared by the three equilibrium correction methods used to generate them. Methods were compared by plotting the C_{free} ratios of the different combinations of correction methods with the target compound's K_{PW} (Figure 3). Plotting the data this way illustrates how well the different equilibrium methods agree for compounds as correction factors increased ($1/f_{eq}$ increased with $\log K_{PW}$). C_{free} values below the quantitation limits were not included, and the data was separated by sampler thickness. Naturally, compounds that reached or nearly reached equilibrium (e.g., CB8, CB18, CB28, CB 44, and CB52) during the deployment showed near perfect agreement for all equilibrium models as little to no corrections were made.

The DIF and NLS methods showed the greatest and most consistent agreement of the three approaches tested (Figure 3a). In fact, the C_{free} values calculated agree within a factor of two for all estimated C_{free} . On average, the C_{free} as estimated by the DIF method were 1.1 times larger than those estimated by NLS. The largest differences in C_{free} were those estimated on the 25.4 μ m thickness where, on average, the C_{free} ratio between the two methods was 1.25. C_{free} ratios ranged from 0.93 to 1.19 for the other thicknesses. This 25.4 μ m thickness discrepancy is likely due to the unexpectedly high and variable f_{ret} for PRC ^{13}C -PCB28 in this sampler, which resulted in variable and relatively high C_{free} estimates of the targeted congeners, as discussed in the *Intra-Method Comparison of Congener C_{free}* section.

The consistent agreement between these two methods resulted in similar comparisons with the FO method (Figures 3b and c). Overall, the FO-predicted C_{free} values were, on average,

higher than the other two methods. In these comparisons variation increased as the K_{PW} increased, and as the f_{eq} decreased, and correction factor increased. Differences larger than a factor of 2, began with PCBs with a log K_{PW} greater than six. These values correlate to estimated f_{eq} as high as 0.5. Unlike the DIF and NLS comparison, there was no one thickness of PE that illustrated any observable patterns in variance in the FO comparisons. There were however some observable patterns. These varying behaviors are likely due to some congeners having different physicochemical characteristics than the PRC used to predict their k_e in the FO method. This trend is most observable for all PE thicknesses with log K_{PW} between 6.80 and 8.25. In both @AB CD/ and 364 3EC CD/ the C_{free} ratios are different by a factor of about ten. As K_{PW} increases to about 7.5 (CB180 has K_{PW} of 7.42 L/kg) the ratio approaches one. As K_{PW} exceeds 7.5, the ratios continue to increase indicating the NLS and DIF methods are estimating a larger C_{free} than the FO method. Much of the variation in these results is a direct result of the large f_{ret} of the PRC, both ^{13}C -CB138 and ^{13}C -CB180, had a different default f_{ret} been defined the patterns may have been different. Many of the large and small ratios observed here incorporated the default f_{eq} of 0.01 used in the FO model. This result gives further evidence of the risks associated with using the FO model beyond the 80:20 rule in that it can both over- and under-predict C_{free} estimates.

ANOVA analysis showed that the estimates of C_{free} demonstrated no statistical differences between results by correction method and C_{free} estimates when no model was used (Equation 1) for all thicknesses for di- and tri-chlorinated congeners (Table S10). At NBH2, the NLS and DIF C_{free} estimates were indistinguishable, in 96% of the comparisons tested, and results from the FO method were not statistically different from the NLS and DIF methods in 40% and 34% of the measurements, respectively. Results of similar statistical analyses for NBH4 and NBH5 are reported in Tables S12 and S14, respectively.

Comparison of total PCB C_{free}

Table 1 reports total PCB C_{free} values calculated using each of the methods as the sum of up to 27 individual congener C_{free} s by thickness at NBH2, NBH4 and NBH5. For NBH2, mean C_{free} s ranged across models and thicknesses with values of 387 to 505 ng/L. For each thickness, the largest total PCB values were generated by the FO method followed by the DIF method, and then the NLS method, where the NLS and DIF methods were always within 5% of each other, and no one thickness of PE consistently demonstrated the largest nor the smallest mean total PCB measurement. No significant differences in total PCB C_{free} values between methods were determined at NBH2 (Table 1). The same trends were observed at NBH4 although the total PCB C_{free} range was an order of magnitude lower: 32.2 to 55.6 ng/L. At NBH5, the total PCB C_{free} were two orders of magnitude below the NBH4 levels with a range of 0.13 to 0.27 ng/L. At NBH4 and NBH5, statistical analyses of total PCB C_{free} s by thickness detected several significant differences in total PCB C_{free} estimates (Table 1). However, at all three stations, statistically significant differences between C_{free} s based on the NLS and DIF methods were never detected. In about 55% of the total PCB C_{free} estimates a significant difference existed between the FO and NLS or DIF modeled results. These results also illustrate how some congeners can statistically dominate the total PCB estimates. For instance, at NBH2 several of the lighter, faster equilibrating congeners

contribute to a large fraction of the total PCB, and as a result, the PRC-modeled results are agreeable with the results to which no PRC corrections were made. However, when these congeners make up a smaller percentage of the mixture significant differences in the results occur. These statistically different results again highlight the importance of using PRCs to estimate accurate C_{free} . A similar statistical analysis as discussed above but focusing on differences between passive sampler thicknesses by model is reported in Table S15.

This comparison of mass transfer-based correction methods for passive samplers found that using multiple PRCs to estimate sampling rates or fractional equilibria for target PCBs (i.e., NLS and DIF methods, respectively) resulted in more consistent and precise estimates of C_{free} than using results from one PRC (i.e., the FO method). In addition, the NLS and DIF methods generated C_{free} values that were statistically similar when expressed as total PCB or on a single congener basis. These findings suggest that contaminated site managers and scientists can apply either mass transfer method to use PRC results to estimate C_{free} for their target contaminants. Assistance running DIF method is available on-line (<https://www.serdpe-stcp.org/Tools-andTraining/Tools/PRC-Correction-Calculator> and <https://www.epa.gov/superfund/superfundcontaminated-sediments-guidance-documents-fact-sheets-and-policies>). Assuming equilibrium is discouraged as it will likely under-estimate C_{free} for contaminants that are slow to equilibrate or under *in situ* conditions with slow kinetics (i.e., quiescent environmental conditions). For all methods, it is important to consider using PRCs that span the physicochemical characteristics (e.g., log K_{OW}) of the target HOCs and that will result in useful f_{reb} guidance on estimating PRC results given environmental conditions can be found in the literature (Apell et al., 2016).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENT

The authors thank the AED reviewers for their comments: Adeyemi Adeleye, David Katz, and Jonathan Serbst. This research was performed while A.S. Joyce held an NRC Research Associateship award at U.S. Environmental Protection Agency, ORD/NHEERL Atlantic Ecology Division. The authors would like to acknowledge Donald Cobb and Barbara Bergen for their assistance in deploying and retrieving these passive samplers.

REFERENCE LIST

- APELL JN & GSCHWEND PM 2014 Validating the Use of Performance Reference Compounds in Passive Samplers to Assess Porewater Concentrations in Sediment Beds. *Environmental Science & Technology*, 48, 10301–10307. [PubMed: 25093866]
- APELL JN & GSCHWEND PM 2016 In situ passive sampling of sediments in the Lower Duwamish Waterway Superfund site: Replicability, comparison with ex situ measurements, and use of data. *Environmental Pollution*, 218, 95–101. [PubMed: 27552042]
- APELL JN, TCACIUC AP & GSCHWEND PM 2016 Understanding the rates of nonpolar organic chemical accumulation into passive samplers deployed in the environment: Guidance for passive sampler deployments. *Integrated Environmental Assessment and Management*, 12, 486–492. [PubMed: 26426907]
- BELLES A, ALARY C & MAMINDY-PAJANY Y 2016 Thickness and material selection of polymeric passive samplers for polycyclic aromatic hydrocarbons in water: Which more strongly

affects sampler properties? *Environmental Toxicology and Chemistry*, 35, 1708–1717. [PubMed: 26647116]

- BOOIJ K, ROBINSON CD, BURGESS RM, MAYER P, ROBERTS CA, AHRENS L, ALLAN IJ, BRANT J, JONES L, KRAUS UR, LARSEN MM, LEPOM P, PETERSEN J, PRÖFROCK D, ROOSE P, SCHÄFER S, SMEDES F, TIXIER C, VORKAMP K & WHITEHOUSE P 2016 Passive Sampling in Regulatory Chemical Monitoring of Nonpolar Organic Compounds in the Aquatic Environment. *Environmental Science & Technology*, 50, 3–17. [PubMed: 26619247]
- BOOIJ K & SMEDES F 2010 An Improved Method for Estimating in Situ Sampling Rates of Nonpolar Passive Samplers. *Environmental Science & Technology*, 44, 6789–6794. [PubMed: 20701278]
- BURGESS RM, LOHMANN R, SCHUBAUER-BERIGAN JP, REITSMA P, PERRON MM, LEFKOVITZ L & CANTWELL MG 2015 Application of passive sampling for measuring dissolved concentrations of organic contaminants in the water column at three marine superfund sites. *Environmental Toxicology and Chemistry*, 34, 1720–1733. [PubMed: 26039657]
- DI TORO DM, ZARBA CS, HANSEN DJ, BERRY WJ, SWARTZ RC, COWAN CE, PAVLOU SP, ALLEN HE, THOMAS NA & PAQUIN PR 1991 Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environmental Toxicology and Chemistry*, 10, 1541–1583.
- FERNANDEZ LA, HARVEY CF & GSCHWEND PM 2009 Using Performance Reference Compounds in Polyethylene Passive Samplers to Deduce Sediment Porewater Concentrations for Numerous Target Chemicals. *Environmental Science & Technology*, 43, 8888–8894. [PubMed: 19943662]
- 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. *Environmental Science & Technology*, 48, 3925–3934. [PubMed: 24564763]
- FERNANDEZ LA, LAO W, MARUYA KA, WHITE C & BURGESS RM 2012 Passive Sampling to Measure Baseline Dissolved Persistent Organic Pollutant Concentrations in the Water Column of the Palos Verdes Shelf Superfund Site. *Environmental Science & Technology*, 46, 11937–11947. [PubMed: 23062073]
- FRIEDMAN CL, CANTWELL MG & LOHMANN R 2012 Passive sampling provides evidence for Newark Bay as a source of polychlorinated dibenzo-p-dioxins and furans to the New York/New Jersey, USA, atmosphere. *Environmental Toxicology and Chemistry*, 31, 253–261. [PubMed: 22095897]
- GHOSH U, KANE DRISCOLL S, BURGESS RM, JONKER MTO, REIBLE D, GOBAS F, CHOI Y, APITZ SE, MARUYA KA, GALA WR, MORTIMER M & BEEGAN C 2014 Passive sampling methods for contaminated sediments: Practical guidance for selection, calibration, and implementation. *Integrated Environmental Assessment and Management*, 10, 210–223. [PubMed: 24288273]
- 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. *Integrated Environmental Assessment and Management*, 10, 224–236. [PubMed: 24343931]
- 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. *Environmental Toxicology and Chemistry*, 30, 1288–1296. [PubMed: 21360577]
- HAWKER DW & CONNELL DW 1988 Octanol-water partition coefficients of polychlorinated biphenyl congeners. *Environmental Science & Technology*, 22, 382–387.
- HUCKINS JN, PETTY JD, LEBO JA, ALMEIDA FV, BOOIJ K, ALVAREZ DA, CRANOR WL, CLARK RC & MOGENSEN BB 2002 Development of the Permeability/Performance Reference Compound Approach for In Situ Calibration of Semipermeable Membrane Devices. *Environmental Science & Technology*, 36, 85–91. [PubMed: 11811495]
- JOYCE AS, PIROGOVSKY MS, ADAMS RG, LAO W, TSUKADA D, CASH CL, HAW JF & MARUYA KA 2015 Using performance reference compound-corrected polyethylene passive

samplers and caged bivalves to measure hydrophobic contaminants of concern in urban coastal seawaters. *Chemosphere*, 127, 10–17. [PubMed: 25613644]

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. *Environmental Science & Technology*, 46, 606–618. [PubMed: 22122117]

LYDY MJ, LANDRUM PF, OEN AMP, ALLINSON M, SMEDES F, HARWOOD AD, LI H, MARUYA KA & LIU J 2014 Passive sampling methods for contaminated sediments: State of the science for organic contaminants. *Integrated Environmental Assessment and Management*, 10, 167–178. [PubMed: 24307344]

MARUYA KA, ZENG EY, TSUKADA D & BAY SM 2009 A passive sampler based on solid-phase microextraction for quantifying hydrophobic organic contaminants in sediment pore water. *Environmental Toxicology and Chemistry*, 28, 733–740. [PubMed: 19391690]

MAYER P, PARKERTON TF, ADAMS RG, CARGILL JG, GAN J, GOUIN T, GSCHWEND PM, HAWTHORNE SB, HELM P, WITT G, YOU J & ESCHER BI 2014 Passive sampling methods for contaminated sediments: Scientific rationale supporting use of freely dissolved concentrations. *Integrated Environmental Assessment and Management*, 10, 197–209. [PubMed: 24288295]

MAYER P, TOLLS J, HERMENS JLM & MACKAY D 2003 Peer Reviewed: Equilibrium Sampling Devices. *Environmental Science & Technology*, 37, 184A–191A.

PERRON MM, BURGESS RM, SUUBERG EM, CANTWELL MG & PENNELL KG 2013a Performance of passive samplers for monitoring estuarine water column concentrations: 1. Contaminants of concern. *Environmental Toxicology and Chemistry*, 32, 2182–2189. [PubMed: 23832638]

PERRON MM, BURGESS RM, SUUBERG EM, CANTWELL MG & PENNELL KG 2013b Performance of passive samplers for monitoring estuarine water column concentrations: 2. Emerging contaminants. *Environmental Toxicology and Chemistry*, 32, 2190–2196. [PubMed: 23595851]

RUSINA TP, SMEDES F, KOBLIZKOVA M & KLANOVA J 2010 Calibration of Silicone Rubber Passive Samplers: Experimental and Modeled Relations between Sampling Rate and Compound Properties. *Environmental Science & Technology*, 44, 362–367. [PubMed: 19954176]

SMEDES F 2007 Monitoring of chlorinated biphenyls and polycyclic aromatic hydrocarbons by passive sampling in concert with deployed mussels In: GREENWOOD R, MILLS GA & VRANA B (eds.) *Passive Sampling Techniques in Environmental Monitoring*. Amsterdam: Elsevier.

THOMPSON JM, HSIEH C-H & LUTHY RG 2015 Modeling Uptake of Hydrophobic Organic Contaminants into Polyethylene Passive Samplers. *Environmental Science & Technology*, 49, 2270–2277. [PubMed: 25607420]

TOMASZEWSKI JE & LUTHY RG 2008 Field Deployment of Polyethylene Devices to Measure PCB Concentrations in Pore Water of Contaminated Sediment. *Environmental Science & Technology*, 42, 6086–6091. [PubMed: 18767670]

VRANA B & SCHÜÜRMAN G 2002 Calibrating the Uptake Kinetics of Semipermeable Membrane Devices in Water: Impact of Hydrodynamics. *Environmental Science & Technology*, 36, 290–296. [PubMed: 11827065]

Figure 1. Performance reference compound (PRC) fraction retained (f_{ret}) from the deployment of four thicknesses of polyethylene passive samplers at station NBH2. PRCs are ^{13}C -labelled PCB 8, 28, 52, 101, 138 and 180. The f_{ret} values are plotted against $\log K_{OW}$ of the PRCs.

Figure 2.

Relative standard deviation (RSD; $n = 12$) of C_{free} values for all four thicknesses at station NBH2 measured with a given equilibrium model: (1) No model, (2) first order kinetic (FO) method, (3) non-linear least squared (NLS) sampling rate method, and (4) Diffusion (DIF) method. The designations (e.g., 'Di', 'Tri', 'Tetra') indicate the chlorination level of congeners along the x-axis.

Figure 3.

Inter-method variability of PRC-equilibrium model estimates of C_{free} , comparing three methods: diffusion based (DIF), sampling rate fit to a nonlinear least square relationship (NLS), and first order kinetic fit (FO) as a function of the polymer partitioning coefficient (K_{PW}).

Table 1.

Mean total PCB C_{free} values (ng/L) estimated as the sum of up to 27 individual PCB congeners using each of the correction methods by thickness at NBH2, NBH4 and NBH5

Station	Thickness (¼m)	Model				ANOVA p-value
		No Model	FO	NLS	DIF	
NBH2	12.5	385 ± 67.6	396 ± 65.4	395 ± 68.1	396 ± 68.1	0.9963
	25.4	427 ± 65.0	505 ± 91.0	444 ± 68.0	463 ± 83.9	0.6533
	50.8	397 ± 56.2	390 ± 58.4	408 ± 61.2	388 ± 58.5	0.9735
	76.2	305 ± 23.5	456 ± 50.2	387 ± 40.3	401 ± 39.4	0.0772
NBH4	12.5	36.0 ± 0.83 ^B	40.4 ± 2.01 ^A	38.1 ± 1.28 ^{A,B}	38.9 ± 0.87 ^A	0.0215
	25.4	39.9 ± 1.05 ^C	55.6 ± 1.75 ^A	43.7 ± 1.01 ^{B,C}	47.8 ± 4.45 ^B	0.0003
	50.8	27.1 ± 1.60 ^C	43.8 ± 1.10 ^A	32.2 ± 1.26 ^B	34.3 ± 1.16 ^B	<0.0001
	76.2	26.8 ± 1.46 ^C	47.1 ± 1.26 ^A	39.7 ± 1.13 ^B	39.3 ± 0.64 ^B	<0.0001
NBH5	12.5	0.18 ± 0.01 ^C	0.25 ± 0.01 ^B	0.26 ± 0.01 ^{A,B}	0.27 ± 0.02 ^A	<0.0001
	25.4	0.09 ± 0.03 ^A	0.13 ± 0.04 ^A	0.17 ± 0.06 ^A	0.18 ± 0.06 ^A	0.1853
	50.8	0.07 ± 0.01 ^B	0.13 ± 0.01 ^A	0.14 ± 0.01 ^A	0.14 ± 0.01 ^A	<0.0001
	76.2	0.06 ± 0.01 ^C	0.13 ± 0.01 ^B	0.16 ± 0.01 ^A	0.17 ± 0.01 ^A	<0.0001