

Polychlorinated Biphenyl Sorption and Availability in Field-Contaminated Sediments[†]

DAVID WERNER,^{*,‡} SARAH E. HALE,[‡]
UPAL GHOSH,[§] AND RICHARD G. LUTHY^{||}

School of Civil Engineering and Geosciences, Newcastle University, Newcastle, NE1 7RU, England, U.K., Department of Civil and Environmental Engineering, University of Maryland Baltimore County, Maryland 21250, and Department of Civil and Environmental Engineering, Stanford University, Stanford, California 94305-4020

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Traditional and new relationships of polychlorinated biphenyl (PCB) distribution among the solid phases, the free aqueous phase, and biolipids are comprehensively reviewed using seven well-characterized freshwater and marine sediments polluted with PCBs. The traditional relationship relating free aqueous concentration and biolipid concentration to sediment total organic carbon, compound octanol–water partitioning coefficient, and solid-phase contaminant concentration overestimates measured free aqueous concentrations and biolipid concentrations by mean factors of 8 and 33, respectively. By contrast, relationships based on measured free aqueous phase concentrations or the PCB mass fraction desorbed from sediment provide reasonable predictions of biolipid concentrations. Solid-phase concentration-based predictions perform better when sorption to amorphous organic matter and black carbon (BC) is distinguished. Contrary to previously published relationships, BC sorption appears to be linear for free aqueous PCB-congener concentrations in the picogram to microgram per liter range.

Introduction

Sorption is a dominant process that affects the ultimate environmental fate of persistent organic pollutants such as polychlorinated biphenyls (PCBs) in sediments. While strong sorption may extend the lifetime and persistence of organic pollutants by reducing their accessibility and hence biodegradability, sorption may also reduce pore water concentrations, ecotoxicity, and biouptake as pollutants become sequestered.

An increasing body of evidence demonstrates that the traditional paradigm used to assess the sorption of hydrophobic organic compounds to sediments, which is based on the fraction of organic carbon (f_{OC}) and the organic carbon–water partitioning coefficient (K_{OC}), cannot correctly explain compound availability and ecotoxicity in field-aged sediments (1–4). The presence of strongly sorbing carbonaceous particles such as soot, char, and coal is postulated to

be the reason for the reduced availability and ecotoxicity (5). Thus, relationships have been proposed to improve correlations between solid phase and free aqueous phase concentrations (3, 6) that consider sediment total organic carbon (TOC) and black carbon (BC) separately. However, a survey of 114 PAH-contaminated sediments was unable to confirm the broad applicability of such correlations (7). For PCBs the database for a comparable evaluation is still very limited.

In clean water batch systems, coal and charcoal were shown to adsorb PCBs much more strongly (8) than anticipated from estimates based on f_{OC} and K_{OC} correlations. However, when present with sediment, these black carbonaceous adsorbent materials may suffer some apparent reduction in the strength of sorption for PCBs, which may be caused by the presence of other organic matter constituents or anthropogenic compounds (9, 10). Furthermore, linear free energy relationships that invoke physicochemical models of the relationship between the amount of PCB sorbed and free aqueous concentrations invoke the assumption of thermodynamic equilibrium. Yet equilibrium may not be attained in field samples, even after a number of years. For example, the great dissimilarity between the physicochemical availability of DDT versus its metabolites, indicates that nonequilibrium may persist in field-contaminated sediments where the DDT has been aged for decades (11). These issues are particularly important for assessing environmental risk and exposure, for example through the use of biota–sediment accumulation factors. These complications have begun to be addressed by quantifying the free aqueous concentration or the readily available fraction of hydrophobic organic contaminants to obtain better predictive relationships for biolipid concentrations than those based on total organic carbon (TOC)-normalized solid phase concentrations (12).

The aim of this work is to comprehensively review traditional and new relationships among solid phase, free aqueous phase, and biolipid PCB concentrations in well-characterized field-contaminated sediments. To this end we compiled data from our previous studies (2, 13–17) and a study from the literature (12) to obtain a representative database comprising seven PCB-contaminated freshwater and marine sediments exhibiting a wide range of PCB concentrations, abundance of native BC, and other physicochemical characteristics.

Methods

Summary of Previous Experimental Studies. The sources of the sediment samples used in this study are described in previous publications (2, 12–17) and the references cited therein. Sediment characteristics are summarized in Table 1. Triplicate sediment samples from Lake Hartwell and Hunters Point were characterized for PCBs following USEPA methods 3550B (hexane:acetone sonication), 3630B (activated granular copper to remove elemental sulfur), 3630C (silica gel column cleanup), and 8082 (PCB congener analysis). Duplicate sediment samples from Grasse River, Milwaukee River, and Niagara River were characterized following USEPA methods 3660B (sulfur cleanup), 3665A (sulfuric acid cleanup), 3630C, and 8082. Triplicate sediment samples from Crab Orchard Lake were characterized using a sulfuric acid and copper cleanup followed by PCB congener analysis.

Free aqueous phase PCB concentrations in Lake Hartwell, Hunters Point, Grasse River, and Milwaukee River sediments were determined using an alum ($Al_2(SO_4)_3 \cdot 18H_2O$) flocculation centrifugation method. Differences between these experimental conditions are highlighted in the Supporting

* Corresponding author phone: 0044 191 22 5099; e-mail: david.werner@ncl.ac.uk.

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[‡] Newcastle University.

[§] University of Maryland Baltimore County.

^{||} Stanford University.

TABLE 1. Sediment Physicochemical Properties for Lake Hartwell (LH), Hunters Point (HP), Grasse River (GR), Milwaukee River Location 1 (MR 1), Milwaukee River Location 2 (MR 2), Niagara River (NR)^a, and Crab Orchard Lake^b Sediments Contaminated with PCBs

physicochemical property	LH	HP	GR	MR 1	MR 2
TOC %	2.8 ± 0.5 ^c	1.7 ^d	5.17 ± 0.31 ^e	3.22 ± 0.07 ^e	3.70 ± 0.00 ^e
black carbon %	no data	0.29 ^f	0.365 ± 0.035 ^e	0.640 ± 0.065 ^e	0.616 ± 0.013 ^e
petrographic information or microscopy observation	a very small amount of fine coal like fragments	presence of charcoal, coal and coke particles	mostly vegetative debris	presence of some coal-derived particles	presence of some coal-derived particles
sediment mass less than 63 μm %	96	19	70	74	76
sediment mass in light sediment fraction %	1.2	4	12.4	7.1	11.6
PCB concentration (μg/kg)	1250	9900	6820	45160	87400
PCB mass in light sediment fraction %	18	68	64.5	40.3	43.5
mass fraction of PCBs associated with D _{app,fast} /R ²	75	43	76	59	62
mass fraction of PCBs desorbed in 1 month	78	35	91	80	85

^a TOC = 0.83 ± 0.03%; black carbon = 0.258 ± 0.056%; arachlor 1254 PCB concentration = 330 (μg/kg). Data taken from ref 14. ^b Crab Orchard Lake sediment: TOC = 0.59%; the sediment comprised 16% clay, 70% silt, 14% sand; arachlor 1254 PCB concentration = 29153 (μg/kg); PCB congener mass fractions desorbed within 14 days ranged from 40 to 80%; black carbon % was not determined. Data taken from ref 12. ^c Data taken from ref 13. ^d Data taken from ref 2. ^e Data taken from ref 14. ^f Black carbon was taken as 29% of TOC which was estimated based on the average BC/TOC ratio for 6 samples described by Cho et al. (18) taken from an adjacent location in the same mudflat where the original HP sediment was sampled.

Information (SI). Free aqueous concentrations were determined in Niagara River sediment using a polyoxymethylene solid phase extraction owing to very low concentrations, and for Crab Orchard Lake sediment free aqueous concentrations were determined using a matrix SPME method (additional details are provided in the SI). Free aqueous PCB concentrations were reported based on duplicate or triplicate analyses. Pollutant desorption from all sediments was measured following a multiple step Tenax bead method. Individual experimental batch conditions and sampling times are provided in the SI. Total organic carbon (TOC) was measured in all cases by combustion in an elemental carbon analyzer following treatment with acid to remove carbonates. Black carbon (BC) was analyzed using a wet chemical oxidation method after pretreatment to remove non-BC materials (19).

Biouptake experiments were carried out on the marine species *Neanthes arenaceodentata* and *Leptocheirus plumulosus* and the freshwater oligochaete *Lumbriculus variegatus* using 28-day sediment toxicity protocols as outlined in the SI. Tissues and digestive fluids were sonicated according to USEPA method 3550B and the lipid content of organisms was measured by spectrophotometric analysis. PCB concentrations in biolipids were reported based on duplicate or triplicate analysis.

Theoretical Relationships. According to Schwarzenbach et al. (20), the distribution coefficient between particulate organic matter and water can be estimated with a linear free energy relationship based on the organochlorine compound's octanol–water partitioning coefficient K_{OW} (-). The free aqueous concentration C_{aq} (g/cm³) can then be related to the solid phase concentration C_s (g/g) based on the fraction of organic carbon f_{OC} (-) in the sediment and the K_{OW} , according to eq 1, assuming the fraction of organic carbon in the sediment is analogous to the organic solvent octanol.

$$\log(C_{aq}) = -0.74 \cdot \log(K_{OW}) - 0.15 - \log(f_{OC}) + \log(C_s) \quad (1)$$

Biolipid concentrations C_{lipid} (g/g) can then be related to free aqueous concentrations according to eq 2

$$\log(C_{lipid}) = 0.91 \cdot \log(K_{OW}) + 0.50 + \log(C_{aq}) \quad (2)$$

By combining eqs 1 and 2, C_{lipid} can be related to C_s according to eq 3

$$\log(C_{lipid}) = 0.17 \cdot \log(K_{OW}) + 0.35 - \log(f_{OC}) + \log(C_s) \quad (3)$$

More recently, Landrum et al. (21) related the concentration of organochlorine compounds in the lipid of oligochaetes to the amount of chemical desorbed from sediment within 6 h as measured via a kinetic test in the form of a Tenax bead extraction. A relationship was obtained between the lipid-normalized concentration in the oligochaetes and the organic carbon normalized concentration in the sediment, f_{6h} (g/g organic carbon), extracted with Tenax as shown in eq 4

$$\log(C_{lipid}) = 0.912 \cdot \log(f_{6h}) + 0.835 \quad (4)$$

Moermond et al. (6) account for two pools of organic carbon in sediment; amorphous organic carbon (AOC) and black carbon (BC). The fraction of AOC equals the difference between the fraction of TOC and the fraction of BC ($f_{AOC} = f_{OC} - f_{BC}$). The amorphous organic carbon–water partitioning coefficient K_{AOC} (cm³/g) and the lipid–water partitioning coefficient K_{lipid} (cm³/g) were both approximated by K_{OW} , and a relationship between C_s and C_{aq} shown in eq 5 was obtained. The black carbon–water Freundlich coefficient ($K_{Fr,BC}$ (g/g BC)(g/cm³)⁻ⁿ) accounts for PCB sorption to BC described by the Freundlich isotherm and was obtained using a K_{OW} based

estimate according to eq 6. The relationship in eq 6 was obtained for a Freundlich exponent n of 0.7. To maintain consistency with the other equations, the units of $K_{Fr,BC}$ were adapted from those used by Moermond et al. (6).

$$C_s = (f_{OC} - f_{BC})K_{AOC}C_{aq} + f_{BC}K_{Fr,BC}C_{aq}^n \quad (5)$$

$$\log(K_{Fr,BC}) = 0.980 \cdot \log(K_{OW}) - 2.209 \quad (6)$$

The C_{aq} values derived from eqs 5 and 6 were related to biolipid concentrations using eq 7, where K_{LIP} is the PCB lipid–water partitioning coefficient

$$C_{lipid} \approx K_{LIP} \cdot C_{aq} \quad (7)$$

Results and Discussion

Sediment Characteristics. Table 1 summarizes the geochemical properties of the sediments in the database and shows that the PCB pollution levels vary up to a factor of 265. Total organic carbon (TOC) content varies up to a factor of 6, and BC as a percentage of TOC varies up to a factor of 4.

PCB Desorption Kinetics. An important consideration when invoking linear free energy relationships is whether thermodynamic equilibrium is attained between sediment and pollutants. Kinetic rates of sorption can indicate the time required for pollutants to reach sorption equilibrium in sediment. Previously published desorption data (2, 13, 14) were therefore interpreted with a two compartment diffusion kinetic release model described by Werner et al. (22). Apparent, first-order diffusion kinetic rates ($D_{app,fast}/R^2$) for the readily released PCB mass fraction ranged from 10^{-5} to 10^{-8} (s^{-1}). As shown in Figure S1, the logarithms of the faster release rates $\log(D_{app,fast}/R^2)$ are comparably inversely related to $\log K_d$ for different PCB congeners in the sediments for which diffusion kinetic rates were fitted. Decreasing desorption rate with increasing compound hydrophobicity is expected and has been documented previously (23). Slower release rates $D_{app,slow}/R^2$ fitted by the two compartment model were mostly between 10^{-7} and 10^{-10} (s^{-1}) and in some cases were too small to be reliably determined from the experimental desorption data, as it was obtained over at most a two month period. The majority of the total PCB mass is generally associated with the faster of the two fitted diffusion kinetic release rates, and the mass fraction released over a one month period is mostly greater than 75%, as shown in Table 1. The exception to this is Hunters Point (HP) sediment where only 43% of the PCB mass is associated with the faster release rate. Furthermore, for the 57% PCB mass associated with the more slowly released fraction, many PCB congeners have sorption kinetic rates $D_{app,slow}/R^2$ below 10^{-10} (s^{-1}), which indicate equilibration times of more than a decade. The slower release of PCBs from HP sediment is likely due to three factors: a dominance of more hydrophobic PCB congeners (mostly heptachlorobiphenyls), a coarser grain size, and/or a high abundance of BC. Given several decades in the field, it seems, however, reasonable to assume that most PCB congeners and sediments have approached thermodynamic equilibrium, with the possible exception of a portion of the PCBs associated with coarse, strong sorbents in HP sediment. Linear free energy relationships between solid phase and free aqueous phase PCB concentrations may therefore be discussed.

Free Aqueous PCB Concentrations in Field-Contaminated Sediments. Figure 1a clearly illustrates that free aqueous PCB concentrations estimated on the basis of K_{OW} values, sediment TOC, and solid phase concentration according to eq 1 exceed actual measurements. This is true for all sediments, even those from relatively rural locations such as Lake Hartwell and Grasse River that did not have major industrial inputs other than PCB releases. The median overestimation is a factor of 8 and ranges from 2 for Grasse

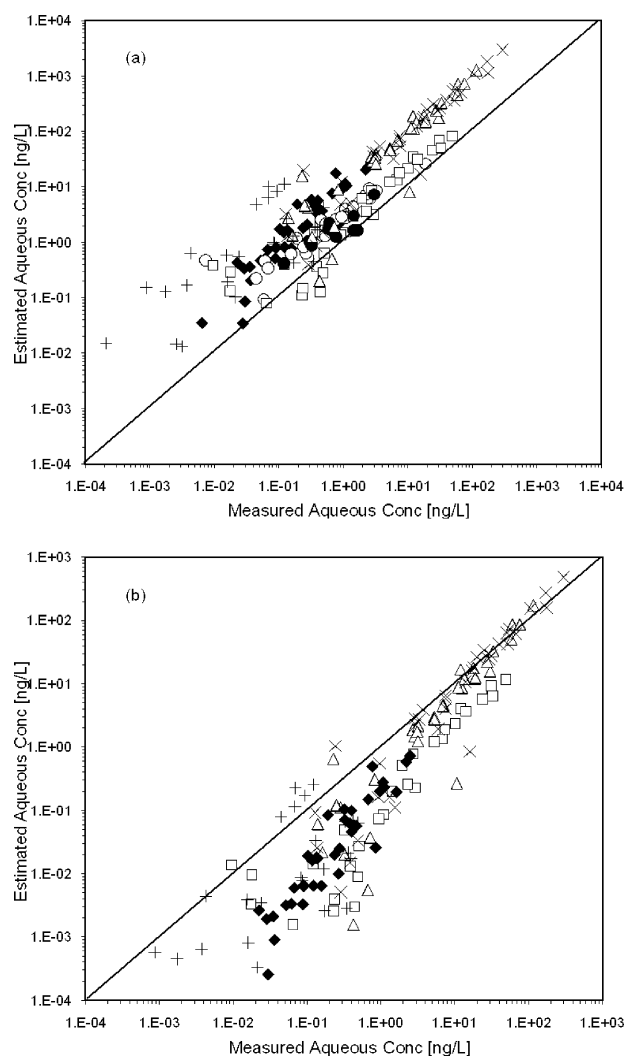


FIGURE 1. Comparison of measured aqueous PCB concentrations with those (a) estimated from K_{OW} values, the sediment f_{OC} and solid phase concentrations according to eq 1, and (b) estimated from solid phase concentrations, the sediment f_{OC} and K_{OW} values according to eqs 5 and 6. Data represent Hunters Point sediment (\diamond), Lake Hartwell sediment (\circ), Grasse River sediment (\square), Crab Orchard Lake sediment (\bullet), Milwaukee River location 1 sediment (Δ), Milwaukee River location 2 sediment (\times), and Niagara River sediment ($+$). The line is drawn to show a 1:1 relationship between estimated and measured data.

River (lowest BC/TOC ratio of 0.07) sediment to 17 for Niagara River (highest BC/TOC ratio of 0.31) sediment. It appears sorption by amorphous organic carbon (AOC) alone (as expressed by sediment TOC) is not sufficient to explain the PCB sorption displayed by any of these sediments, in accordance with similar previous observations (3, 24). Figure 1b compares measured free aqueous PCB concentrations and those estimated using eqs 5 and 6, which are based on the solid phase concentration, K_{OW} values, and sediment TOC but additionally account for adsorption to BC. The agreement between estimated and measured concentrations is improved; in agreement with previous observations (25–27), and here this is especially evident at free aqueous concentrations greater than 30 ng/L. Yet, it is notable that eqs 5 and 6 underestimate measured free aqueous concentrations in the lower concentrations range of approximately less than 30 ng/L. This is reflected in the statistics reported in Table 2. The median ratio of estimated to measured free aqueous PCB concentrations shows an underestimation of a factor of

TABLE 2. Statistical Analysis of the Predictive Relationships

	data points	median $C_{\text{estimated}}/C_{\text{measured}}$	Pearson's correlation coefficient $\log C_{\text{estimated}}$ vs $\log C_{\text{measured}}$	linear regression slope $\log C_{\text{estimated}}$ vs $\log C_{\text{measured}}$
Aqueous Concentration Estimates				
Figure 1a estimates based on eq 1	204	8	0.90	0.88
$\log(C_{\text{aq}}) = -0.74 \cdot \log(K_{\text{OW}}) - 0.15 - \log(f_{\text{OC}}) + \log(C_{\text{S}})$				
Figure 1b estimates based on eqs 5 and 6	166	1/4	0.93	1.26
$C_{\text{S}} = (f_{\text{OC}} - f_{\text{BC}})K_{\text{AOC}}C_{\text{aq}} + f_{\text{BC}}K_{\text{Fr,BC}}C_{\text{aq}}^{0.7}$				
$\log(K_{\text{Fr,BC}}) = 0.980 \cdot \log(K_{\text{OW}}) - 2.209$				
Figure 3a estimates based on eqs 5, 9 and 10 ^a	166	1	0.94	0.93
$C_{\text{S}} = (f_{\text{OC}} - f_{\text{BC}})K_{\text{AOC}}C_{\text{aq}} + f_{\text{BC}}K_{\text{BC,lin}}C_{\text{aq}}$				
$\log(K_{\text{BC,lin}}) = 0.912 \cdot \log(K_{\text{OW}}) + 1.370$				
$\log(K_{\text{AOC}}) = 0.74 \cdot \log(K_{\text{OW}}) + 0.15$				
Biolipid Concentration Estimates				
Figure 2a estimates based on eq 3	157	33	0.83	0.85
$\log(C_{\text{lipid}}) = 0.17 \cdot \log(K_{\text{OW}}) + 0.35 - \log(f_{\text{OC}}) + \log(C_{\text{S}})$				
Figure 2b estimates based on eqs 5, 6 and 7	138	1/6	0.93	1.38
$C_{\text{S}} = (f_{\text{OC}} - f_{\text{BC}})K_{\text{AOC}}C_{\text{aq}} + f_{\text{BC}}K_{\text{Fr,BC}}C_{\text{aq}}^{0.7}$				
$\log(K_{\text{Fr,BC}}) = 0.980 \cdot \log(K_{\text{OW}}) - 2.209$				
$C_{\text{lipid}} \approx K_{\text{LIP}} \cdot C_{\text{aq}}$				
Figure 2c estimates based on eq 4	99	1	0.90	1.04
$\log(C_{\text{lipid}}) = 0.912 \cdot \log(f_{\text{th}}) + 0.835$				
Figure 2d estimates based on eq 2	135	1	0.84	0.97
$\log(C_{\text{lipid}}) = 0.91 \cdot \log(K_{\text{OW}}) + 0.50 + \log(C_{\text{aq}})$				
Figure 3b estimates based on eqs 5, 9, 10 ^a and (2)	138	1	0.92	0.98
$C_{\text{S}} = (f_{\text{OC}} - f_{\text{BC}})K_{\text{AOC}}C_{\text{aq}} + f_{\text{BC}}K_{\text{BC,lin}}C_{\text{aq}}$				
$\log(K_{\text{BC,lin}}) = 0.912 \cdot \log(K_{\text{OW}}) + 1.370$				
$\log(K_{\text{AOC}}) = 0.74 \cdot \log(K_{\text{OW}}) + 0.15$				
$\log(C_{\text{lipid}}) = 0.91 \cdot \log(K_{\text{OW}}) + 0.50 + \log(C_{\text{aq}})$				

^a Relationship parameters were fitted from the data.

4 when eqs 5 and 6 are used, compared to a median overestimation of a factor of 8 for the TOC based relationship. The Pearson's correlation coefficient used to test the linearity of the relationship between estimated and measured data is also slightly improved from 0.90 to 0.93 when TOC is split to AOC and BC. Still, the fitted slope of the data in Figure 1b is higher than the theoretical value of 1 because of the systematic underestimation of free aqueous PCB concentrations below 30 ng/L. The HP sediment data have been included in the statistical analysis, despite the slower kinetics discussed above, as data points generally fall within the range of data for the other, finer sediments indicating that the PCBs in HP sediment are also close to sorption equilibrium. Statistics without the HP data set show the same overall trends and are provided in Table S1.

Biolipid PCB Concentrations for Organisms Exposed to Field-Contaminated Sediments. Figure 2a–d show the relationships among estimated and measured PCB biolipid concentrations in sediment dwelling organisms. Figure 2a shows that estimated data derived from K_{OW} values, sediment TOC, and solid phase concentration according to eq 3 overestimate measured biolipid concentrations by a median factor of 33. By contrast, estimates in Figure 2b where data are derived from eqs 5, 6, and 7 that distinguish between sorption to AOC and BC agree within a median factor of 6 as reported Table 2. The correlation coefficient is improved from 0.83 to 0.93 when sorption to AOC and BC are both considered. Again, the BC-corrected relationship performs well in the higher PCB concentration range, but underpredicts biolipid concentrations in the lower PCB concentration range. Consequently, the slope for the data in Figure 2b is greater than 1. Predicting biolipid concentrations from bioavailability measurements such as the PCB mass fraction desorbed, measured via a Tenax bead extraction and shown in eq 4, or using actual measured free aqueous concentrations according to eq 2 instead of solid phase concentrations, gives much better agreement with measured data. This is shown in Figure 2c and d and reflected by the median factor of 1 for the ratio

of estimated to measured biolipid concentrations and fitted slopes in the log–log plots close to unity. The relationship presented by Landrum et al. (21) using the PCB mass fraction desorbed from sediment within 6 h, f_{th} , has only been validated for oligochaetes, but apparently also yields reasonable predictions for the marine species *Neanthes arenaceodentata* and *Leptocheirus plumulosus* discussed here. Figure 2d confirms the contention of Kraaij et al. (28) that measured pore-water concentrations work better than sediment concentrations in estimating equilibrium biolipid PCB concentrations. *Leptocheirus plumulosus* is a particle-browsing amphipod whereas the polychaete *Neanthes arenaceodentata* and the oligochaete *Lumbriculus variegatus* ingest the fine sediment fraction. While different feeding strategies may result in different PCB exposure pathways and may explain some of the smaller differences in Figure 2c and d, the data suggest that the relationships are quite robust for three different sediment dwelling organisms.

Linearity of Native Black Carbon Adsorption at Low Free Aqueous PCB Concentrations. One possible explanation for the underestimation of both free aqueous and biolipid concentrations at very low aqueous concentrations may be due to assumptions on the degree of linearity or nonlinearity of the sorption isotherm for BC in sediment. If the sorption is more linear below the microgram/L concentration range, then the relationship that accounts for sediment AOC and BC content (eqs 5–7) as shown in Figures 1b and 2b, should be modified as the Freundlich sorption isotherm for BC materials in the low free aqueous concentration range is not adequately represented by the assumed value of 0.7 for the Freundlich exponent n . Assuming a linear isotherm (and therefore a Freundlich exponent n of unity instead of 0.7), BC–water partitioning coefficients $K_{\text{BC,lin}}$ (cm³/g) were recalculated from the data with eq 5 and yielded the following correlation with K_{OW}

$$\log(K_{\text{BC,lin}}) = (0.912 \pm 0.064) \cdot \log(K_{\text{OW}}) + (1.370 \pm 0.403) \quad (9)$$

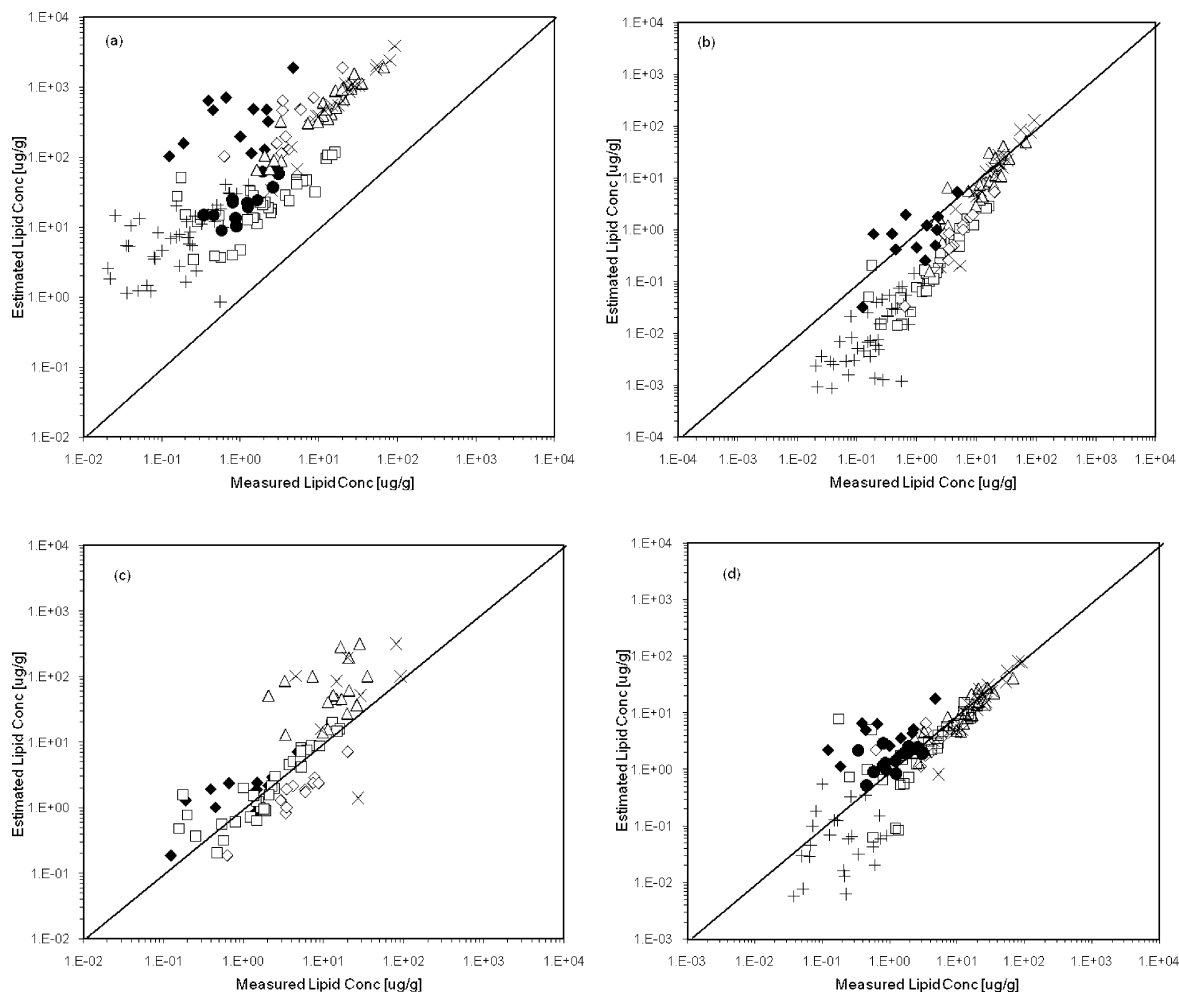


FIGURE 2. Comparison of measured biolipid PCB concentrations with those estimated from (a) K_{OW} values, the sediment f_{OC} , and solid phase concentrations according to eq 3; (b) solid phase concentrations, the sediment f_{OC} , and f_{BC} and K_{OW} values according to equations (5 – 7); (c) the contaminant mass fraction desorbed from sediment using a tenax extraction according to eq 4; and (d) actual measured free aqueous concentrations according to eq 2. Data represent Hunters Point sediment, *Neantes areaceodontata* (◆) and *Leptocheirus plumulosus* (◇); Grasse River sediment, *Lumbriculus variegatus* (□); Crab Orchard Lake sediment, *Lumbriculus variegatus* (●); Milwaukee River location 1 sediment, *Lumbriculus variegatus* (Δ); Milwaukee River location 2 sediment, *Lumbriculus variegatus* (×); and Niagara River sediment, *Lumbriculus variegatus* (+). The line is drawn to show a 1:1 relationship between estimated and measured data.

Figure 3a and b show the improved agreement compared to Figures 1b and 2b, respectively, between measured free aqueous and biolipid concentrations with respective estimates based on a linear AOC partitioning coefficient K_{AOC} calculated according to the relationship presented in Schwarzenbach et al. (20) shown in eq 10 (instead of assuming K_{AOC} is equal to K_{OW} (6)) and a linear BC partitioning coefficient $K_{BC,lin}$, calculated according to eq 9 (instead of using $K_{Fr,BC}$ and $n = 0.7$).

$$\log(K_{AOC}) = 0.74 \cdot \log(K_{OW}) + 0.15 \quad (10)$$

Equation 2 was used to estimate the biolipid concentrations shown in Figure 3b from estimated free aqueous concentrations shown in Figure 3a. Table 2 illustrates median ratios of estimated to measured aqueous and biolipid concentrations of 1 and slopes close to unity for data in Figure 3a and b. As demonstrated by Jonker and Koelmans (8), BC is a heterogeneous material with distinct sorption properties and therefore the use of a single K_{BC} value could be challenged. Yet, for the data in Figure 3 spanning free aqueous concentrations of 7 orders of magnitude and biolipid concentrations of 4 orders of magnitude, normalization to f_{AOC} and f_{BC} appears to minimize systematic differences among the

five sediments that were apparent when estimates were based on sediment TOC alone. It is logical that the BC sorption isotherm should eventually become more linear in the very low free aqueous PCB concentration range, since there must be a finite limit to the affinity of PCBs for any type of adsorption site, and the BC sorbent strength for PCBs cannot increase indefinitely with decreasing free aqueous PCB concentrations.

Implications for Monitoring and Management Practices.

An increasing body of evidence suggests that free aqueous PCB concentrations or surrogate measures such as the PCB concentration assimilated by passive samplers (for example single phase polyoxymethylene or SPME), or the Tenax-extractable PCB concentration, correlate better with biolipid concentrations than relationships based only on TOC-normalized solid phase concentrations. Therefore, the use of these experimental techniques can make a significant contribution to the assessment of contaminant risk at polluted sediment sites. Quantification and separate consideration of AOC and BC materials in sediment may also result in more accurate assessment of risk. However it appears that nonlinear Freundlich sorption isotherms to BC should

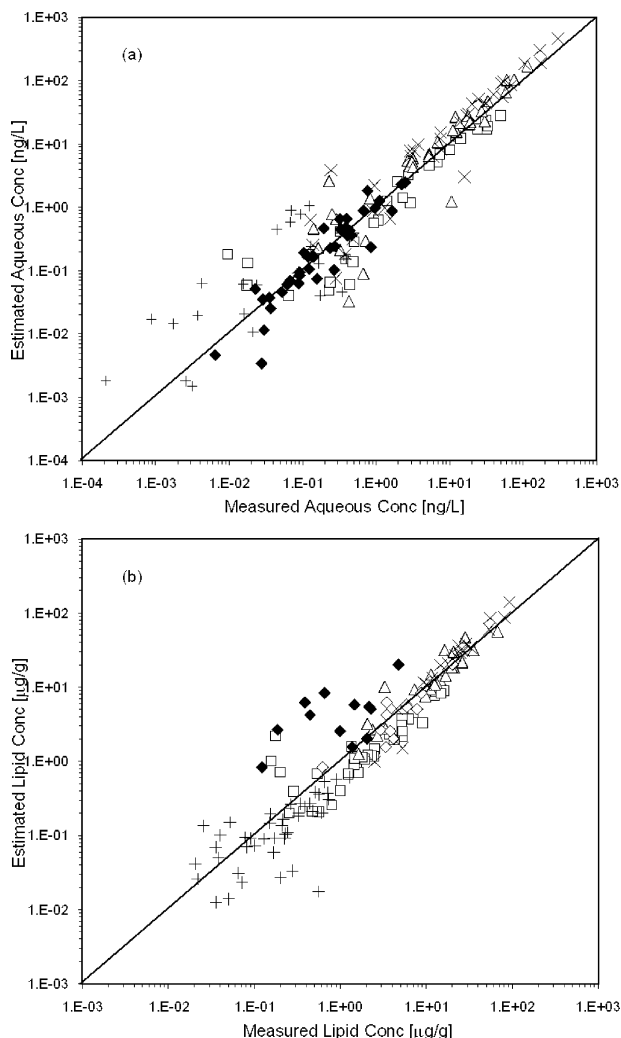


FIGURE 3. (a) Comparison of measured aqueous PCB concentrations with those estimated from solid phase concentrations, the sediment f_{OC} and f_{BC} and K_{OW} values according to eqs 5 and 9, using $K_{BC,lin}$ and $n = 1$ instead of $K_{fr,BC}$ and $n = 0.7$, and (10). Data represent Hunters Point sediment (\blacklozenge), Grasse River sediment (\square), Milwaukee River location 1 sediment (\triangle), Milwaukee River location 2 sediment (\times) and Niagara River sediment ($+$). (b) comparison of measured biolipid PCB concentrations with those estimated from solid phase concentrations, the sediment f_{OC} and f_{BC} and K_{OW} values according to eq 5, 9, using $K_{BC,lin}$ and $n = 1$ instead of $K_{fr,BC}$ and $n = 0.7$, and (10). Equation 2 was used to estimate biolipid concentrations from estimated aqueous concentrations in Figure 3a. Data represent Hunters Point sediment, *Neanthes arenaceodentata* (\blacklozenge) and *Leptocheirus plumulosus* (\diamond); Grasse River sediment, *Lumbriculus variegatus* (\square); Milwaukee River location 1 sediment, *Lumbriculus variegatus* (\triangle); Milwaukee River location 2 sediment, *Lumbriculus variegatus* (\times); and Niagara River sediment, *Lumbriculus variegatus* ($+$). The line is drawn to show a 1:1 relationship between estimated and measured data.

not be extrapolated to the very low free aqueous concentration range as this appears to overestimate the sorption strength.

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Supporting Information Available

Details of previous experimental studies, the statistical analysis of the predictive relationships without Hunters Point data and the logarithm of fitted release rates, $\log D_{app,fast}/R^2$, of the readily desorbed PCB mass fraction versus the logarithm of the sediment–water distribution coefficient, $\log K_d$. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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