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Improving Predictability of Sediment-Porewater Partitioning Models using Trends Observed with PCB-Contaminated Field Sediments

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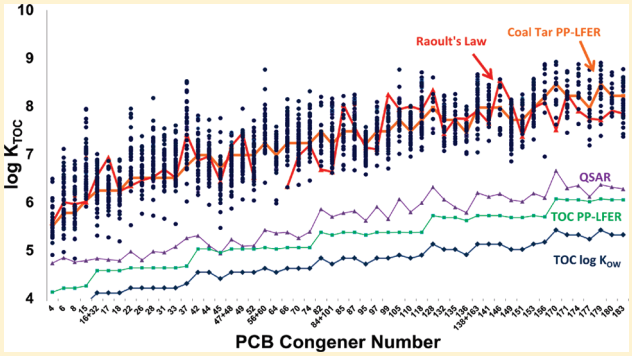
S *Supporting Information*

ABSTRACT: More than 1900 sediment-water partitioning coefficients were measured for 58 polychlorinated biphenyl (PCB) congeners in 53 historically contaminated sediments collected from 10 urban and rural waterways in the United States and Canada. Freely dissolved porewater concentrations were determined using passive sampling with polyoxymethylene. Measured total organic carbon (TOC)/water partitioning coefficients, K_{TOC}, ranged from one to nearly three orders-of-magnitude higher than typical literature values based on spiking experiments and model predictions. Although total PCB concentrations ranged from 0.08 to 194 mg/kg, the more highly contaminated sediments showed only slightly lower K_{TOC} values than less-contaminated sediments. No correlation was observed between log K_{TOC} values and sediment TOC, black carbon (BC), or BC/TOC fractions (r^2 typically <0.1). Utilizing a two-carbon model incorporating anthropogenic BC did not improve predictions over a one-carbon TOC model. A comparison of models recently validated for field data showed that a coal-tar poly parameter linear-free energy relationship (PP-LFER) and a Raoult's Law model were successful at predicting average log K_{TOC} values, without the need for any calibration or fitting (within a factor of 10 more than 90% of the time, and within a factor of 30 more than 99% of the time). Predictions were further improved by the introduction of a Weathering Factor (WF) that accounts for the relative depletion of lower molecular weight congeners due to weathering. Highly weathered sediments (with a WF near 1) tended to follow the coal-tar PP-LFER and Raoult's Law model the closest. Less-weathered sediments (with WF $\ll$ 1) sorbed less than predicted by these models. Noncalibrated WF inclusive coal-tar PP-LFER and Raoult's Law models performed as well or better than a quantitative-structure activity relationship (QSAR) model calibrated specifically to the data. These recommended partitioning models here can readily be used for all 209-PCB congeners.



INTRODUCTION

There has been increasing interest in developing models better able to predict freely dissolved concentrations of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated dioxins, and other hydrophobic organic compounds (HOCs) in contaminated sediments, since conventional equilibrium partitioning approaches using limited experimental and (most often) modeled partitioning coefficients usually over predict freely dissolved concentrations and, therefore, overestimate the potential impacts of such HOCs.[1−4] Sediment-water partitioning constants, K_D, for HOCs determined in historically impacted sediments have been found to vary by several orders-of-magnitude, regardless of whether they are normalized to sediment fractions typically associated with sorption like total organic carbon (TOC)[1,2] or a combination of amorphous organic carbon (AOC) and black carbon (BC).[3,4]

While it is becoming generally accepted that measured freely dissolved HOC concentrations (i.e., the aqueous concentration not associated with colloids or dissolved organic matter) are superior to sediment concentrations in accounting for bioavailability and related environmental impacts, determinations in historically contaminated sediments are limited by the lack of proper analytical methods capable of determining freely dissolved concentrations at levels of interest (often part-per-quadrillion or lower). Further, existing site data are almost exclusively limited to sediment concentrations. Consequently, improvements in models to predict freely dissolved concentrations are needed to better understand and predict the environmental impacts of HOCs. Adequate accounting of field K_D values and their variability is also required for improving the performance of multimedia fate models of HOCs as well as screening models for emerging HOCs.

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Other than for PAHs,[1,3] to date there has been no suitably large set of field data for other classes of HOCs to support the validation and improvement of predictive partitioning models for historically contaminated sediments. With recently developed techniques for measuring freely dissolved concentrations for large numbers of target HOCs,[5,6] it is now possible to better understand the distribution behavior of K_D values in impacted environments. In this work, the largest collection of PCB partitioning data to date that has been determined on historically contaminated sediments using consistent methods is presented. These data are used as a validation data set to test established partitioning models developed based on laboratory-spiked sediments as well as emerging models developed based on historically contaminated sediments. In order to test the robustness of these models, no calibration is done as part of the validation work presented. Additionally, the influences of carbon content, sediment concentration, and the apparent degree of weathering are investigated to determine if they are worth including in partitioning models for impacted sites.

MATERIALS AND METHODS

Samples and Analyses. Sediment samples were collected from several urban and rural rivers including the Buffalo ($n = 19$), Hudson ($n = 11$), Fox ($n = 10$), Grasse ($n = 3$), and one sample each from four other freshwater and brackish rivers. Six marine sediments were also collected, four of which were associated with an aluminum smelter. Sediments were collected using a Ponar grab sampler, or in a few cases, using a shovel. Sediments were sieved through 2-mm screens, homogenized, and stored at 4 °C in the dark until analyzed. Samples typically had ca. 30−50 wt % water during storage. All partitioning experiments were performed at room temperature. All partitioning studies were initiated within two weeks of sample receipt to minimize changes which could occur between the field and the lab.

Total organic carbon (TOC) was determined on air-dried sediment (80 °C for 2 h) after grinding to a fine powder and acidification with 1 M HCl to remove inorganic carbonates. A replicate sample was oxidized for 24 h at 375 °C in a gas chromatographic oven and acidified to determine black (or "soot") carbon (BC).[7] TOC and BC on the prepared samples were determined by elemental (C,H,N) analysis.

Freely dissolved porewater concentrations (i.e., not associated with DOC or colloids in the porewater), C_{pw}, of 58 di- to heptachloro- PCB congeners were determined using a passive sampling method with polyoxymethylene (POM) coupons as previously described.[6] This method can measure C_{pw} in the pg/L range. In brief, 100 mg POM coupons were mixed with ca. 30 g of sediment (wet wt.) and an additional ca. 30 mL water for 28 days, the POM coupon was briefly rinsed to remove colloids, extracted with 1:1 hexane/acetone, and the PCB concentrations were determined by GC/MS with selected ion monitoring (SIM) after the addition of several internal standards.[6] It should be noted that POM does not sorb DOC and DOC-associated PCBs. However, even in the unlikely event that DOC-associated PCBs are measured as an artifact in the POM, there is no significant effect on the measured freely dissolved concentrations since the mass of PCBs associated with DOC in a sediment sample is insignificant ($\ll$1%) compared to the mass in the 100 mg POM coupon.

To determine sediment concentrations, C_{sed}, sediments (5 g) were mixed with sodium sulfate to a dry powder and extracted with 150 mL of hexane/acetone for 18 h in a Soxhlet apparatus. Internal standards were added, and the extracts were concentrated under a gentle stream of nitrogen and analyzed in the same manner as the POM extracts. All POM equilibration experiments and Soxhlet extractions were performed with duplicate sediment samples.

Modeling. There are a great variety of models proposed for PCB partitioning to sediments. For the modeling work here, a representative cross-section of these models is tested in order to see how well they account for the new field data set *without* requiring further calibration. The selection of models presented here are based on (a) their perceived current popularity, (b) the differences in their underlying assumptions, and (c) observations from a previous critical review which assessed the best performing one-carbon based models for historically contaminated sediments.[2]

One and Two Carbon Models. On the basis of the long-held assumption that the fraction of TOC is responsible for the majority of sorption occurring in sediments,[10] K_D values have been normalized to the mass fraction of TOC, f_{TOC}, as below:

$$K_D = K_{TOC} f_{TOC} = C_{sed}/C_{pw} \quad (1)$$

Over the past decade, there has been increasing advocacy for a two-carbon model that accounts for the contributions of BC (typically defined as carbon that is thermo-resistant at 375 °C)[7,8] and amorphous organic carbon (AOC) (defined as all TOC that is not BC) separately:

$$K_D = f_{AOC} K_{AOC} + f_{BC} K_{BC,F} C_{pw}^{nF-1} \quad (2)$$

where nF is the Freundlich exponent, and is typically assumed to be one for PCBs.[4,9]

Carbon Sorption Models. K_{TOC} values for HOCs have traditionally been estimated using log−log correlations with the octanol−water partition coefficient, K_{OW}, such as the following relationship from Schwarzenbach et al.[10] for PCBs, which was recently used for PCBs by Werner et al[9] and is representative of similar log K_{TOC}−log K_{OW} relationships used by others for historically contaminated sediments:[11−13]

$$\log K_{TOC} = 0.74 \log K_{OW} + 0.15 \quad (3)$$

Several quantitative-structure activity relationship (QSAR) approaches have also been used to account for the lack of K_{OW} data for all 209 PCB congeners.[14] More recently, poly parameter linear-free energy relationships (PP-LFERs), which explicitly account for specific and nonspecific interactions, have been used to predict K_{TOC} values for PCBs[15] and also the K_{OW} for PCBs,[16] such as in the relationships below:

$$\log K_{TOC} = 1.08E - 0.83S + 0.28A - 1.85B + 2.55V - 0.12 \quad (4)$$

$$\log K_{OW} = 0.58E - 1.09S + 0.03A - 3.40B + 3.81V + 0.03 \quad (5)$$

where S, A, and B are descriptors for specific interactions made by PCBs, and E and V are descriptors for nonspecific interactions. An updated list of these descriptors for all 209 PCB congeners has recently been published in ref 17.

Traditional one-carbon K_{TOC} models, such as those mentioned in eqs 3−5, are known to under-predict field K_{TOC} values for PCBs and other HOCs by several orders-of-magnitude, largely because they were initially calibrated in the lab using spiked sediments and generally at high concentrations.[2]

Table 1. Summary of 53 Sediment Characteristics

	min	max	mean	median
TOC, wt %	0.45	24.6	4.0	2.5
BC, wt %	0.12	4.4	0.88	0.34
BC/TOC	0.03	0.87	0.24	0.18
AOC, wt%	0.06	20.2	3.1	2.1
Sediment PCB Concentrations, μg/kg				
Di	4	134200	7340	150
Tri	2	84400	5780	510
Tetra	24	44000	3790	498
Penta	23	22600	1550	219
Hexa	4	13000	717	98
Hepta	ND	1960	202	36
Freely-Dissolved PCB Concentrations, ng/L				
Di	0.17	64600	3140	18
Tri	0.17	1490	129	16
Tetra	0.09	279	36	5.6
Penta	0.03	37	3.7	0.8
Hexa	ND	6.67	0.59	0.09
Hepta	ND	0.71	0.07	0.01
total sediment PCBs (mg/kg)[a]	0.08	164	19.4	26.3
total dissolved PCBs (ng/L)[a]	0.5	65200	3310	48
WF[b]	8%	91%	66%	74%

[a] Based on 58 dichloro- to heptachlorobiphenyl congeners listed in the Supporting Information. [b] Weathering Factor, defined as the sum of sediment concentration for the tetra- to hepta-chloro congeners measured divided by the sum of sediment concentration for all congeners measured.

To account for this, many researchers have adopted the two-carbon model introduced in eq 2, with the implicit assumption that all sorption not attributable to traditional TOC models is attributable to BC.[6,18] Recently, a way of estimating K_{BC} values for PCBs was introduced:[9]

$$\log K_{BC} = 0.91 \log K_{OW} + 1.37 \quad (6)$$

Instead of using a two-carbon model, an alternate approach is a one-carbon TOC model where the TOC is allowed to sorb more than traditionally derived from lab experiments.[2,19] In a recent critical review that screened a variety of TOC modeling approaches for their ability to model sediments historically contaminated with HOCs, models that were based on TOC sorbing similar to coal-tar were the most successful. One such model was a PP-LFER[2,20]

$$\log K_{TOC} = 0.50E - 0.35S - 1.16A - 4.46B + 3.86V + 0.16 \quad (7)$$

The second such model was based on Raoult's Law parameterization:[2]

$$\log K_{TOC} = -\log(S_L^* MW_{TOC}) \quad (8)$$

where S_L^* is the subcooled saturated molar water solubility (mol/L_{water}), MW_{TOC} is the molar weight of the sediment's organic phase, which is assumed to be that of coal tar at 223 g/mol.[2,20] (Note this MW_{TOC} is used as it was derived for the proxy coal tar, and is likely much smaller than the MW_{TOC} of sediments, which is highly variable). Measured S_L^* values were obtained from compilations in van Noort,[21] otherwise nonsub-cooled data were from the PhysProp database (Syracuse Research Corporation, www.syrres.com, accessed February 4, 2009) and corrected for using fugacity ratios as in van Noort.[21] S_L^* values used here are listed in the Supporting Information (SI).

In the present work, we will compare how well each of the model equations presented above account for the average behavior of measured field data, by using these data as a validation data set. No model calibration is done as part of this comparison.

RESULTS AND DISCUSSION

Sediment Characteristics. The characteristics of the 53 test sediments are summarized in Table 1. Total PCB concentrations (sum of 58 congeners) varied over a range of 0.08 to 164 mg/kg, and total dissolved concentrations ranged from 0.5 to 65 000 ng/L. A complete list of sediment and freely dissolved concentrations is given in the SI, Tables S2, and S3. Sediment TOC varied from 0.5 to 25 wt %, of which BC comprised 3 to 87%.

PCB Partitioning Coefficients. As shown in Figure 1 for the 1925 K_{TOC} values measured in this study, K_{TOC} values for each PCB congener show a range from more than one to over two orders-of-magnitude. (The minimum, maximum, mean, and median log K_{TOC} values are summarized in Table S4 of the SI). A previous study on PAH K_{TOC} values showed a range for each PAH's K_{TOC} values of ca. three orders-of-magnitude, which is larger compared to two orders-of-magnitude for the PCBs in the present work. This is most likely because of the association of some PAHs with coproduced materials such as soot, or as major components of particles such as coal tar pitch.[22]

Figure 1 also shows K_{TOC} values based on commonly used models developed from spiking studies, including the log K_{TOC}−log K_{OW} correlation from Schwarzenbach et al. presented in eq 3,[10] the TOC PP-LFER from Nguyen et al. presented in eq 4,[15] and the QSAR approach used by Hansen et al.[14] Note that almost every measured K_{TOC} value in our study of historically contaminated sediments is higher than other sets of literature values used to calibrate these models, with our measured values ranging as much as three orders-of-magnitude higher. Thus, applying these traditional models and sediment concentrations to predict dissolved concentrations would overpredict the dissolved concentrations in nearly every case, and up to three orders-of-magnitude for some sediments. Although our K_{TOC} values are much higher than predictions after Hansen et al.,[14] Nguyen et al.,[15] and Schwarzenbach et al.,[10] our results are consistent with the range of PCB K_{TOC} values for historically contaminated sediments that were collected in a recent critical review.[2] Furthermore, as evident from Figure 1a, the same models that worked well for that critical review (the coal-tar based models, such as the PP-LFER model (eq 7) and the Raoult's Law model (eq 8)), also worked much better with the new field data than the other more popular models. This further validates the suitability of the coal-tar PP-LFER and Raoult's Law models for HOC partitioning in historically contaminated sediment, and that coal-tar is a suitable TOC proxy. Other coal-tar based TOC models presented in Endo et al.[20] such as the SPARC model, COSMOtherm model, or the log K_{TOC}−log K_{OW} relationship (log K_{TOC} = 1.15 log K_{OW} −0.2), are also expected to give better agreement than traditional TOC models for historically contaminated sets. Only the PP-LFER and Raoult's Law models were tested here, as these were the best performing for coal tar,[20] and were validated for HOCs in a previous study.[2]

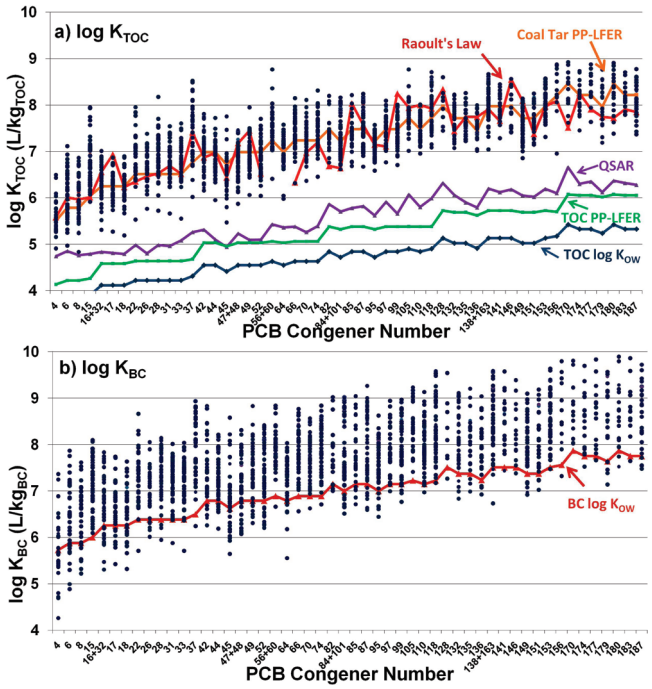

Figure 1. (a) log K_{TOC} values ($n = 1925$) and (b) log K_{BC} values ($n = 1925$) from the one-carbon model (eq 1) and two-carbon model (eq 2), respectively. Also shown in (a) are log K_{TOC} estimates from the TOC log K_{OW} correlation model (eq 3) from Schwarzenbach et al.,[10] the TOC PP-LFER model (eq 4) from Nguyen et al.,[15] the QSAR model from Hansen et al.,[14] the Raoult's Law model (eq 8) from Arp et al.,[2] and the Coal-Tar PP-LFER model (eq 7) from Arp et al. and Endo et al.[2,20] Also shown in (b) is the log K_{BC} estimations from the BC log K_{OW} correlation model (eq 6) from Werner et al.[9]

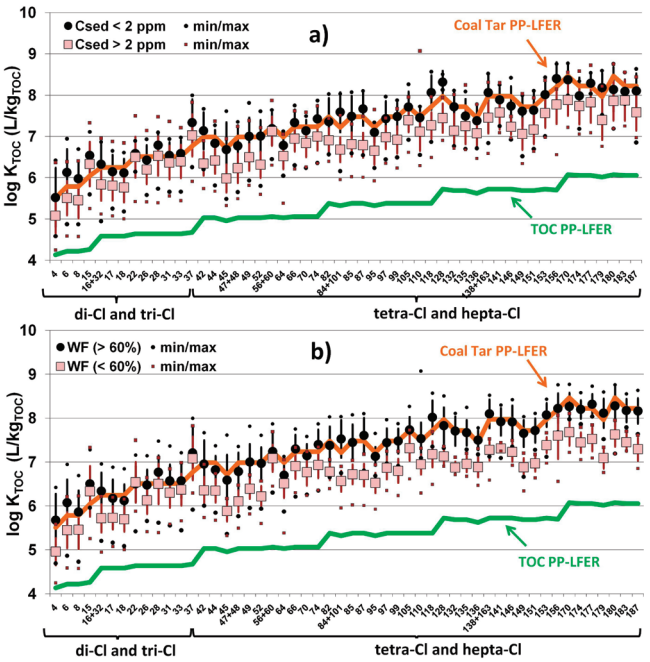

Figure 2. log K_{TOC} values for PCBs plotted (a) based on their C_{sed} concentration being below ($n = 1174$) or above 2 mg/kg ($n = 751$) and (b) based on their weathering factor (WF) being above ($n = 971$) or below 60% ($n = 954$). Also shown are predictions based on the TOC PP-LFER model from Nguyen et al.[15] and the Coal Tar PP-LFER model.[2,20].

Two-Carbon Model. Log K_{BC} values calculated using the K_{AOC} values from Hansen et al.[14] and eq 2 are shown in Figure 1b. If the two-carbon model was effective at improving the prediction of dissolved concentrations, then the 53 sediments would show a narrower range of log K_{BC} for each congener compared to the log K_{TOC} values in Figure 1a. Unfortunately, as shown in Figure 1b and Table S5 of the SI, K_{BC} values for each congener vary by ca. three orders-of-magnitude, thus demonstrating a decrease in precision from the single carbon K_{TOC} model. (Using the other traditional methods to determine K_{AOC} resulted in no improvement in K_{BC} values.) K_{BC} values for our sediments ranged from values similar to those reported by Werner et al. (based on seven sediments),[9] to almost two orders-of-magnitude higher (Figure 1b).

Although we did not apply the Freundlich correction to determine the K_{BC} values shown in Figure 1, it should be recognized that there is a discussion among investigators whether the Freundlich isotherm exponent should be optimized when comparing concentration effects on different sediments. It is the view of the present authors that no adjustment should be made (i.e., nF should be left at 1), unless a concentration study is being performed on a single sediment having a consistent distribution of carbon types. However, we did investigate whether more consistent values of K_{BC} would result when nF was varied from 0.5 to 1 (Table S6 of the SI), and found no significant improvement in the scatter of K_{BC} values compared to those shown in Figure 1b. Since the two-carbon model provides no measurable, practical, or testable advantages over the one-carbon type model despite all the extra assumptions made for the two-carbon model, it is not considered further here.

Effect of Sediment Characteristics and PCB Distributions on K_{TOC}. To try and account for the scatter of measured K_{TOC} values, the influence of carbon type, sediment PCB concentration, and weathering was investigated. These factors have a plausible effect on log K_{TOC} as they can influence, respectively: (a) the dominating sorption phase (TOC or BC), (b) the possibility of nonlinear partitioning (with sorption increasing with decreasing C_{sed} following Freundlich or Langmuir sorption paradigms), and (c) depletion of PCBs from weakly sorbing components with increased field exposure.

The 53 field sediments had a wide range in TOC, BC, and BC/TOC ratios. However, linear correlation coefficients (r^2 values) between log K_{TOC} values and log f_{TOC} and log f_{BC} were extremely low, ranging from 0.00 to 0.13 and 0.00 to 0.12, respectively (Table S7 of the SI). Correlations with fractions of BC/TOC were even worse, and r^2 values were consistently less than 0.06, with the majority less than 0.02 (and the significance factor, p, was greater than 0.2 in all cases).

In contrast to the carbon types, there were low, but statistically significant correlations for several of the di-, tri-, and tetra-chloro congeners between log K_{TOC} and log C_{sed} values (r^2 typically between 0.3 and 0.4), though this was not the case for the higher molecular weight congeners (r^2 typically < 0.1) (Table S7 of the SI). As shown in Figure 2a, sediments with higher concentrations (total of 58 congeners >2 mg/kg) had slightly lower log K_{TOC} values than those with lower concentrations as might be expected, but there is still substantial overlap and the overall shift in values is fairly small. Note that Figure 2a also shows a general trend that sediments with lower PCB concentrations were generally better predicted (but only slightly) by the coal tar PP-LFER model.

Since a direct measure of weathering does not exist, we used the sum sediment concentration of tetra- and larger congeners relative to the total sediment concentration of all congeners as a proxy for weathering. This is referred to as a weathering factor (WF). The basis for WF as a weathering proxy is that lower molecular weight congeners are expected to deplete more rapidly by diverse weathering processes (desorption, transformation) than higher molecular weight congeners, thus over time the WF should increase to a value of 1. As presented in Figure 2b, when WF is high (i.e., > 60%), the log K_{TOC} values for most congeners with five or more chlorines are significantly larger than when WF is lower (i.e., < 60%.) Although there is overlap of the log K_{TOC} values for the lower molecular weight congeners, with increasing molecular weights the log K_{TOC} values for sediments with WF values >60% show nearly complete separation from those with WF values <60%. Similarly, the linear correlation coefficients, r^2, between log K_{TOC} and WF range from ca. 0.2 for di- and trichloro- congeners to an r^2 of ca. 0.6 for the hexa- and hepta-chloro congeners (Table S7 of the SI). These results suggest that weathering can influence (or be indirectly correlated to) K_{TOC} values, and adding a factor incorporating the distribution of PCB congeners could be worthwhile in developing models to predict dissolved concentrations from sediment concentrations, as presented in the next section.

Improving K_{TOC} Predictive Models by Accounting for Weathering. In order for WF to be of practical value it should be based on commonly measured PCBs rather than requiring the measurement of the 58 congeners in our study (or all 209 congeners). On the basis of an assessment of the peer-reviewed literature and the frequency of detection in our own data, PCB-28, PCB-52, and PCB-153 were judged to be the most frequently measured. Therefore, for practical reasons, WF is defined in the remainder of this paper as follows:

$$\mathrm{WF} = (C_{\mathrm{sed,\,PCB\text{-}52}} + C_{\mathrm{sed,\,PCB\text{-}153}})/(C_{\mathrm{sed,\,PCB\text{-}28}} + C_{\mathrm{sed,\,PCB\text{-}52}} + C_{\mathrm{sed,\,PCB\text{-}153}}) \quad (9)$$

The WF term can then be used to estimate the effect of weathering using eq 9:

$$\log K_{\mathrm{TOC}} = \log K_{\mathrm{TOC,\,ref}} + \log \mathrm{WF} \quad (10)$$

Where log $K_{TOC,ref}$ refers to a reference log K_{TOC} value for highly weathered sediments having a WF value near 1. This equation predicts that, as sediments become more weathered (or as the relative abundance of low molecular weight congeners decreases compared to higher molecular weight congeners) the log K_{TOC} value approaches log $K_{TOC,ref}$. On the basis of the good agreement for sediments with high WF values in Figure 2b with the coal tar models, predictions from these two models (eqs 7 and 8) are tested here for their use as $K_{TOC,ref}$. Measured $K_{TOC,ref}$ (calculated as log K_{TOC} − log WF) values for individual sediments are compared to coal tar PP-LFER and Raoult's Law estimations in Table S8 of the SI and plotted in Figure S1 of the SI. For all congeners, the average difference between experimentally derived and predicted log $K_{TOC,ref}$ values were 0.00 ± 0.20 for the PP-LFER model and 0.03 ± 0.41 for the Raoult's Law model. The bigger scatter for the Raoult's Law model is likely due to the experimental uncertainty in S_L^* values. Without including the WF correction in eq 10, log K_{TOC} measured values were, on average, lower than predicted values by −0.25 ± 0.19 using the coal tar PP-LFER and by −0.22 ± 0.42 using the Raoult's Law model. Thus, this recommended WF correction, which did not require any calibration, resulted in increased accuracy of the predicted log K_{TOC} values.

Calibrated vs Non-Calibrated Models. If one was simply interested in estimating the typical log K_{TOC} value for all 209-PCB congeners and not in the partitioning mechanism of HOCs in general, then a PCB-specific QSAR approach that simply accounts for the molecular structure and size of the PCB would be the most straightforward approach. Such QSARs include that by Hansen et al.[14] based on the total surface area of the PCB, or the following QSAR based on the number and position of the Cl groups:[2]

$$\log K_{\mathrm{TOC}} = \mathrm{m}(N_{\mathrm{Cl}} - N_{\mathrm{ortho\text{-}Cl}}) + b \quad (11)$$

where N_{Cl} is the total number of chlorines, $N_{ortho\text{-}Cl}$ is the number of ortho-chlorines, and m and b are least-squares regression coefficients. Using the data in the present work, the m and b values are 0.52 ± 0.11 and 5.13 ± 0.55, respectively. Calibrating this equation additionally with all known data in the literature (compiled from refs 2 and 9), resulting m and b values are 0.53 ± 0.12 and 4.98 ± 0.79, respectively.

On the basis of the work presented here for modeling log K_{TOC} values of PCBs in historically impacted sediments, the following three models are recommended in which eq 12 is a calibrated QSAR model, eq 13 is the noncalibrated WF-adjusted coal tar PP-LFER model and eq 14 is the WF-adjusted Raoult's Law model.

$$\log K_{\mathrm{TOC}} = 0.53(N_{\mathrm{Cl}} - N_{\mathrm{ortho\text{-}Cl}}) + 4.98 \quad (12)$$

$$\log K_{\mathrm{TOC}} = 0.50E - 0.35S - 1.16A - 4.46B + 3.86V + 0.16 + \log \mathrm{WF} \quad (13)$$

$$\log K_{\mathrm{TOC}} = -\log(S_L^* \mathrm{MW}_{\mathrm{TOC}}) + \log \mathrm{WF} \quad (14)$$

These three models are compared in Figure 3, and their summary statistics are presented in Table S9 of the SI. Overall, the WF-adjusted coal-tar PP-LFER model (eq 13) exhibits the best performance. It predicts K_{TOC} values (and therefore would predict dissolved concentrations from sediment concentrations) within factors of 3, 10, and 30 with frequencies of 72%, 97%, and 100%, respectively. In comparison, the calibrated QSAR model predicts within the same factors with frequencies of 64%, 97%, and 100%, respectively (Table S9 of the SI). Thus, the noncalibrated models in eq 13 work better than the QSAR specifically calibrated to the same field data. The WF inclusive coal-tar PP-LFER (eq 13) is therefore considered quite robust.

Implications for Future Studies. The measurements presented here are the largest collection of K_{TOC} values of PCBs for historically impacted sediments available using a consistent method. These data confirmed earlier expectations in the literature that two-carbon models are not superior to one-carbon models for estimating partitioning of PCBs, and that average sorption behavior can be reasonably accounted for by Raoult's Law (eq 8) and the coal tar PP-LFER model (eq 7).[2,3] This provides further support that these models are suitable for deriving typical K_{TOC} values of other HOCs in impacted sediments. The average K_{TOC} values could be better accounted for by including a congener molecular weight fraction, WF, as a proxy for weathering. Further studies are recommended to test, modify, or gain deeper insight into the correlations between WF and log K_{TOC}.

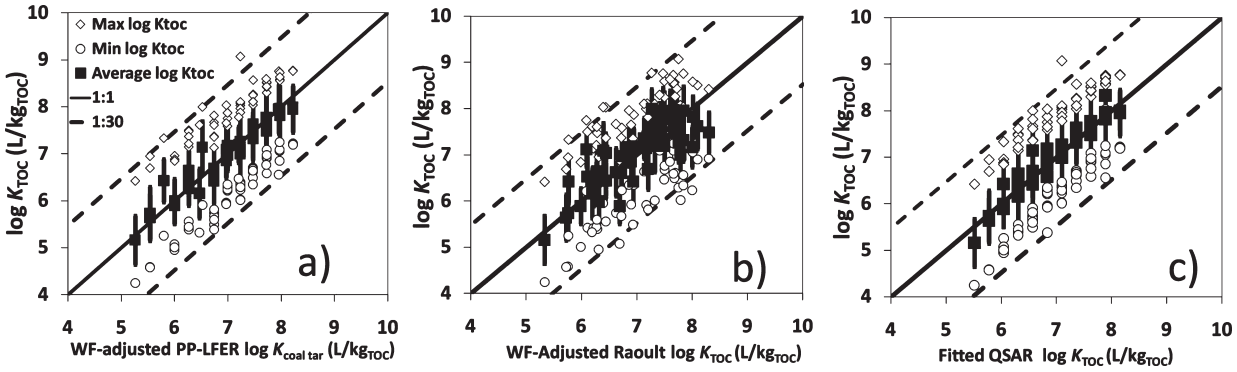

Figure 3. Comparison of experimental log K_{TOC} values for PCB congeners in 53 impacted field sediments with the estimations from the best performing noncalibrated models: (a) WF-adjusted coal tar PP-LFER (eq 13) and (b) WF-adjusted Raoult's Law (eq 14). Also shown is (c) a comparison with estimations based on a calibrated Cl-substituent based QSAR model (eq 12).

Although the redox potentials of the sediments were not measured, the success of the WF factor suggests that redox potentials could be useful, since bacterial dechlorination occurs under anoxic conditions, and would therefore influence WF values. Further tests could be done to study the influence of sediment site, such as marine vs freshwater (which was not done here as only six of the sediments are from marine water). PCB sources, if known, could also be included to refine the modeling.

The predictive models recommended here (eqs 12−14) should be applicable to all 209 PCB-congeners and are superior to previous models used for risk assessments. Consideration of these models in guidelines and risk assessments is warranted. However, it should be kept in mind that the error associated with these predictions is up to a factor of 3, 72% of the time. In situations where this is not acceptable, directly measured freely dissolved porewater concentrations should be obtained.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. TOC, BC, and PCB sediment concentrations and porewater freely dissolved concentrations are reported for all sediments and all congeners measured in this work. Electronic copies of the concentration data are available as Excel spread sheets from the corresponding author. Additional model results, a list of acronyms, and a data quality statement are also included. This material is available free of charge via the Internet at http://pubs.acs.org.

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