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Estimating the in situ Sediment−Porewater Distribution of PAHs and Chlorinated Aromatic Hydrocarbons in Anthropogenic Impacted Sediments

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It has become increasingly apparent that the *in situ* sediment−porewater distribution behavior of organic compounds within anthropogenic impacted sediments is quite diverse, and challenging to generalize. Traditional models based on octanol−water partitioning generally overestimate native porewater concentrations, and modern approaches accounting for multiple carbon fractions, including black carbon, appear sediment specific. To assess the diversity of this sorption behavior, we collected all peer-reviewed total organic carbon (TOC)-normalized in situ sediment−porewater distribution coefficients, K_{TOC}, for impacted sediments. This entailed several hundreds of data for PAHs, PCBs, PCDD/Fs, and chlorinated benzenes, covering a large variety of sediments, locations, and experimental methods. Compound-specific K_{TOC} could range up to over 3 orders of magnitude. Output from various predictive models for individual carbonaceous phases found in impacted sediments, based on peer-reviewed polyparameter linear free energy relationships (PP-LFERs), Raoult's Law, and the SPARC online-calculator, were tested to see if any of the models could consistently predict literature K_{TOC} values within a factor of 30 (i.e., ~1.5 orders of magnitude, or half the range of K_{TOC} values). The Raoult's Law model and coal tar PP-LFER achieved the sought-after accuracy for all tested compound classes, and are recommended for general, regional-scale modeling purposes. As impacted sediment−porewater distribution models are unlikely to get more accurate than this, this review underpins that the only way to accurately obtain accurate porewater concentrations is to measure them directly, and not infer them from sediment concentrations.

Introduction

Since the industrial revolution anthropogenic particulates, residues, and chemicals have impacted coastal and harbor sediments by processes such as urban runoff, sewage discharge, oil spills, shipping, and the dumping of manufactured gas plant and smelter residues. The term "anthropogenic impacted sediments" has often been used to describe these sediments, heavily burdened with both anthropogenic particles and contaminants. A central process governing their ecological consequence is how organic contaminants are distributed between the sediment and porewater phases. Whereas sediment-bound contaminants are generally benign, if they can enter the porewater phase they can be considered bioavailable to benthic organisms and able to contaminate the overlying water (*1*−*3*). However, due to the diversity of impacted sediment types and contamination sources, a validated, general predictive model for the distribution behavior of all impacted sediments is still lacking.

Classically, it has been assumed that the dominating sorption phase in both natural and impacted sediments and soils is the total organic-carbon fraction, TOC. Thus, measured sediment−porewater and soil−porewater distribution coefficients are commonly normalized to TOC, and are referred to as K_{TOC} or K_{OC} values (e.g., *1, 2*). This was largely because early environmental chemists attributed sorption in natural sediments and soils to natural organic matter (NOM) (e.g., (*3*)), and assumed TOC was a suitable measure of the NOM content. Another early assumption by researchers was that K_{TOC} values in general are log−log linearly proportional to the octanol−water partition constant, K_{OW}, as octanol was put forth as a suitable surrogate for TOC (or NOM) (*2, 4*). This view has long been orthodox, and has functioned well in laboratory experiments for sediments spiked with high concentrations of PAHs and chlorinated hydrocarbons. However for impacted sediments, as will be elaborated presently, the appropriateness of normalizing sediment−porewater distribution to TOC, the assumption that TOC consists solely of NOM, and the appropriateness of octanol as a TOC surrogate have all been questioned by many.

Hawthorne and co-workers (*5*) established a large, consistent, and comprehensive data set of log K_{TOC} values of various native polycyclic aromatic hydrocarbons (PAHs) for over 114 highly varying impacted sediments. From this they were clearly able to distinguish that PAH-specific K_{TOC} values are distributed over 3 orders of magnitude. Further they noted that traditional log K_{TOC}−log K_{OW} relationships correspond to only the lowest range of measured K_{TOC} values. Several other researchers have also observed that in situ field K_{TOC} are ≫ than those predicted with this classical relationship with K_{OW} (*6*−*8*). There are several possible reasons to account

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for this deviation: (1) partitioning to impacted sediments and other environmental phases has been found to often be nonlinear, in that log K_{TOC} values at high concentrations (typical for spiked sediments in laboratory experiments) are $\ll$ log K_{TOC} at low concentrations (typical for field conditions) (*9–14*); which is significant as traditional log K_{TOC}–log K_{OW} relationships were based on spiked sediments at relatively high concentrations; (2) for impacted sediments, NOM is just a subset of the TOC phase, which needs to be taken into consideration as other carbonaceous phases present (e.g., soot, coal) can potentially sorb much stronger than NOM and log K_{TOC}–log K_{OW} relationships (*8, 15*); (3) specifically for PAHs, a portion of the native PAHs can be entrapped in soot and coal fractions during their genesis, and thus not fully available for partitioning (*16, 17*). Log K_{TOC}–log K_{OW} relationships in general have also been criticized for the fact that they are inherently compound-class specific (*18*). Thus, in order to be successful, log K_{TOC}–log K_{OW} relationships do not only have to be recalibrated for different sediments, but different compound classes as well.

To understand why natively occurring contaminated sediments sorb stronger than traditional TOC models, several researchers have sought to isolate strong-sorbing phases and characterize nonlinear sorption behavior. One of the most supported candidates for being responsible for both strong sorption and nonlinear sorption behavior is the black carbon (BC) fraction, which is composed mainly of graphite-like nanostructures formed from incomplete combustion processes, such as diesel soot (*19*), and exhibits a strong propensity for adsorption (*8, 20, 21*). Thus, the use of a dual mode two-carbon type model, i.e., $K_{AOC}K_{BC}$, has been advocated, which accounts for additive *nonlinear adsorption* to BC components (*20, 22, 23*) with *linear absorptive* partitioning into amorphous organic carbon components (AOC) (which is generally defined as the non-BC fraction, and assumed to be NOM though it may contain other phases). This approach has met some success, especially for specific sediments and location-specific modeling studies (e.g., *23, 24*). However, some doubts about whether this model works well for all types of impacted sediments has recently emerged. Hawthorne et al. (*25*), using the same set of 114 sediments as in ref *5*, demonstrated $K_{AOC}K_{BC}$ models show no significant improvement over K_{TOC} models for the general prediction of the sediment–porewater distribution. Further, alternative strong sorption phases in impacted sediments have been identified that may be a subset of the AOC fraction, these include coal tar (*26, 27*), thermally unstable CGCs such as unburnt coal and inertinites (*8, 15, 28–30*), oil (*31*), and weathered oil residues (*32*). Further, challenging the notion that there are generic K_{AOC} and K_{BC} values that can be used in predictive models, a number of processes can influence sorption to the various adsorbing and absorbing phases, such as pore blocking (e.g., *33–35*), surface attenuation by water, organic matter, and organic compounds (*36, 37*), aging processes (e.g., (*32*)), sorption hysteresis (e.g., (*38*)), and variations in sorption nonlinearity of both the adsorbing and absorbing components (e.g., *35, 39*).

The complexity of factors that can influence partitioning to diverse impacted sediments indicates that to develop a general partitioning model there are two general avenues of approach: (1) try and be more mechanistically explicit than the K_{AOC}–K_{BC} model by accounting for the contribution of all sorbents, attenuation factors, aging factors, hysteresis factors, and nonlinear behavior; (2) stick with the empirical approach, accepting high heterogeneity of K_{TOC} over 3 orders of magnitude as the status quo, and thus develop or validate a K_{TOC} model that cut rights through the middle of this scatter. This second approach is the most attainable one for general predictive purposes, and is followed up here within this critical review.

Here a thorough literature search was conducted to obtain and analyze as many measured values of in situ log K_{TOC} as possible for anthropogenic impacted sediments. To identify a suitable general partitioning model, rather than simply *calibrate* a new general log K_{TOC}–log K_{OW} or dual mode K_{AOC}–K_{BC} relationship for all impacted sediments, here we set out to *validate* if established models for individual carbonaceous phases found in impacted sediments correlate well with median literature K_{TOC} values. The models tested here include polyparameter linear-free energy relationships (PP-LFERs) for coal tar, lignite, peat, humic acids (HA), aliphatic-NAPLs (diesel, hexadecane, *n*-octanol), and granular activated carbon (GAC); additionally, models based on Raoult's Law and the SPARC online calculator (*40, 41*) are also tested. The approach used here has two distinct advantages over calibrating new K_{TOC}–log K_{OW} or K_{AOC}–K_{BC} relationships. First, as no sorption surrogate (e.g., octanol, BC) is being assumed, it allows for a fresh evaluation of various sorption surrogates. Second, most of tested models have been found to be suitable for diverse polar and nonpolar compounds, which increases the likelihood that chemicals outside of the validation data set exhibit accuracy comparable to those tested. As will be presented below, some of the tested models gave predictions within the desired accuracy, i.e., able to predict literature log K_{TOC} consistently within a factor 30 (~1.5 orders of magnitude), and are thus considered the most accurate general in situ partitioning models feasible for PAHs and chlorinated aromatic hydrocarbons in impacted sediments. Implications of these modeling approaches are herewith discussed for the purposes of regional-scale multimedia modeling and risk/remediation assessments.

Methods

Sediment–Porewater Partitioning. The TOC-normalized sediment–porewater distribution coefficient is defined as:

$$K_{TOC}\ (L_{pw}/kg_{TOC}) = C_{sediment}/(C_{pw} \cdot f_{TOC}) \qquad (1)$$

where $C_{sediment}$ (mol/$kg_{sediment\ d.w.}$) is the amount of contaminant sorbed to dry-weight of sediment at equilibrium, C_{pw} (mol/L_{pw}) is the equilibrium porewater concentration, and f_{TOC} ($kg_{TOC}/kg_{sediment\ d.w.}$) is the weight fraction of TOC in the dry sediment.

K_{TOC} Data Acceptance and Exclusion. All K_{TOC} values based on native, in situ sediment–porewater concentration ratios, and not from spiked sediments, we could find in the peer-reviewed literature were collected. In cases where K_{TOC} values were not provided they were calculated from available sediment and porewater concentration data, provided that the data were for the same sediment sample (and not averages of many samples), and porewater data was for the "freely dissolved" and not "total aqueous" phase. K_{TOC} values calculated from sediment–overlying water concentration data were not included, as the overlying water is commonly not in equilibrium with the sediment porewater (*42–44*). Further, only data for settled sediments are used, and not from sediment sources (such as urban runoff particles, industrial residues, etc.). There was no differentiation made according to how the sediment and porewater concentrations were determined, be they solvent extraction, passive sampler extraction, etc., nor was there any differentiation according to temperature, aqueous phase properties (including salinity), or how the TOC was determined. Though in cases where "slow sorbing" and "fast sorbing" fractions were differentiated, the "slow sorbing" fractions were used (e.g., (*45*)). Further, no discrimination was made according to the location (e.g., river, harbor, or ponds) or contaminant sources. Thus the data set includes a wide variety of experimental methods, locations, sediment types, and contaminant sources. Following these criteria, data for four classes of contaminants

TABLE 1. PP-LFER Sorbent Descriptors for Carbonaceous Phases and Surrogates of Carbonaceous Phases Typically Found in Sediments (20−25 °C)[a]

	e	*l*[b]	*v*	*a*	*b*	*s*	*c*	*n*	ref
coal tar	0.50	n.a.	3.86	−1.16	−4.46	−0.35	0.16	69	*64*[c]
peat (low)	0.31	n.a.	3.71	−0.10	−3.94	1.27	−1.04	51	*10*
peat (high)	0.43	n.a.	3.51	0.02	−3.83	0.19	−0.82	51	*10*
lignite (low)	0.44	n.a.	3.74	−0.26	−3.43	0.45	−0.28	58	*10*
sedimentary NOM	1.08	n.a.	2.55	0.28	−1.85	−0.83	−0.12	75	*61*[d]
Leonardite HA	n.a.	0.29	2.52	−0.49	−3.08	−0.93	0.27	95	*62*[e]
hexadecane	0.67	n.a.	4.34	−3.59	−4.87	−1.62	0.09	n.d.	*65*
diesel	0.63	n.a.	4.34	−3.42	−4.82	−1.47	0.26	n.d.	*66*
n-octanol	0.57	n.a.	3.88	−0.05	−3.45	−1.06	0.03	314	*67*
GAC (low)	0.63	n.a.	5.15	−0.54	−4.50	0.04	0.72	14	*68*[f]
GAC (high)	0.02	n.a.	4.03	−0.51	−4.53	−0.28	0.85	14	*68*[f]

[a] n.a. = not applicable; n.d. = no data; (low) = calibrated at infinite dilution; (high) = calibrated at high concentration, near water saturation; *n* = number of unique compounds used for calibration; ref = reference. [b] For the PP-LFER developed for Leonardite HA the "*lL*" is used instead of "*eE*", where *L* is the compounds hexadecane−air partition coefficient and *l* is the sorbents complementary descriptor (for more information see refs *62 and 69)*. [c] Several PP-LFERs for coal tar are presented in this reference; here the one calibrated for all compounds is used. [d] The data for this PP-LFER was calibrated mainly for natural sediments, and not impacted sediments, and using all compound data in the cited reference and not just averaged data. [e] HA = humic acid, PP-LFER calibrated at 25 °C was used from the cited reference. [f] GAC = granular activated carbon.

could be found: chlorinated benzenes (CBs) (*44−49*), PAHs (*5, 7, 26, 44, 46, 47, 50−56*), polychlorinated biphenyls (PCBs) (*7, 44, 46, 47, 50, 51, 57*), and polychlorinated dibenzodioxins/furans (PCDD/Fs) (*7, 57−59*).

K_{TOC} data sets from individual literature sources were then reduced into up to three values per compound and per literature source: the average log K_{TOC}, the maximum log K_{TOC}, and the minimum log K_{TOC}. If only one compound-specific log K_{TOC} was given, it was considered the average, only. Thus, the "average" values here range from values taken from a diverse set of sediments (e.g., 114 sediments in ref *5*), and those from only one sediment (e.g., ref *55*). A list of all the values obtained can be found in the Supporting Information (SI, Table S1).

Partitioning Models. *PP-LFERs.* The polyparameter linear free-energy relationships tested here relate partitioning constants to five diverse sorbate−sorbent interactions descriptors based on the Abraham model (*60*). These PP-LFERs are well established as being highly accurate for both polar and apolar compounds for a large variety of environmental and biological phases (e.g., *16, 61−63*). The PP-LFERs to describe sorbent/water partitioning typically have the following form:

$$\mathrm{Log}\, K = eE + vV + aA + bB + sS + c \qquad (2)$$

where the capital letters *E*, *V*, *A*, *B*, and *S* are the compound-specific parameters describing the excess molar refraction, the molar volume, electron acceptor (i.e., H-bond donor) capability, electron donor (i.e., H-bond acceptor) capability, and the polarizability/dipolarizability, respectively. Corresponding to the compound-specific parameters are the complementary sorbent-specific parameters, *e*, *v*, *a*, *b*, and *s*. The constant *c* is dependent on the sorbent and units of *K*.

Sorbent-specific parameters have been calibrated for several individual carbonaceous components that can be found in impacted sediments. These include the absorbents coal tar, peat, sedimentary NOM, humic acids (HA), aliphatic NAPLs (e.g., hexadecane, diesel, and *n*-octanol) and adsorbents lignite and GAC. These are presented in Table 1. Note the PP-LFERs for peat, lignite, and GAC in Table 1 are labeled "(low)" or "(high)" to differentiate whether they were calibrated for low porewater concentrations (at infinite dilution) or at high porewater concentrations (near water saturation), thereby accounting for the nonlinearity of the sorption isotherms. Compound-specific descriptors for the compounds considered in this study are included in the SI.

Raoult's Law. Applied to sorbent−aqueous partitioning, Raoult's Law would assume that the nonaqueous phase, in this case the impacted sediment TOC, is an ideal solvent, i.e., that the compound is as equally miscible in the TOC phase as it is miscible within a phase consisting of the compound itself. From this, it can be derived that (*2*):

$$K_{TOC}\ (\mathrm{L_{water}/kg_{TOC}}) = \frac{1}{C_w^{sat}\mathrm{MW_{TOC}}} \qquad (3)$$

where C_w^{sat} is the *subcooled* saturated molar water solubility ($\mathrm{mol/L_{water}}$) and $\mathrm{MW_{TOC}}$ is the molar weight of the sediment's organic phase ($\mathrm{kg_{TOC}/mol_{TOC}}$). To test this model, experimental C_w^{sat} data at 25 °C were obtained by compilations by van Noort (*70−72*). Otherwise, nonsubcooled data were obtained from the PhysProp database, (Syracuse Research Corporation (www.syrres.com) accessed February 4, 2009 and additionally on April 16, 2009), and corrected to the subcooled state using the experimental or estimated fugacity ratios following van Noort (*70−72*). Predicted C_w^{sat} values using the SPARC online-calculator (see the next section) were also obtained for model testing. The $\mathrm{MW_{TOC}}$ estimation method for use in this model is presented later.

SPARC Online-Calculator. SPARC is a free, online Web application (http://ibmlc2.chem.uga.edu/sparc/) that explicitly calculates sorbate−sorbent interactions by using various empirical molecular descriptors that are derived explicitly from molecular structure (*40, 41*). Unlike the above approaches, no experimental data are needed as a prerequisite (such as PP-LFER descriptors or C_w^{sat}). Instead, a suitable molecular structure (or combination of molecular structures) is needed to represent the sorbing phase. Here, various molecules are tested as surrogates for impacted sediment TOC, as will be presented based on the PP-LFER analysis below. Model predictions were done at 25 °C and for the subcooled state of the sorbates. Data were retrieved using v4.2, accessed Febuary 5−15, 2009, and additionally on April 15, 2009.

Results and Discussion

Literature Search. All experimental average, maximum, and minimum in situ log K_{TOC} values that met the selection criteria are presented in Table S1 in the SI. The distribution of log

TABLE 2. Comparison of Various PP-LFER log K_{TOC} Estimations with Collected Experimental Average, Maximum, and Minimum in situ Values from the Literature for Impacted Sediments[a]

PP-LFER	PAH	PCB	CB	all
	compound class			
	average difference between estimated and measured log K_{TOC}			
coal tar	**−0.3 ± 0.9**	**0.4 ± 0.5**	−0.5 ± 0.7	**−0.1 ± 0.9**
peat (low)	0.4 ± 1.1	1.1 ± 0.7	−0.8 ± 0.7	0.5 ± 1.1
peat (high)	−1.1 ± 1.0	−0.5 ± 0.6	−1.5 ± 0.7	−1.0 ± 0.9
lignite (low)	0.4 ± 1.0	1.0 ± 0.6	−0.5 ± 0.7	0.5 ± 1.0
sedimentary NOM	−1.2 ± 1.0	−1.8 ± 0.5	−2.1 ± 0.7	−1.5 ± 0.9
Leonardite HA	−1.6 ± 1.0	−1.3 ± 0.5	−1.3 ± 0.7	−1.5 ± 0.8
hexadecane	−1.3 ± 1.0	−0.5 ± 0.5	−1.0 ± 0.7	−1.0 ± 0.9
diesel	−1.0 ± 1.0	−0.2 ± 0.5	−0.7 ± 0.7	−0.7 ± 0.9
n-octanol	−1.0 ± 0.9	−0.6 ± 0.5	−1.2 ± 0.7	−0.9 ± 0.8
GAC (low)	3.3 ± 1.2	4.3 ± 0.8	1.9 ± 0.8	3.4 ± 1.3
GAC (high)	−0.6 ± 1.0	0.5 ± 0.6	**−0.1 ± 0.7**	−0.2 ± 1.0
	number of unique compounds and K_{TOC} values			
unique Compounds	21	24	10	55
unique K_{TOC} values	267	142	64	473

[a] Negative values indicate under-predictions by the respective PP-LFER model; best agreements are in bold font.

K_{TOC} of PAHs over 3 orders of magnitude measured for 114 samples by Hawthorne et al. (*5*) using a consistent experimental method reflects the distribution of log K_{TOC} values for PAHs found in the literature as a whole, covering 13 citations which used varying experimental methods. There was no instance of PAH log K_{TOC} values being lower than that of Hawthorne's data set, and only rare instances of values being higher. The higher values were all for sediments from Lake Ketelmeer, The Netherlands, mostly determined using a cosolvent method. Jonker et al. (*46*) reported log K_{TOC} benzo(ghi)perylene, benzo(e)pyrene, Indeno[1,2,3-cd]pyrene, benzo(a)pyrene, and dibenz[a,h]anthracene that were 0.4, 0.4, 0.4, 0.7, and 0.8 log units higher than the maximum value by Hawthorne et al., respectively. ten Hulscher et al. (*47*) reported a value for 2-methyl naphthalene that was 1.1 log unit higher than the maximum value by Hawthorne et al.

For compound classes other than PAHs, much fewer data are available. The most diverse data set is available for PCBs, covering 142 average, minimum, and maximum in situ K_{TOC} values, 24 compounds, and 7 citations. Data for CBs were found for 10 compounds, covering 64 average, minimum, and maximum in situ K_{TOC} values over 6 citations. Data for PCDD/DFs were available for 26 congeners, covering 83 average, minimum, and maximum in situ K_{TOC} values from 4 citations. Obtained K_{TOC} values for the CBs varied from 1 to over 2 orders of magnitude, with the maximum deviation for 1,4-dichlorobenzene (2.37 log units) (Table S2). Deviations for the compound-specific K_{TOC} values for the PCBs and PCDD/Fs generally varied between 1 and 2 orders of magnitude (Table S2). Thus, there does appear to be less variability of the log K_{TOC} values of these chlorinated compounds compared to PAHs; however, this cannot be said definitively, as the data set for PAHs is much more diverse. Thus, as a safe assumption, it is assumed here that compound-specific in situ log K_{TOC} can vary up to 3 orders of magnitude for varying impacted sediments.

PP-LFER Analysis. In Table 2, experimental average, maximum, and minimum log K_{TOC} values are compared with PP-LFER predictions for phases that could potentially represent the TOC phase of impacted sediments (listed in Table 1). Note that PCDD/Fs are not included in the validation data set, as the necessary compound descriptors are not yet available for these compounds. From Table 2, it is evident that the coal tar PP-LFER predictions were generally the closest to experimental values (average −0.1 ± 0.9 log units). The only other PP-LFER to give comparable predictions was for GAC (high) (average −0.2 ± 1.0 log units). The GAC (low) predictions gave the most overestimated values (average 3.5 ± 1.2 log units). Predictions using peat (low) and lignite (low) overestimated log K_{TOC} values on average (by 0.5 ± 1.1 and 0.5 ± 1.0 log units, respectively). Thus, GAC, peat, and lignite at low sorbate concentrations appear to be even stronger sorbents than impacted sediment TOC. The sedimentary NOM model gave the most underestimated values (−1.5 ± 0.9), with predictions often being smaller than the lowest reported log K_{TOC} value (see the SI Part 5). Other models to give underestimations, typically by an order of magnitude, were peat(high), Leonardite HA, diesel, hexadecane, and *n*-octanol (with deviations being −1.0 ± 0.9, −1.5 ± 0.8, −0.7 ± 0.9, −1.0 ± 0.9, and −0.9 ± 0.8 log units, respectively). Based on the findings by Niederer et al. (*73*) that Leonardite HA is one of the strongest sorbing HAs available, PP-LFERs for other HAs will thus result in even larger understimations.

To illustrate the agreement between literature in situ K_{TOC} values with coal tar PP-LFER predictions, average literature predictions are plotted against coal tar PP-LFER predictions in Figure 1a; additional maximum and minimum log K_{TOC} values are included in Figure 1b.

As can be seen in Figure 1, the coal tar PP-LFER predictions are generally within a factor 30 of the most extreme reported values for PAHs, PCBs, and CBs, and thus, this model performs within the desired accuracy. The only noticeable outlier in Figure 1a is the value for 2-methyl naphthalene reported in ref *47*.

Raoult's Law and SPARC Models. Based on the results of the PP-LFER analysis, the MW_{TOC} value needed for the Raoult's Law predictions in eq 3 is assumed to be that of coal tar, which is here considered to be 0.223 kg_{TOC}/mol, based on a MW reported for coal tar consisting of 90% TOC being 0.248 kg/mol (*64*). As MW_{TOC} is a property of the sorbing phase, any error in this value when applied to eq 3 would appear as a systematic error for all compounds (i.e., if this value were too low, systematic overestimations would result).

With the SPARC online calculator, essentially any organic molecular input structure could have been tested to represent the TOC phase. However, as the PP-LFER analysis revealed coal tar and GAC(high) to give the best predictions, only suitable molecular surrogates for these phases were considered here. Both phases can be considered to be "PAH-like", as coal tar contains a large fraction of PAHs and aromatic structures (*66, 74, 75*), and GAC is essentially comprised of very large PAH structures. Correspondingly, Endo et al. (*64*) have validated the use of naphthalene and an 85:15 mixtures of naphthalene/quinoline as suitable SPARC input surrogates

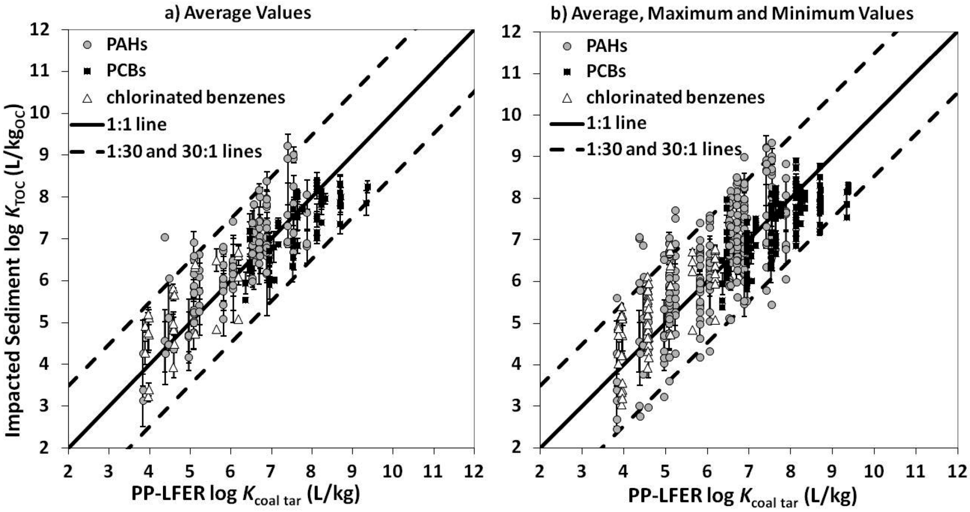

FIGURE 1. Impacted sediment in situ literature log K_{TOC} (~room temperature) values vs those predicted using the PP-LFER for coal tar (20 °C), showing (a) average values from the literature, and (b) average, maximum, and minimum values from the literature.

TABLE 3. Comparison of Various Raoult's Law and SPARC log K_{TOC} Estimations with Collected Experimental Average, Maximum, and Minimum in situ log K_{TOC} Values for Impacted Sediments from the Literature[a]

	compound class					
model	PAH	PCB	PCDD/F	CB	all	all except PCDD/F
	average difference between estimated and measured log K_{TOC}					
Raoult's law models						
experimental C_w^{sat}	**0.0 ± 1.0**	**0.2 ± 0.6**	**0.1 ± 0.8**	−0.3 ± 0.8	**0.0 ± 0.9**	**0.0 ± 0.9**
SPARC C_w^{sat}	**0.0 ± 1.0**	1.1 ± 0.8	1.8 ± 1.2	−0.6 ± 0.9	0.5 ± 1.2	0.2 ± 1.1
SPARC models						
coronene	**0.0 ± 1.0**	1.6 ± 0.9	2.1 ± 1.2	−0.3 ± 1.0	0.7 ± 1.4	0.4 ± 1.2
naphthalene	0.2 ± 1.0	1.8 ± 0.9	2.3 ± 1.2	−0.1 ± 1.0	0.9 ± 1.3	0.7 ± 1.2
naphthalene/quinoline (85:15)	0.2 ± 1.0	1.8 ± 0.9	2.2 ± 1.2	**−0.1 ± 0.9**	0.9 ± 1.3	0.7 ± 1.2
naphthalene/water (95:5)	−0.1 ± 1.0	1.2 ± 0.8	1.4 ± 1.1	−0.3 ± 0.9	0.4 ± 1.2	0.3 ± 1.1
naphthalene/water (92:8)	−0.5 ± 1.0	0.7 ± 0.8	0.8 ± 1.0	−0.6 ± 0.8	**0.0 ± 1.1**	−0.2 ± 1.1
naphthalene/water (90:10)	−0.9 ± 1.0	0.3 ± 0.7	0.3 ± 1.0	−0.8 ± 0.8	−0.4 ± 1.0	−0.5 ± 1.0
	number of unique compounds and K_{TOC} values					
unique compounds	21	24	26	10	81	55
unique K_{TOC} values	267	143	83	64	557	474

[a] Negative values indicate under predictions by the respective model. Best agreements are in bold font.

for coal tar, and thus these surrogates were tested here. Additionally, various naphthalene/water mixtures (ranging from 0−10% water) were tested to account for potential water saturation of the TOC phase. In Table 3, experimental values are compared with Raoult's law predictions along with SPARC-predictions using these various molecular TOC surrogates. The predicted values themselves are presented in Part 3 of the SI.

Comparing the Raoult's Law and SPARC predictions with each other in Table 3, it is evident that predictions based on experimental Raoult's Law C_w^{sat} values outperformed all other models tested, deviating on average a maximum of 0.3 log units for an individual contaminant class, and 0.0 ± 0.9 overall, and thus performed within the desired accuracy, and even better than the coal tar PP-LFER. It should be noted here that correcting for the subcooled liquid C_w^{sat} was essential, especially for large PCBs and PCDD/Fs. Nonsubcooled values were orders of magnitude different from subcooled values for larger congeners, and when used resulted in an extremely poor agreement with log K_{TOC} values (see the SI, Figure S1). None of the tested SPARC models performed as well as the Raoult's Law model, nor the coal-tar PP-LFER. The best model overall was the 92:8 naphthalene/water mixture, with deviations on average of −0.2 ± 1.1 log units, though with unsatisfactory estimations for the PCBs and PCDD/Fs (particularly for the larger PCBs and PCDD/Fs, see the SI Part S4).

The agreement between literature log K_{TOC} and estimations from experimental C_w^{sat} based Raoult's Law model and the 92:8 napthalene/water SPARC model is shown in Figure 2.

To obtain a better overview of systematic biases in each of the model predictions, such as those related to compound class and molecular size, vertical plots comparing several of the model predictions with the range of experimental values are presented in Section S5 of the SI.

Experimental Biases. Experimental biases were ignored in this study, as they are assumed to be minimal compared to variations attributable to sediment diversity. However, large generic biases across all experimental methods may have influenced the comparisons here. One potential generic bias is that highly chlorinated PCBs and PCDD/Fs are challenging to detect in the porewater phase regardless of the experimental method used, and have a tendency to be positively biased (e.g., due to concentrations lower than the detection limit reported as the detection limit, contamination by DOC, uncertainty in $K_{sampler/porewater}$ values, etc.). This may have contributed to literature K_{TOC} values of the largest PCBs and PCDD/Fs being negatively biased, which would be a

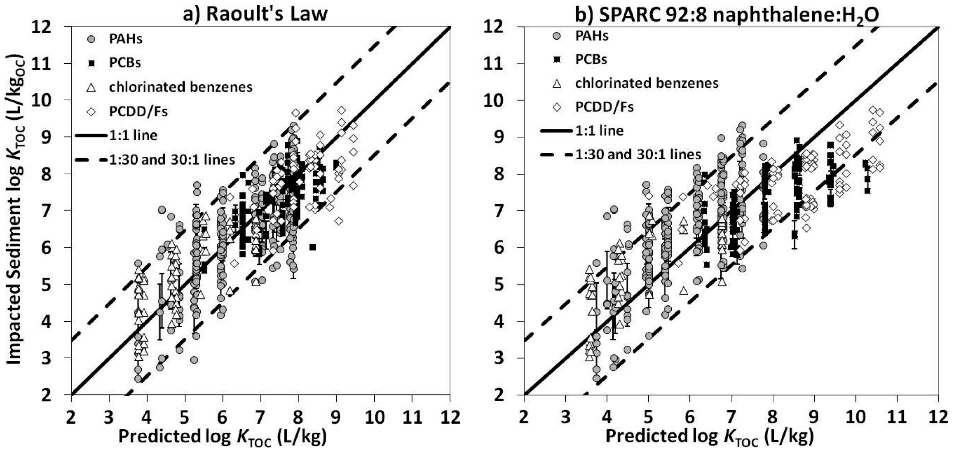

FIGURE 2. Literature maximum, minimum, and average in situ log K_{TOC} (∼room temperature) values for impacted sediments vs values predicted based on (a) Raoult's law and (b) using a 92:8 naphthalene/water mixture as a TOC sorbent surrogate with the SPARC online calculator (v 4.2, 25 °C).

contributing factor for the increasing deviation between literature and predicted log K_{TOC} values as log K_{TOC} values increase for many models (in Figures 1 and 2, S1-10). A possible generic bias for PAHs may be caused by these compounds being formed alongside many particulate phases during their genesis (e.g., coal, soot, etc.), and thus fusing deep within the particle matrix. If some of this matrix-bound PAH fraction is not at all exchangeable with porewater though readily solvent-extractable (*17, 76*), this would cause experimental log K_{TOC} values to be positively biased. This could account somewhat for the largest scatter of log K_{TOC} being for PAHs, and the largest under-predictions of the best performing models being for PAHs (see Figures 1 and 2). Similarly, deviations may have also arisen from the tested models not being calibrated with experimental data for very large molecules, such as those studied here, which would lead to extrapolation-related biases (*10*).

Recommended Models. *PP-LFERs.* The coal tar model is considered the most appropriate PP-LFER model, not only because of it resulting in the best correlations with experimental data, but also because it was calibrated with a larger number of compounds than the second best performing GAC(high) model ($n = 69$ vs $n = 14$, respectively). TOC sorbent phase descriptors can be strongly influenced by the diversity of the calibration data set (*10*), thus it is possible the calibrated GAC(high) descriptors might change somewhat if they are calibrated for a larger set of compounds. Recommending the coal tar PP-LFER does not suggest that coal tar is the dominating sorption phase of impacted sediments, but merely that it is an appropriate sorption surrogate for general predictive purposes. However, coal tar as an appropriate sorption surrogate can be defended empirically: (1) coal tar itself has been clearly identified as the major sorbing phase in several impacted sediments and sources, such as in urban harbors (*27*), manufactured gas plants (*26*), and smelter residues (*74, 77*); (2) coal tar like other anthropogenic carbonaceous phases in impacted sediment is rich in aromatic (BC, PAHs) and aliphatic structures (NAPLs) (*66, 74, 75*), thus also contains an AOC/BC type matrix; (3) coal tar and weathered oil residues have been reported to exhibit K_{TOC} values (*32*) that are quite similar to other components found in sediments such as BC, coal, or kerogen (*8, 15*).

Raoult's Law. The Raoult's model was the best performing, and is the most recommended when *subcooled* C_w^{sat} are available. The success of the Raoult's Law model implies that the assumption behind it, that sorbate–sorbate interactions are similar to sorbent–sorbent interactions, is appropriate. Incidentally, it has been also found that the Raoult's Law assumption works well for describing sorption to coal tar for a broad set of polar and apolar compounds, as it is apparently capable of making a broad variety of strong polar and apolar interactions (*64*). Thus, it is conceivable that anthropogenic impacted sediments may be considered an "ideal solvent", like coal tar. Further validations would be needed to verify this for other compounds.

SPARC. Though SPARC models resulted in inferior performance, they are considered the best alternative when compound-specific PP-LFER descriptors or C_w^{sat} data are not available. The best SPARC model to use depends on the compound class. Models based on Raoult's Law and coronene surrogates are recommended for PAHs and alkyl PAHs, as they gave the best correlations for PAHs. For the PCDD/Fs and other large chlorinated compounds, the 90:10 naphthalene/water SPARC model gave the best correlations, and is thereby recommended.

Average log K_{TOC} and Molecular Fragments. Though this review found that *absolute* K_{TOC} *values* for a specific compound can vary over several orders of magnitude across impacted sediments, it is still likely to be the case that *relative differences* in K_{TOC} for a specific compound class are similar within a specific sediment sample. As an example, sediment-specific K_{TOC} values measured for benzo(a)pyrene are likely to be always larger than those for naphthalene. For partitioning to pure phases, it is common to characterize the typical influence of a molecular fragment (e.g., CH_2– alkyl group, Cl– atom, etc.) with a change in the *K*- value (*2*). Thus, here, it was investigated if significant correlations could be found between literature/sample-specific K_{TOC} values and a particular molecular fragment, $N_{fragment}$ of the following form:

$$\log K_{TOC} = m \cdot N_{fragment} + b \tag{4}$$

where *m* and *b* are the slope and intercept, respectively, from a linear regression. For PAHs, $N_{fragment}$ was the number of aromatic carbons present, $N_{aro\text{-}C}$. For chlorobenzenes and PCDD/Fs, this increment was the number of chlorines present, N_{Cl}. For PCBs, this increment was also based on the number of chlorines present, however *ortho*-Cl (i.e., in the 2 or 2′ positions) only counted as "half a chlorine", because *ortho*-Cl causes the planar conformation of PCBs to be energetically unfavorable, which in turn causes lower adsorption and absorption with the surrounding media (as indicated by the "*ortho*-effect" on the S, B, and L compound descriptors, see ref *78*). Thus the increment used was "$N_{Cl} - 0.5N_{ortho\text{-}Cl}$". Based on correlations outlined in the SI (section 6), the following equations were obtained:

$$\text{for CBs:}\quad \Delta\log K_{\mathrm{TOC}} = (0.40 \pm 0.06) \times \Delta N_{\mathrm{Cl}} \tag{5}$$

$$\text{for PAHs:}\quad \Delta\log K_{\mathrm{TOC}} = (0.29 \pm 0.05) \times \Delta N_{\text{aro-C}} \tag{6}$$

$$\text{for PCBs:}\ \Delta\log K_{\mathrm{TOC}} = (0.45 \pm 0.09) \times \Delta(N_{\mathrm{Cl}} - 0.5N_{\text{ortho-Cl}}) \tag{7}$$

$$\text{for PCDDs:}\quad \Delta\log K_{\mathrm{TOC}} = (0.36 \pm 0.01) \times \Delta N_{\mathrm{Cl}} \tag{8}$$

$$\text{for PCDFs:}\quad \Delta\log K_{\mathrm{TOC}} = (0.42 \pm 0.05) \times \Delta N_{\mathrm{Cl}} \tag{9}$$

Equations 5−9 are recommended for extrapolations when log K_{TOC} values are available for only a few congeners. If data for several compound-class specific congeners for a sediment sample are available, it is more appropriate to determine the influence of a molecular fragment for that particular sample.

Role of Compound Diversity. Because the models tested here were primarily for PAHs and nonpolar compounds, we would anticipate they would give comparable predictions for other nonpolar compounds such as alkanes, brominated flame retardants (such as polybrominated diphenyl ethers), and pesticides (e.g., DDT, chlordane, dieldrin etc.); though these were not included in the validation data set. Though PP-LFERs and SPARC explicitly account for apolar and polar interactions and the Raoult's Law model may also in this case, how well these models perform for compounds with polar functional groups remains uncertain. At present, no studies on in situ impacted sediment K_{TOC} values for compounds with polar functional groups could be found, and only few studies were available reporting values for spiked polar compounds. These include values for the hormones estradiol and ethinylestradiol (*79*), and the nonionic surfactants alkyl phenols (*80, 81*) and alcohol ethoxylates (*82*). Of these compounds, currently only PP-LFER parameters exist for estradiol (SI, Table S3), of which coal tar PP-LFER prediction exhibited a nice agreement with the average literature values (deviation of 0.1 log units) (see the SI, Table S8). Of the various SPARC models, the best predictions for these compounds were from the 85:15 naphthalene/quinoline mixture (with the overall deviation being 0.0 ± 0.8 log units for all compounds, see SI, Table S9), likely because adding quinoline increases the electron donor ability of the model sorbent (*64*). However, despite these results, as the data set is limited few conclusions can be drawn from this on the suitability for all polar compounds. Additionally, for the sorption behavior of certain compounds, such as surfactants, it may be necessary to take the clay or other fractions into consideration (*83, 84*). Thus, the presented models here must be re-evaluated for polar and other compound classes, once sufficient data on their in situ porewater distribution become available.

Roles of Sorbent Heterogeneity, Mixing, Aging, and Sorption Nonlinearity. The large scatter of log K_{TOC} values found in the literature review can be attributed to the diverse sorption behavior of the various absorbing and adsorbing components found in impacted sediments. The potential diversity of this sorption behavior is evident by the sorbent PP-LFER coefficients and predictions in Tables 1 and 2 and S5 for various carbonaceous phases. As is evident, though some absorbing components have similar PP-LFER coefficients and result in similar predictions (e.g., the aliphatic-NAPLs hexadecane and diesel) others exhibit very different PP-LFER coefficients and result in very different predictions from one another (e.g., peat, coal tar, and hexadecane). Similarly, the adsorbing CGC phases lignite and GAC(high) exhibit different sorption behavior from each other. Traditional models have assumed that only CGC components exhibit substantial nonlinearity (*8*); however, substantial nonlinear partitioning isotherms have been observed in AOC components such as peat and natural organic matter (NOM) (*10, 12, 39*). This nonlinearity in natural OM can result in K_{TOC} values for natural OM to be greater than that for impacted sediments at low concentrations, though less than that for impacted sediments at higher concentrations, as is the case for peat in Table 2.

The diversity of log K_{TOC} values can be further exacerbated by the individual sediment components not always sorbing additively nor consistently, due to phenomena mentioned in the introduction such as pore blocking (e.g., (*33*)), soot-surface attenuation (e.g., *36, 37*), aging processes (*32*), and hysteresis (*38*). Thus, conceptualizing all the competing effects and concentration dependencies in lieu of the sorbent diversity indicates that it is unlikely that any single carbon fraction (e.g., AOC, BC, CGC, coal tar, aliphatic-NAPL, etc.) will be able to account for general partitioning behavior better than TOC. Further, it is also unlikely to be the case that realistic, practical multiphase carbon models can be developed for all impacted sediments. Thus, though the determination of different carbon fractions other than TOC in impacted sediments, such as BC, is extremely useful and necessary for many mechanistic studies, it is not necessary for general predictive purposes or risk assessments. This is especially the case if the ultimate purpose of a *K*-value is to infer porewater concentrations from sediment concentrations, as it has become more economical and practical to measure porewater concentrations directly, such as by use of equilibrium passive samplers (*51*).

Recommendations for Improving Predictions. To possibly improve estimation methods for impacted sediments, partitioning data could be classified into various subsets, such as by sediment source (e.g., smelter residues, coal shipping, etc.), sediment age (e.g., modern, legacy, etc.), concentration (high vs low), and known contents of various phases (e.g., BC rich, NAPL rich). This could lead to generic trends being identified, and thus form the basis for improved models. Hawthorne et al. (*5*) adopted such an approach to investigate the scatter of K_{TOC} values for PAHs, accounting for location, concentration, and the presence of NAPLs, though they were unable to find significant trends. However, such trends may be clearer to identify for other compound classes.

Models could also be improved by conducting systematic investigations of a large number of diverse sediments and probe compounds. This may lead to information on whether certain contaminants may consistently sorb on particular sorption component (e.g, surfactants preferring minerals (*83, 84*) or OM-water interfaces (*85*)), regardless of the mixture. However, a comprehensive understanding of all types of impacted sediments, even for nonpolar compounds, is a long way off. Several innovative approaches are needed, beyond simple sorption experiments, such as imaging and X-ray techniques (e.g., (*86*)) which can potentially identify the relative abundance of various organic chemicals on and within various particulates. To this end, for further mechanistic studies on the sorption of diverse organic carbon fractions to sediments, it is still important to account for sorption to various components, e.g., BC, CGC, minerals, oils, etc.

Relevance for Regional Fate Modeling. This study emphasizes that at regional scales the diversity of in situ sediment−porewater distribution of anthropogenic impacted sediments may cover 3 orders of magnitude. Thus, here we recommend that regional-scale fate modelers should account for a median sorption behavior of impacted sediments, either from the literature values in the SI or from the recommended model predictions, and account for the possibility that different areas of the impacted sediments may have maximum and minimum K_{TOC} values of ± a factor 30 of this median, such as with a sensitivity analysis.

Relevance for Risk and Remediation Assessment. For cases in which it is necessary to have determinations of porewater concentrations as accurate as possible, then these concentrations should be directly measured and not inferred from sediment concentrations. Use of inappropriate partitioning models has probably led to several inaccurate risk assessments and remediation strategies, and thus in wasted spending. Though more accurate ways of estimating sediment−porewater distribution may exist in the future, they cannot give results as accurate as directly measured porewater concentrations, and are unlikely to be more economical or as environmentally friendly due to the added resources and solvents needed to determine sediment concentrations compared to many modern porewater determination methods. Thus, researchers, regulators, and managers of impacted sediment sites are encouraged to base risk assessments and remediation strategies on measured porewater concentrations rather than inferred values.

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Supporting Information Available

Experimental and estimated K_{TOC} data, compound properties, additional plots and information. This information is available free of charge via the Internet at http://pubs.acs.org.

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