Critical Review

Polyparameter Linear Free Energy Relationships for Estimating the Equilibrium Partition of Organic Compounds between Water and the Natural Organic Matter in Soils and Sediments

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Values of the organic-carbon-based partition coefficient (K_{oc}) have often been estimated using one-parameter linear free energy relationships (op-LFERs), which include both correlations between log K_{oc} and log K_{ow}, where K_{ow} is the octanol−water partition coefficient, and op-LFERs that are based on first-order molecular connectivity indices. For chemicals with tendencies toward strong hydrogen-bonding or other specific interactions with the organic phase, however, these methods are not sufficiently accurate. Polyparameter LFERs (pp-LFERs) address these shortcomings by explicitly considering contributions toward free energy change from multiple kinds of molecular interactions with both water and bulk organic phases. This paper reviews pp-LFER theory and presents the development of a new pp-LFER for organic chemical partitioning with soil/sediment organic matter (SOM) using a data set of 356 carefully selected experimental values of log K_{oc} for 75 chemicals, including apolar, monopolar, and bipolar compounds. The paradigm of representing SOM by a single pp-LFER is qualitatively supported by our results, and the set of coefficients for the regression log K_{oc} = (1.10 ± 0.10)**E** − (0.72 ± 0.14)**S** + (0.15 ± 0.15)**A** − (1.98 ± 0.14)**B** + (2.28 ± 0.14)**V** + (0.14 ± 0.10) represents a proposed set of water−SOM-specific properties for estimating log K_{oc}. The developed correlation outperformed other currently recommended approaches with the given K_{oc} data set and also compared favorably against the use of new multiple class-specific op-LFER regressions. Overall, the pp-LFER approach is recommended over other current methods for the purpose of K_{oc} estimation and especially for polar chemicals.

Introduction

Sorption to soil and sediment organic matter (SOM) affects (and often controls) the fate of nonionic organic pollutants in the environment. The equilibrium partition of an organic chemical between aqueous solution and soil or sediment is often described by the soil/sediment−water distribution coefficient (K_d), which is the ratio of the equilibrium concentration of the chemical in the soil or sediment (q_e) to the corresponding equilibrium aqueous concentration (C_e). Numerous studies over 40 years have shown that K_d strongly depends on the fraction of organic carbon (f_{oc}) and that sorption of many nonionic solutes can often be accurately expressed by the soil/sediment−water distribution coefficient normalized to organic carbon K_{oc} (i.e., $K_d = f_{oc}K_{oc}$) (*1−7*). Although a growing body of evidence shows that this simple paradigm does not always apply (*5, 8*), linear absorption with macromolecular SOM is nonetheless a major component of sorption that can dominate solute behavior under many circumstances. Because K_{oc} is thus a critical component of fate and transport modeling (*9, 10*), it is important that this parameter be estimated as accurately as possible.

One-parameter linear free energy relationships (op-LFERs) for log K_{oc} estimation have been developed and used for several decades. Three widely used kinds of op-LFERs are (i) quantitative structure−activity relationships (QSARs) developed with molecular connectivity indices (MCI) (*11, 12*); (ii) correlations between log K_{oc} and log K_{ow}, where K_{ow} is the octanol−water partition coefficient (*1, 3−5*); and (iii) correlations between log K_{oc} and log S_w, where S_w is the water solubility (*1, 3−5*). Environmental fate modeling has often been conducted on the basis of nonclass-specific op-LFERs that have been developed from data sets containing multiple compound classes (*9, 10, 13, 14*). Generic (nonclass-specific) op-LFER approaches (using either K_{ow}, S_w, or MCI) are, however, theoretically inappropriate for estimating K_{oc} when specific interactions occur with SOM (see Theory), and op-LFER failings under such circumstances have been experimentally confirmed (*12, 15−17*). Although MCI can include information on molecular properties, the first-order MCIs that are most commonly used in QSARs for K_{oc} estimation contain more information for molecular shape and size than electronic properties (*15, 18*). Overall, it is generally well-recognized that accurate estimation of log K_{oc} with any op-LFER approach will require specific and separate regressions for individual chemical classes. Moreover, even such specialized regressions are neither appropriate nor accurate when the regressed data set includes a variety of highly polar sorbates for which multiple types of specific chemical interaction may occur with SOM (*5, 15, 19*).

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TABLE 1. Log K_{oc} Data for Multiple Soils or Sediments

chemicals	avg $\pm$ SD	min.–max.	no. of soils and/or sediments	ref
tetrachloromethane	1.90 ± 0.13	1.65–2.16	70	*30, 91*
1,2-dichlorobenzene	2.59 ± 0.15	2.35–3.10	73	*2, 30, 91, 92*
pyrene	4.93 ± 0.22	4.64–5.45	22	*4, 17, 93*
acetophenone	1.55 ± 0.13	1.34–1.68	10	*94*
acridine	4.14 ± 0.16	3.74–4.34	10	*64*
carbaryl[a]	2.49 ± 0.21	1.80–2.78	33	*69*
phosalone[a]	3.74 ± 0.24	3.20–4.09	33	*69*
4-nonylphenol	3.94 ± 0.16	3.47–4.39	51	*68*

[a] Data are not included for one soil with significant amount of lipids/waxes (Pk6; (*95*)), for 5 soils with more than 4% black carbon (*96*), or for 9 soils containing 32% clay (*69*).

Specific Interactions

On the basis of their ability to interact with the surrounding media, solute chemicals can be roughly divided into three groups: apolar, monopolar, and bipolar (*20, 21*). Apolar compounds are those whose interaction with SOM is very strongly dominated by nonspecific van der Waals interactions. Examples of apolar chemicals are alkanes and compounds with diminished π-electron density by electron-withdrawing substituents (e.g., Cl) such as tetrachloroethene, chlorobenzenes, and PCBs. In addition to the aforementioned nonspecific interactions, monopolar and bipolar chemicals are also capable of direct polar interaction, including hydrogen-bonding. The importance of specific interactions between polar chemicals and SOM has been recognized previously in the work of Karickhoff (*22*), Spurlock and Biggar (*16*), Chiou and Kile (*17*), and others. Monopolar compounds can be either H-acceptors (e.g., PAHs and alkyl-aromatic hydrocarbons) or H-donors (e.g., ketones and some halogenated alkyl hydrocarbons). Bipolar compounds are H-accepting and H-donating. Examples are phenols, anilines, and ureas. In this paper, we refer to all chemicals with strong hydrogen-bonding interactions simply as polar compounds. These include both strongly monopolar chemicals (e.g., pentachlorophenol, *N,N*-dimethylbenzamide) and bipolar chemicals (2,3-dichlorophenol, benzamide). The term "nonpolar" is used for those chemicals with interactions dominated by nonspecific van der Waals interactions, including chemicals that are either apolar (e.g., many PCBs and chlorinated benzenes) or weakly monopolar (e.g., PAHs).

Meylan et al. (*12*) developed an improved MCI–K_{oc} relationship for both polar and nonpolar chemicals by using a combination of the first-order MCI and a series of statistically derived fragment correction factors. This alternative to the op-LFER approach has been encoded into a computer program, PCKOCWIN, which is available from the U.S. EPA as a part of the Estimation Program Interface (EPI) Suite (*23*).

Borisover and Graber (*24*) used a data set of 59 organic chemicals (including polar chemicals) to develop a two-parameter LFER for estimating log K_{oc}. One parameter was the logarithm of the hexadecane/air partitioning coefficient (log L_h). Because hexadecane is an inert solvent that is incapable of specific interaction with solute molecules, hexadecane was considered as an appropriate reference medium for nonspecific van der Waals interactions, and log L_h was used to represent this contribution. The second parameter, log water solubility (log L_w), contains the effects of remaining interactions with water, including H-donor, H-acceptor, and van der Waals interactions. Log L_w is thus a complex parameter that does not account for individual specific interactions with SOM. In the pp-LFER approach presented subsequently, different types of chemical interaction with both water and SOM are specifically accounted. Before describing the theory behind this approach, however, it is useful to briefly review a fundamental assumption behind all of the approaches discussed—that is, that a chemical's interaction with SOM in various soils and sediments can in fact be reasonably well-characterized by a single value of K_{oc}.

Validity of the K_{oc} Concept. The assumptions of linear partitioning and approximately uniform average SOM quality (i.e., the existence of a "representative" value of K_{oc}) are central to use of the $f_{oc}K_{oc}$ paradigm, irrespective of the approach taken for K_{oc} estimation. These assumptions have been thoroughly investigated in the context of op-LFER application (*1*–*7*) but remain as principal sources of imprecision and inaccuracy for any developed regression. In fact, concentration-dependent adsorption phenomena can be relevant for any sorbate that is capable of displacing water on naturally occurring adsorption sites, and this may include nonpolar chemicals for the case of sorbents containing substantial quantities of thermally altered "hard" carbon surface (*5, 8*). Under such circumstances, however, there is nonetheless a value in estimating the extent of linear absorption with "soft" macromolecular SOM. Even for the absorption components, however, partition will not be well-modeled by a single K_{oc} if there is significant variability in the quality of the average natural organic matter among different soils and sediments.

Fortunately, there is a substantial body of data to suggest that the average SOM of many whole soils and sediments is of reasonably uniform quality (*1*–*7*). Although sorption variability has been widely reported for isolated SOM fractions of variable polarity (e.g., O/H atomic ratios, aromaticity, aliphatic components) (*25*–*29*) or of various extents of thermal alteration (*6*), existing K_{oc} data for multiple samples of bulk soils and sediments suggest that the variation in overall SOM K_{oc} at high relative solute concentration is not large. This presumably reflects the fact that absorption dominates for most of the reported data (at least at higher relative concentrations) and that the relative mass proportions of various SOM fractions are reasonably consistent among most whole sediments and soils, and that most of the examined systems contain similarly low concentrations of kerogen, black carbon, or other thermally altered SOM. Even in the absence of adsorption, however, some distinctions can be made. For example, in a sorption study with two nonpolar compounds (1,2-dichlorobenzene and carbon tetrachloride) and a large number of surface soils and aquatic sediments, Kile et al. (*30*) found a small but significant difference (0.22 log units) in log K_{oc} values for soils relative to sediments, which the authors attributed to differences in polarity of the SOM in the two categories. Importantly, they found no substantial variation in K_{oc} among samples comprised of only soils or only sediments.

To further examine K_{oc} variability, Table 1 shows the range of K_{oc} values observed for eight chemicals of varying polarity, each of which has been evaluated using at least 10 different soils and sediments. The standard deviation of log K_{oc} values for each chemical is smaller than 0.3, which is an indication that there is practical utility in the development of a single pp-LFER for the log K_{oc} of both polar and nonpolar chemicals

with SOM. Although the data of Kile et al. (*30*) would suggest that separate regressions with soil and sediments would improve accuracy, such an analysis would require a large amount of sorption data with polar chemicals for each type of solid. Because such data are currently unavailable, our current work focuses only on the development of a combined soil and sediment regression.

Development and Evaluation of a New pp-LFER. In this paper, we present a new critically reviewed data set of log K_{oc} values for both polar and nonpolar chemicals and describe our application of this data set toward the development of both a new pp-LFER and new op-LFERs for specific classes of chemical sorbates. Results from the two approaches are then compared, both against each other and against results from previously published methods, to demonstrate that a pp-LFER (using a single set of SOM-phase specific parameters for all SOM) can accurately describe K_{oc} for multiple compound classes and with a large variety of soils and sediments. Before presenting the details of these results, we review the theory and methods behind the compared approaches for K_{oc} estimation.

Theory

One-Parameter LFER. The dimensionless partition coefficient K_{ow} is related to the total change in Gibbs free energy for the transfer of one mole of chemical i from aqueous solution to octanol:

$$K_{ow} = A_1 \exp(-\Delta G_{ow}^i/RT) = \exp(-\Delta G_{ow}^i/RT + \ln C_1) \quad (1)$$

where C_1 is a preexponential constant that depends on volume entropy effects and the standard states chosen (*31, 32*). The SOM partition coefficient K_{oc} (in units of volume of water per mass of organic carbon) can be similarly expressed as follows:

$$K_{oc} = K_d/f_{oc} = C_2/\rho_{oc} \exp(-\Delta G_{oc}^i/RT) = \\ \exp(-\Delta G_{oc}^i/RT + \ln C_2/\rho_{oc}) \quad (2)$$

where C_2 again depends on volume entropy effects and standard states, and ρ_{oc} is the mass of carbon per unit volume of the SOM (*7*).

Assuming a linear relationship between ΔG_{ow}^i and ΔG_{oc}^i, one can obtain an op-LFER for log K_{oc} and log K_{ow} of the following form:

$$\log K_{oc} = a \log K_{ow} + b \quad (3)$$

Theoretically, eq 3 should be used only when a linear relationship exists between ΔG_{ow}^i and ΔG_{oc}^i. Such a relationship holds if either (i) octanol and SOM have identical sorption properties or (ii) the studied log K_{oc} data are limited to a given class of compounds for which all interactions vary proportionally in both ΔG_{ow}^i and ΔG_{oc}^i (i.e., $\Delta G_{oc}^i =$ constant $\times \Delta G_{ow}^i$). Usually this is only the case for compound classes in which H-bond functional groups stay constant and only the remaining nonpolar portion of the molecule changes. For these reasons, the op-LFER approach has been found successful at estimating log K_{oc} for both apolar compounds and for weakly polar compounds that have only a small contribution from H-acceptor or donor interaction (chlorinated alkanes, alkynes, PAHs). Equation 3 yields poor results, however, if applied to a data set that includes polar chemicals that also interact substantially with SOM through hydrogen bonds of varying strengths (*15, 24*). Another source of error with op-LFERs is in the determination of log K_{ow}. For example, accurate measurement of K_{oc} has been found to be especially difficult for large and hydrophobic chemicals such

as DDT, and numerous erroneous values for these chemicals have been reported and propagated through literature (*33*).

In addition to correlations with log K_{ow}, several investigators have developed correlations for log K_{oc} estimation that are based on aqueous solubility (see Gawlik et al. (*15*) and Allen-King et al. (*5*) for reviews). This approach has the same basic problems as the octanol approach as well as some additional pitfalls for polar chemicals. In the case of strongly polar compounds, the interactions with SOM are being compared to those in a variety of pure chemical phases that may vary substantially in their tendency toward hydrogen-bonding and other types of specific interaction.

One approach for understanding differences of sorption among chemical classes is based on Flory−Huggins theory, which was originally introduced to describe hydrophobic organic compound sorption by SOM or dissolved organic matter (DOM) by Chiou et al. (*2*) and more recently improved by Georgi and Kopinke (*34*). Although the modified Flory−Huggins concept can offer means of better understanding and isolating empirical log K_{oc}−log K_{ow} correlations for different chemical classes, it cannot describe specific interactions such as hydrogen bonding (*34*) and is therefore not applicable for chemicals subject to such effects.

Polyparamter LFERs. A pp-LFER overcomes the disadvantages of the op-LFER by specifically considering various interactions between an aqueous chemical and an organic phase. This approach has found increasing acceptance and application in medicinal chemistry (*35*) and is slowly gaining acceptance for use in the context of environmental chemistry and contaminant fate modeling. In addition to several recent descriptions of the method by Goss and colleagues (*36, 37*), Breivik and Wania (*38*) have proposed the use of a pp-LFER approach in multimedia fate modeling for polar chemicals. On the other hand, the pp-LFER approach has not yet been widely applied in environmental contexts, and we know of only three peer-reviewed publications that describe the application of a pp-LFER approach with respect to sorption of hydrophobic organic chemicals to SOM (*39−41*). These prior results have some shortcomings, however, in regard to either the chemical parameters used (*39, 40*) or the data set evaluated (*41*). These issues are further described under Previously Published pp-LFERs in the Discussion section. First, we find it useful to better describe the theory behind the pp-LFER approach.

The change in Gibbs free energy for absorption from the aqueous phase into SOM includes a term for cavity formation for solute molecules (*21, 42*) and additional terms for intermolecular interactions between the solute and the surrounding SOM (*31, 41, 42*). Overall, the following equation applies:

$$-\Delta G_{oc}^i = G_{cavity-water}^i + G_{interaction-water}^i - G_{cavity-oc}^i - \\ G_{interaction-oc}^i \quad (4)$$

Here, $G_{cavity-water}^i$ and $G_{cavity-oc}^i$ are Gibbs free energies required to close and form a cavity inside water or SOM, respectively. $G_{interaction-water}^i$ and $G_{interaction-oc}^i$ are the Gibbs free energies of the interaction between molecule i and water molecules or SOM molecules, respectively. The energy for the formation of a cavity is positive, and because water molecules interact more strongly with each other through hydrogen bonding than do molecules of SOM, $G_{cavity-water}^i$ is generally greater than $G_{cavity-oc}^i$.

Combining eqs 2 and 4 gives the following equation for K_{oc}:

$$\log K_{oc} = (G_{cavity-water}^i + G_{interaction-water}^i - G_{cavity-oc}^i - \\ G_{interaction-oc}^i)/2.3RT + \log(C_2/\rho_{oc}) \quad (5)$$

The Gibbs free energy for cavity formation is proportional

to the size of molecule i, which can be related to the McGowan's characteristic molecular volume ($\mathbf{V}$) (43). Consequently, we can write:

$$G_{\text{cavity}-\text{water}}^{i} - G_{\text{cavity}-\text{oc}}^{i} = \nu\mathbf{V} \qquad (6)$$

where ν is a parameter that represents the difference in the cohesive energy of the two bulk phases—water and SOM (44).

The interaction terms can be further decomposed into four terms as follows:

$$G_{\text{interaction}-\text{water}}^{i} - G_{\text{interaction}-\text{oc}}^{i} = e\mathbf{E} + s\mathbf{S} + a\mathbf{A} + b\mathbf{B} \quad (7)$$

Here, the terms $\mathbf{E}$, $\mathbf{S}$, $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{V}$ represent the latest nomenclature introduced by Abraham's group (45). (In older work (46, 47) by the same group $\mathbf{E}$, $\mathbf{S}$, $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{V}$ are referred to as R_2, π_2^{H}, $\Sigma\alpha_2^{\mathrm{H}}$, $\Sigma\beta_2^{\mathrm{H}}$ or $\Sigma\beta_2^{0}$, and V_x.) The excess molar refraction ($\mathbf{E}$) stands for the difference in polarizability compared to an alkane of the same size. Hence, this term accounts for nonspecific interactions that involve the induction of dipoles within the solute—that is, London dispersive forces (induced dipole—induced dipole interactions) and Debye forces (dipole—induced dipole interactions) (42,45). The $\mathbf{S}$ term was originally defined by Abraham (47) as a combined descriptor for polarity and polarizability. Arey and co-workers (48, 49) have used molecular-scale calculations to show that the $\mathbf{S}$ term does in fact include some small effects of polarizability (cross effect of $\mathbf{E}$) but that it is predominantly a description of electrostatic interactions controlled by stable charge separation—that is, dipole—dipole interactions. Finally, $\mathbf{A}$ is a descriptor for the *overall* hydrogen-bond acidity (H-donor or electron acceptor); and $\mathbf{B}$ is a descriptor for the *overall* hydrogen-bond basicity (H-acceptor or electron donor) (47).

Combining eqs 5–7 gives the following pp-LFERs for log K_{oc}:

$$\log K_{\text{oc}} = e\mathbf{E} + s\mathbf{S} + a\mathbf{A} + b\mathbf{B} + \nu\mathbf{V} + c \qquad (8)$$

The coefficients e, s, a, b, and ν in this equation are parameters that depend on the difference in chemical properties between water and the SOM phase. The constant e depends on the difference in the tendency of the two absorption media to interact through solute polarization (Debye and London forces). The constant s depends primarily upon the difference in the solvents' tendency for dipole—dipole interactions but is also influenced by difference in the solvents' tendency toward solute polarization; the constant a depends on the differences in phases' tendency toward hydrogen bonding between H-bond-acceptor sites in the absorption medium and an H-bond-donor solute; the constant b depends on the differences in the phases' tendency toward hydrogen bonding between H-bond-donating sites in the absorption medium and a H-bond acceptor solute; and the constant ν is as previously described in eq 6 (44). The constant c is a solvent specific free energy contribution that depends on volume entropy effects (50). The descriptors $\mathbf{V}$ and $\mathbf{E}$ can be estimated by fragment addition (42). The descriptors $\mathbf{S}$, $\mathbf{A}$, and $\mathbf{B}$ can be determined chromatographically using appropriate stationary and mobile phases (42–45, 51–54) or through appropriate regressions of available data in other solvent—solvent systems. A review of methods for determining chemical descriptors can be found in the Supporting Information.

Methods for Development and Evaluation of LFERs for Log K_{oc}

To critically review the viability of the pp-LFER approach for estimating K_{oc} in SOM, we conducted the following tasks:

(i) development of a critically reviewed data set of K_{oc} values for SOM; (ii) evaluation of K_{oc} prediction by the approaches developed by Meylan et al. (12) and Seth et al. (14); (iii) development of new class-specific op-LFERs (log K_{oc}—log K_{ow} correlations) based on the compiled data set; (iv) development of new pp-LFERs on the compiled data set; and (v) a quantitative evaluation and comparison of the performance of these various approaches.

Data Collection. For this work, we considered only organic chemicals for which peer-reviewed literature could be found to provide both values of chemical descriptors and K_{oc} data obtained by methods that could be critically evaluated. More specifically, 75 different organic chemicals were selected (Table 1S in the Supporting Information), and sorption data for these chemicals were included in the data set only if they met the following criteria: (i) sorption isotherms from aqueous solution were measured at multiple solute concentrations and were approximately linear over the concentration range studied (Freundlich coefficient $n = 0.9$–1.1); (ii) data were obtained by batch sorption experiments with well-documented procedures that involved a careful control and accounting of losses; and (iii) soil properties met specific conditions of SOM and clay content, as further described below. For some systems, it is likely that the first criterion was met only because the original investigators conducted their studies at comparatively high aqueous concentrations (5, 17). For these cases, it is likely that the impact of high-energy sorption to minor soil/sediment components (such as black carbon) was minimal because concentrations studied were sufficiently high that absorption to SOM could dominate over any such effects (5, 17). Also, because adsorption to thermally altered carbon may dominate sorption in sediment of low SOM content (5), we did not include data for soils or sediments with organic carbon fractions lower than 0.1%. We also carefully excluded sorption data for phenolic compounds in combination with high-clay materials to avoid evaluating K_{oc} data for cases where interaction with clay cannot be ignored (55). More specifically, we did not include the sorption data for 2-nitrophenol with a 70% clay sediment (56) and 4-methylphenol, 3,5-dimethylphenol, and 2,3,5-trimethylphenol with a 60% clay sediment (57). Finally, data for soils and sediments where original authors reported knowledge or suspicion of abnormally high sorption contribution from thermally altered organic matter (such as that in shale, coal, and black carbons) were not considered.

The final data set comprised 356 log K_{oc} data points for the 75 chemicals. These compounds were classified into four general groups: unhalogenated monoaromatic hydrocarbons (10 compounds), halogenated hydrocarbons (33 compounds), PAHs (11 compounds), and polar chemicals (21 compounds). The halogenated hydrocarbon group includes 8 chlorobenzenes, 16 polychlorinated biphenyls (PCBs), and 9 halogenated alkyl hydrocarbons. The 21 polar chemicals include chemicals that are capable of strong hydrogen bonding (such as phenols, anilines, amides, and ureas) at pH values that ensured negligible contribution of ionic species. Table 1S in the Supporting Information lists the studied chemicals and their descriptors as well as the selected value of log K_{ow} and the associated reference. Table 2S in the Supporting Information lists the collected log K_{oc} data as well as organic carbon and clay contents. The clay contents of the studied materials varied between 0.6% and 69%. For polar chemicals, all data were obtained for soils with clay content below 35% (i.e., silts and loams only), except that three of the 10 soils studied with regard to acetophenone and acridine sorption had clay contents of 55.2, 42.9, and 39.5%. These results were kept in the data set because they showed log K_{oc} with the range of results observed for the other soils. Organic carbon fractions (f_{oc}) of the materials

studied varied between 0.1% and 9.4%. Data presented as log K_{om} were converted to log K_{oc} assuming a conversion factor of 1.72 g of SOM/g of organic carbon (*7*).

Data Evaluation. We used the final data set to evaluate two previously published correlations and to develop several new correlations, including both class-specific log K_{oc}–log K_{ow} correlations and two alternative pp-LFERs (based on either individual or average log K_{oc} values, as described below). The previously developed correlations were (i) the QSAR approach developed by Meylan et al. (*12*) and (ii) the nonclass-specific K_{oc}–K_{ow} correlation developed by Seth et al. (*14*), which was developed from a data set of 118 log K_{oc} values for both polar and nonpolar chemicals. Specifically, we used both Meylan et al.'s published and distributed QSAR computer program PCKOCWIN (version 1.66) (*12*) and Seth et al.'s correlation (log K_{oc} = 1.03 log K_{ow} − 0.61) to estimate log K_{oc} for all chemicals in our data set (*14*). We then compared the results with the reported experimental values. These two approaches were selected because they have been recommended by several recent critical review papers on K_{oc} estimation (*5, 15, 19*). We note that an independent study conducted by Xia (*58*) reported a nonclass-specific op-LFER (log K_{oc} = 1.10 log K_{ow} − 0.99), which has been shown to give similar results as the Seth et al. correlation (*5*). We also note that the Seth et al. correlation has been recommended for use in multimedia models that estimate environmental pollutant persistence and long-range transport (*10*).

For the class-specific op-LFERs, values of log K_{ow} were taken primarily from Schwarzenbach et al. (*21*). Additional sources of information were Karickhoff et al. (*4*), Shiu and Mackay (*59*), Briggs (*60*), Hansch et al. (*61*), and Borisover and Graber (*24*). For the pp-LFER, solute descriptor data were taken from Abraham and Roses (*62*), Abraham et al. (*44*), Poole and Poole (*41*), and Platts et al. (*63*). Details are provided in the Supporting Information (Table 1S).

For both the op- and pp-LFER approaches, we performed two types of regressions: one using all collected data and one using average values for each of the 75 chemicals (i.e., with average K_{oc} values based on all available data for a given chemical from multiple soils). Regressions were performed using Sigma Plot 2000 (SPSS, Chicago, IL). Regressions based on average log K_{oc} values were used because such regression should not be overly influenced by some specific chemicals that have been evaluated in especially high numbers of studies. For example, our data set of 356 total log K_{oc} values includes 73 points for 1,2-dichlorobenzene and 70 points for tetrachloromethane, reflecting the impact of a major study by Kile et al. that used these two chemicals to study sorption with 68 natural solids (*30*). Regression with average K_{oc} data has most commonly been used in previous work on log K_{oc} estimation (*3, 11, 12*). On the other hand, regressions based on all collected data provide equal weight to the entire data set and perhaps better reflect the effect of variations that may occur as a result of variability in SOM quality, experimental imprecision, and/or potential differences in experimental bias among the different investigators.

Results

QSAR Approach for K_{oc} Estimation. The log K_{oc} values predicted using the computer program PCKOCWIN are plotted versus the experimental data in Figure 1a. In general, this approach gives a reasonable K_{oc} estimation for most compounds. The average absolute values of Δlog K_{oc} (i.e., the difference between measured and predicted values of log K_{oc}) were 0.43, 0.27, 0.20, and 0.29 for monoaromatic hydrocarbons, halogenated hydrocarbons, PAHs, and polar chemicals, respectively. (Such average absolute values are hereafter referred to as $|\Delta|_{avg}$.) This approach, however, substantially underestimated K_{oc} for high molecular weight
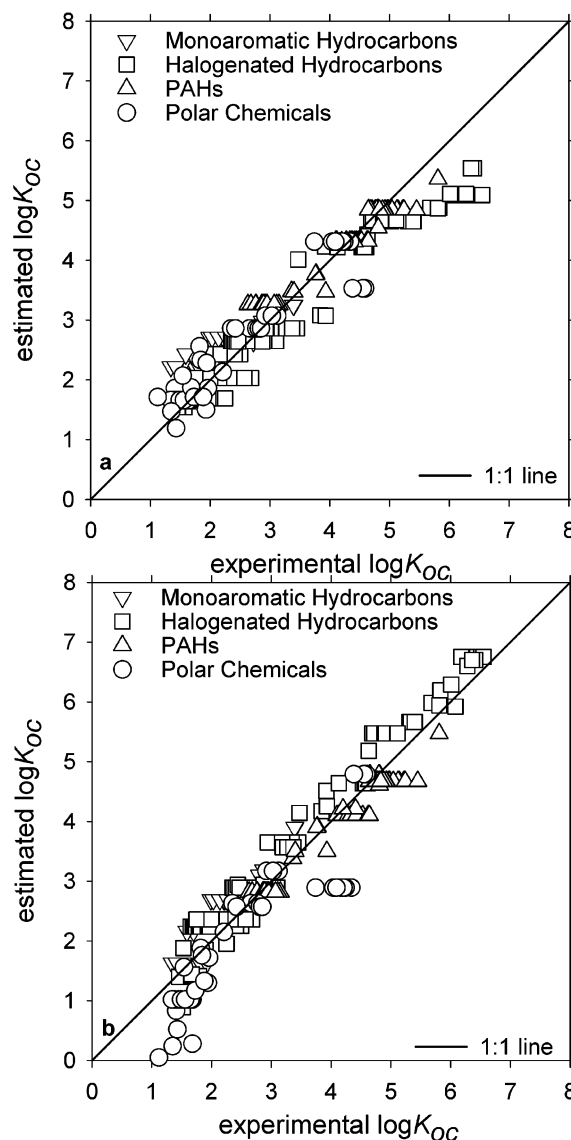

FIGURE 1. Plots of fitted data for log K_{oc} vs experimental data using the QSAR approach developed by Meylan et al. (*12*) and the K_{oc}–K_{ow} correlation developed by Seth et al. (*14*).

PCB congeners, for which Δ log K_{oc} varied between +0.80 and +1.46. For monoaromatic hydrocarbons, this approach overestimated K_{oc} for all compounds (Δ log K_{oc} = −0.03 to −1.12) except *n*-butylbenzene. Although developed specifically for the consideration of polar chemicals, this approach substantially underestimated log K_{oc} for pentachlorophenol (Δ log K_{oc} = +1.4) and overestimated log K_{oc} for fluometuron, monolinuron, benzamide, and *N,N*-methylbenzamide (Δ log K_{oc} = −0.74, −0.49, −0.59, and − 0.58, respectively).

Nonclass-Specific One-Parameter LFER. For the nonpolar chemicals in our data set, the op-LFER of Seth et al. (*14*) (log K_{oc} = 1.03 log K_{ow} − 0.61) provided a reasonably good estimation for log K_{oc} ($|\Delta|_{avg}$ = 0.30). As expected, this op-LFER performed poorly for polar chemicals, with examples of both substantial underestimation [e.g., Δlog K_{oc} = +1.44 for acridine (*64*)] and overestimation [e.g., Δ log K_{oc} = −0.41 for pentachlorophenol (*57*)]. The experimental data are plotted versuss the fitted data in Figure 1b.

Class-Specific One-Parameter LFERs. Class-specific regressions using both all collected data and average K_{oc} values are shown in Table 4S of the Supporting Information. When all collected data were used for op-LFERs, four different
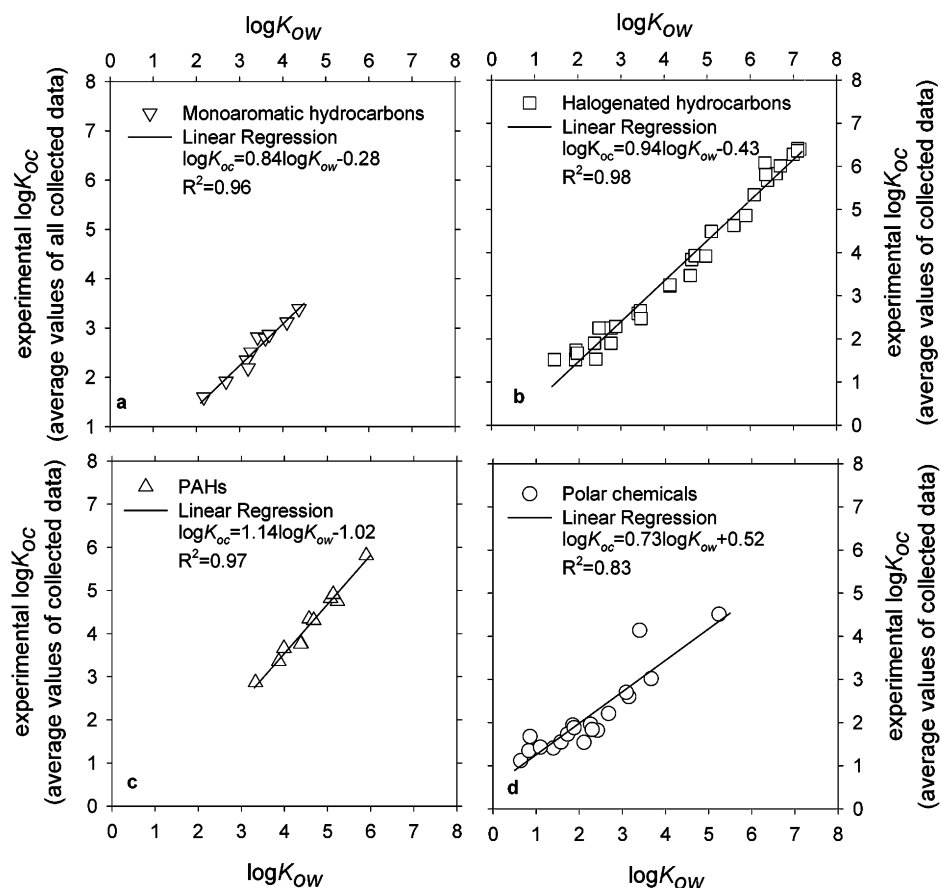
FIGURE 2. One-parameter LFERs between log K_{oc} and log K_{ow} based on average log K_{oc} values for each chemical as obtained by averaging data collected with multiple sediments and soils.

group-specific equations were developed (Figure 1S of the Supporting Information). The regression worked best for halogenated hydrocarbons ($R^2 = 0.97$) and, not surprisingly, showed the worst results for polar chemicals ($R^2 = 0.79$). The absolute value of the difference between measured and fitted values of log K_{oc} (shown as Δ in Table 4S) was highest for polar chemicals: $|\Delta|_{avg} = 0.42$, versus $|\Delta|_{avg} = 0.16$ for all nonpolar chemicals. The error was especially high for acridine ($\Delta \log K_{oc} = +1.03$).

When the average values for log K_{oc} were used, the regression parameters remained nearly the same for nonpolar chemicals and regression parameters of polar chemicals showed only slight improvement ($R^2 = 0.83$ instead of 0.79), but with acridine results lying especially far from the model regression ($\Delta \log K_{oc} = +1.15$). These average K_{oc} regression results are shown in Figure 2.

Polyparameter LFERs. Two polyparameter LFERs were obtained: one with all collected data (eq 9a, Figure 3a) and another with average values (eq 9b, Figure 3b):

$$\log K_{oc} = (1.08 \pm 0.04)\mathbf{E} - (0.83 \pm 0.09)\mathbf{S} + (0.28 \pm 0.08)\mathbf{A} - (1.85 \pm 0.08)\mathbf{B} + (2.55 \pm 0.08)\mathbf{V} - (0.12 \pm 0.05) \quad (9a)$$

$$\log K_{oc} = (1.10 \pm 0.10)\mathbf{E} - (0.72 \pm 0.14)\mathbf{S} + (0.15 \pm 0.15)\mathbf{A} - (1.98 \pm 0.14)\mathbf{B} + (2.28 \pm 0.14)\mathbf{V} + (0.14 \pm 0.10) \quad (9b)$$

A generally similar quality of regression was observed using either all collected data ($R^2 = 0.97$) or average values ($R^2 = 0.98$), indicating a substantially better regression than that obtained by the op-LFERs for polar chemicals. When the average values for log K_{oc} were used, the average value of $|\Delta|$

was 0.18, with a maximum value of 0.48 (for 2-methylnaphthalene). When all collected data were used, all of the fitted regression parameters (e, s, a, b, c) were statistically significant to the regression (i.e., different from 0 with greater than 95% confident). On the other hand, when the average values for log K_{oc} were used, the coefficient a was found to be statistically insignificant to the regression (0.15 $\pm$ 0.15). Overall, the choice of the most appropriate regression to use is unclear. Average K_{oc} may be preferable if we wish to minimize the potential effect of soil and sediment variability on the equation or if we are especially concerned about the effect of specific chemicals on the equation. On the other hand, the equation with individual sample results can more completely show variability among the measurements.

Discussion

Previously Published pp-LFERs. Park and Lee (*39*) used the K_{oc} data set of 42 compounds from ref *65* to develop the following pp-LFER:

$$\log K_{oc} = 0.22(\pm 0.19) + 4.87(\pm 0.29)V_I/100 - 0.51(\pm 0.33)\Pi^* - 0.60(\pm 0.27)\delta - 1.17(\pm 0.46)\beta - 0.12(\pm 0.37)\alpha \quad (R^2 = 0.97) \quad (10)$$

Here, $V_I/100$ is the cavity term similar to the $\mathbf{V}$ term in eqs 9a and 9b. The terms Π^* and δ both relate to the solute−solvent dipole−dipole and dipole−induced dipole interactions, and the terms β and α relate to the hydrogen accepting and donating capabilities, respectively. A difficulty with Park and Lee's application of the pp-LFER approach, however, is that the descriptors used in eq 10 are the so-called Kamlet−Taft solvatochromic parameters. Because these parameters

are defined in terms of spectroscopic properties, they are not related to Gibbs free energy (*42, 66, 67*) and should not be used to develop K_{oc}.

Baker et al. (*40*) compiled a new data set of log K_{oc} for 68 compounds to develop a pp-LFER:

$$\log K_{oc} = 0.93(\pm 0.25) + 3.36(\pm 0.26)V_I/100$$
$$-2.09(\pm 0.23)\beta \ (R^2 = 0.72) \quad (11)$$

Although Baker et al. (*40*) concluded that the pp-LFER approach was less accurate then other methods tested, this result was undoubtedly related to the fact that, as with the work of Park and Lee (*39*), inappropriate (i.e., solvatochromic) descriptors were used.

More recently, Poole and Poole (*41*) used the Gibbs-free-energy-related scale of parameters proposed by Abraham et al. (*46*) to develop the following pp-LFER based on a data set of 131 compounds:

$$\log K_{oc} = 0.21(\pm 0.09) + 2.09(\pm 0.10)V_x$$
$$+ 0.74(\pm 0.04)R_2 - 0.31(\pm 0.09)\Sigma\alpha^H_2 - 2.27(\pm 0.11)\Sigma\beta^0_2$$
$$(R^2 = 0.98) \quad (12)$$

A difficulty with this pp-LFER is that it was developed on a large data set that was not critically reviewed (*41*). Rather, the data set is a simple compilation of all available data from Sabljic et al. (*11*), Meylan et al. (*12*), and Bahnick and Doucetter (*65*) without removing multiply referenced data or critically considering the data sources in regard to linearity, experimental protocol, or other criteria used in our current work (see Data Collection). Furthermore, by arbitrarily removing seven "outliers", Poole and Poole increased the regression's correlation coefficient significantly (R^2 from 0.94 to 0.98) (*41*). We believe that our updated pp-LFER regression equations (eqs 9a and 9b) are likely to more accurately reflect absorption to SOM than eq 12 because of the use of a more carefully screened data set. Nonetheless, the prior work by Poole and Poole (*41*) represents an important early effort in this area, and we are encouraged by the qualitative similarity of our results.

Fractional Contributions to Log K_{oc} with the pp-LFER. The good regression obtained with the pp-LFER approach (using either all data or average K_{oc}) illustrates that data collected for both polar and nonpolar chemicals can be effectively expressed through the combined consideration of the six parameters identified in eqs 9a and 9b. These regression equations do not, however, provide any insight about the relative contribution to log K_{oc} that is made by each type of interaction. This latter information is provided by considering the fractional contributions (to total ΔG) that derive from the $s\mathbf{S}$, $v\mathbf{V}$, $e\mathbf{E}$, $a\mathbf{A}$, $b\mathbf{B}$, and c terms. Individual results for each chemical are shown in Tables 6S and 7S (Supporting Information)—note that the calculated fractional contributions are based on sums of absolute values to provide a fair comparison among chemicals with both positive and negative ΔG contributions. Table 2 shows the average, standard deviation, and range of values for each of the various classes of chemicals. For all 75 chemicals, the strongest influence on log K_{oc} was from the cavity term ($v\mathbf{V}$). Notice that the terms reflecting nonspecific van der Waals interactions (i.e., $e\mathbf{E}$ and $s\mathbf{S}$) were the second and third largest contributors to free energy change for all compound classes (Table 2). For polar chemicals, substantially greater contribution from H-acceptor and H-donor terms was observed (Table 2). Pentachlorophenol had the highest fractional contribution from the H-acceptor term $a\mathbf{A}$ (2.6%) *N,N*-methylbenzamide had the highest fractional contribution from the H-donor term $b\mathbf{B}$ (27.8%), but chemicals usually classified as nonpolar (e.g., trichloromethane, 1,2-dichlo-
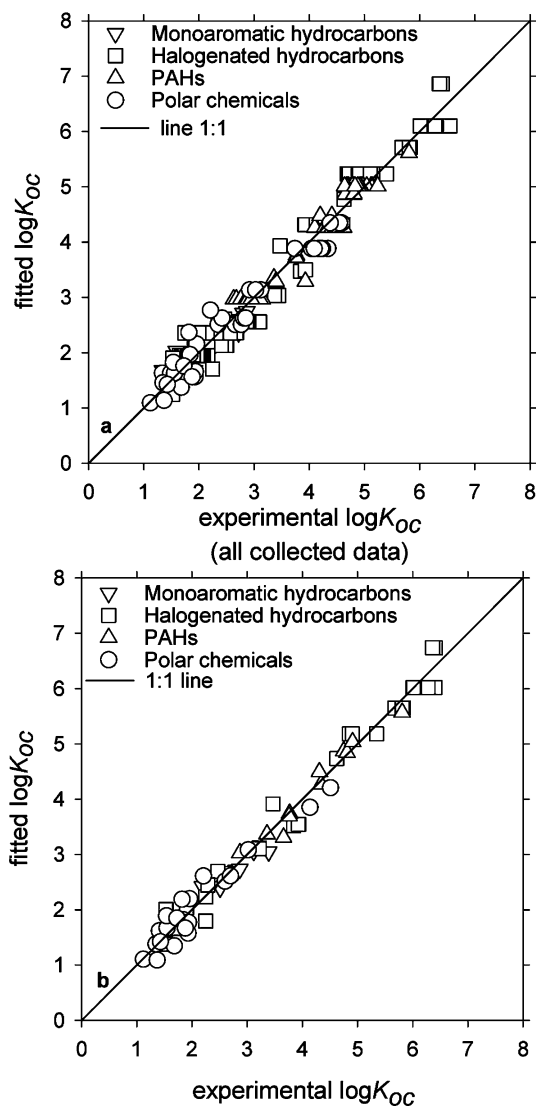
FIGURE 3. Plots of fitted data for log K_{oc} vs experimental data using polyparameter LFER. (a) Plot based on collected data and associated regression [log K_{oc}= (1.08 ± 0.04)E − (0.83 ± 0.09)S + (0.28 ± 0.08)A − (1.85 ± 0.08)B + (2.55 ± 0.08)V − (0.12 ± 0.05)]. (b) Plot based on average values for each chemical and associated regression [log K_{oc} = (1.10 ± 0.10)E − (0.72 ± 0.14)S + (0.15 ± 0.15)A − (1.98 ± 0.14)B + (2.28 ± 0.14)V + (0.14 ± 0.10)].

roethane, and 1,1,2,2-tetrachloroethane) also showed some contribution from $b\mathbf{B}$ (in the range of 1.6 to 9.5%) and $a\mathbf{A}$ (in the range of 0.4−0.9%). Only the truly apolar chemicals (e.g. the trichlorobenzenes) showed no significant contribution from H-acceptor and H-donor terms (Table 7S, Supporting Information).

The above results are consistent with expectations. Compared to bulk water, water-wet SOM is less cohesive (positive v) and has greater capacity for polarizing effects (stronger positive e). Thus, the dominant driving force for sorption from water to water-wet SOM is the rejection of solute molecules by bulk water. Water-wet SOM has weaker electrostatic interactions than water (strong negative s) and is a weaker hydrogen-bond acid (strong negative b); therefore, polar solutes (high $\mathbf{S}$) and solutes with significant hydrogen-bond basicity (high $\mathbf{B}$) prefer bulk water. Water-wet SOM is a slightly stronger hydrogen-bond base (small positive a), but interactions with SOM basic sites are only significant for solutes with very high acidity (high $\mathbf{A}$; e.g.. pentachlorophenol).

TABLE 2. Fractional Contributions of Various Terms to Log K_{oc}[a]

	monoaromatic hydrocarbons	halogenated hydrocarbons	PAHs	polar chemicals
eE (%)	15.1−21.7 (18.1 ± 1.8)	13.8−28.7 (24.8 ± 4.3)	25.6−35.8 (30.5 ± 3.7)	12.7−32.3 (20.8 ± 4.3)
sS (%)	8.4−12.1 (9.9 ± 1.1)	9.9−16.9 (13.8 ± 1.5)	10.9−14.3 (12.6 ± 1.1)	11.6−23.2 (15.2 ± 3.0)
aA (%)	0.0−0.0	0.0−0.9 (0.1 ± 0.2)	0.0−0.0	0.0−2.6 (0.9 ± 0.8)
bB (%)	6.8−9.0 (8.1 ± 0.7)	0.0−9.5 (2.3 ± 2.9)	5.0−7.7 (6.8 ± 0.7)	0.0−27.8 (16.3 ± 7.3)
vV (%)	52.7−66.6 (60.4 ± 3.8)	47.5−64.7 (56.0 ± 3.3)	41.7−54.2 (48.0 ± 4.1)	37.4−57.7 (44.4 ± 5.6)
c (%)	2.9−4.5 (3.5 ± 0.5)	1.5−5.7 (3.0 ± 1.4)	1.5−2.7 (2.1 ± 0.4)	1.7−3.3 (2.4 ± 0.5)

[a] Note that the contributions from sS, bB, and c to log K_{oc} are negative (eq 9b). Data are calculated as percent contributions to the sum of absolute values of log K_{oc}. Data represent the range of values observed for individual chemicals, with the average ± 1 standard deviation shown in parentheses. Further detail can be found in Table 6S and 7S of the Supporting Information.

Role of Cavity Effect in op-LFER for Polar and Nonpolar Chemicals. For partitioning between two phases, the so-called hydrophobic effect is associated with the high energy required to break hydrogen bonds between water molecules to form a cavity. For nonpolar chemicals, both octanol−water and SOM−water partitioning are dominated by cavity and London dispersion effects, such that both log K_{ow} and log K_{oc} should be linearly correlated to the characteristic volume (**V**). Figure 4a illustrates the linear correlation between **V** and log K_{oc}, and Figure 4c illustrates a similar correlation between **V** and log K_{ow}. Because both of these relations are linear, an op-LFER approach based on log K_{ow} can predict log K_{oc} with reasonable accuracy for nonpolar chemicals. On the other hand, chemicals that undergo strong H-bonding do not show a linear correlation between either log K_{ow} or log K_{oc} and **V** (Figure 4b,d) because other parameters in eqs 9a and 9b also play important roles. It is for this reason that log K_{oc} versus log K_{ow} correlations are not accurate for polar chemicals.

SOM versus Other Organic Solvents. As shown in Theory, the coefficients e, s, a, b, and v represent the differences in chemical properties of two absorbing media. In this context, it is of interest to compare the pp-LFER for SOM (eq 9b) with the pp-LFER for other organic solvents using the same chemical data set. Using the K_{ow} data compiled for the 75 chemicals evaluated in this review leads to the following pp-LFER for K_{ow}:

$$\log K_{ow} = (0.78 \pm 0.11)\mathbf{E} - (1.17 \pm 0.16)\mathbf{S} + (0.14 \pm 0.17)\mathbf{A} - (2.85 \pm 0.16)\mathbf{B} + (3.25 \pm 0.15)\mathbf{V} + (0.47 \pm 0.11) \quad (R^2 = 0.98) \quad (13)$$

A somewhat similar pp-LFER has been reported before by Abraham and Chadham (35) using a much larger data set (n = 613).

In theory, the subtraction of eq 13 from eq 9b will give a pp-LFER for estimating a chemical's distribution between water-wet SOM and water-wet octanol. In comparison to water-wet SOM, water-wet octanol is less cohesive (more positive v), has less electrostatic and polar interactions (more negative s), and has weaker hydrogen-bond acidity (more negative b). The coefficient a is statistically insignificant for both correlations, indicating that water-wet octanol and water-wet SOM have similar hydrogen-bond basicity. Abraham and Chadham (35) reported a list of pp-LFERs for various water−organic solvent systems. The coefficients of pp-LFER

for the water−SOM system (equation 9b) are not the same as those of any other solvent examined but are closest to those for water−2-butanol (35). We do not, however, recommend the use of water-wet isobutanol or any other solvent as a surrogate for water-wet SOM. As previously discussed in the context of octanol, such approaches conceal the specific sorption properties of the SOM phase and can lead to disproportionately large errors for some classes of chemicals.

Improved Prediction with the pp-LFER: Selected Examples. (i) Because pentachlorophenol and acridine have very different log K_{ow} (5.24 vs 3.4), any op-LFER based on log K_{ow} must forcibly predict very different log K_{oc} for these two chemicals. This is in contrast to the experimental observations, which show that these two chemicals have very similar log K_{oc} (both in the range of 4.2−4.4). In fact, the class-specific op-LFERs for polar chemicals were inaccurate for both chemicals, with Δ log K_{oc} of +0.18 for pentachlorophenol and Δ log K_{oc} of 1.15 for acridine (Table 3S, Supporting Information). The reason that these two chemicals can interact similarly with SOM but differently with octanol is that octanol does not offer the same potential as SOM for H-donor and H-acceptor interactions. Specifically, pentachlorophenol has a strong tendency to react with basic sites of SOM ($\mathbf{A} = 0.97$; $\mathbf{B} = 0$), whereas acridine tends to react with acidic sites of SOM ($\mathbf{A} = 0$; $\mathbf{B} = 0.58$). Because the pp-LFER approach specifically takes into account both kinds of interaction (H-donor and H-acceptor), eq 9b is able to predict log K_{oc} within 0.3 log units from the experimental value for *both* chemicals (Table 3S, Supporting Information).

(ii) Two other chemicals that showed different log K_{ow} (1.1 vs 2.1) but similar experimental log K_{oc} (1.43 vs 1.54) are benzyl alcohol and anisole. The class-specific op-LFERs underestimated log K_{oc} for benzyl alcohol (Δ log K_{oc} = +0.11) and overestimated log K_{oc} for anisole (Δ log K_{oc} = −0.51) (see Table 3S, Supporting Information). The difference in log K_{ow} between those two chemicals derives from their size, but the similarity of their log K_{oc} values derives primarily from the compensating tendency of benzyl alcohol to react with basic sites of SOM ($\mathbf{A} = 0.33$), which is a characteristic that anisole does not share ($\mathbf{A} = 0$). By specifically considering the interactions of both solutes and SOM, the pp-LFER approach (i.e., equation 9b) reduced the error for log K_{oc} estimation from −0.51 to −0.35 for anisole and from +0.11 to +0.01 for benzyl alcohol.

(iii) The pp-LFER improved estimation of log K_{oc} not only for polar chemicals but also for monopolar chemicals such as 1,2-dichloroethane and 1,2-dibromoethane. The class-specific op-LFER developed here for halogenated hydrocarbons underestimated log K_{oc} for those chemicals by about +0.57 and +0.32, respectively (Table 3S, the Supporting Information). Underestimation of the class-specific LFER is likely because these chemicals have been grouped together with other apolar halogenated hydrocarbons that do not have H-bonding ability. In fact, these chemicals do have H-bonding ability ($\mathbf{A} = 0.1$ and 0.1; $\mathbf{B} = 0.11$ and 0.17). The pp-LFER approach (i.e., eq 9b) was able to predict K_{oc} with the deviations from experimental values of −0.04 (1,2-dibromoethane) and +0.14 (1,2-dichloroethane).

(iv) As mentioned under Results, the QSAR approach substantially underestimated log K_{oc} by between +0.8 and +1.46 for nine high molecular weight PCBs. The pp-LFER approach offered some improvement with the deviation from experimental values of less than 0.45 for all PCBs (Table 3S, Supporting Information). For the five polar chemicals for which the QSAR approach mispredicted log K_{oc} by between 0.49 and 1.0, the pp-LFER was able to reduce the deviation from experimental values to between 0.02 and 0.37 (Table 3S, Supporting Information).
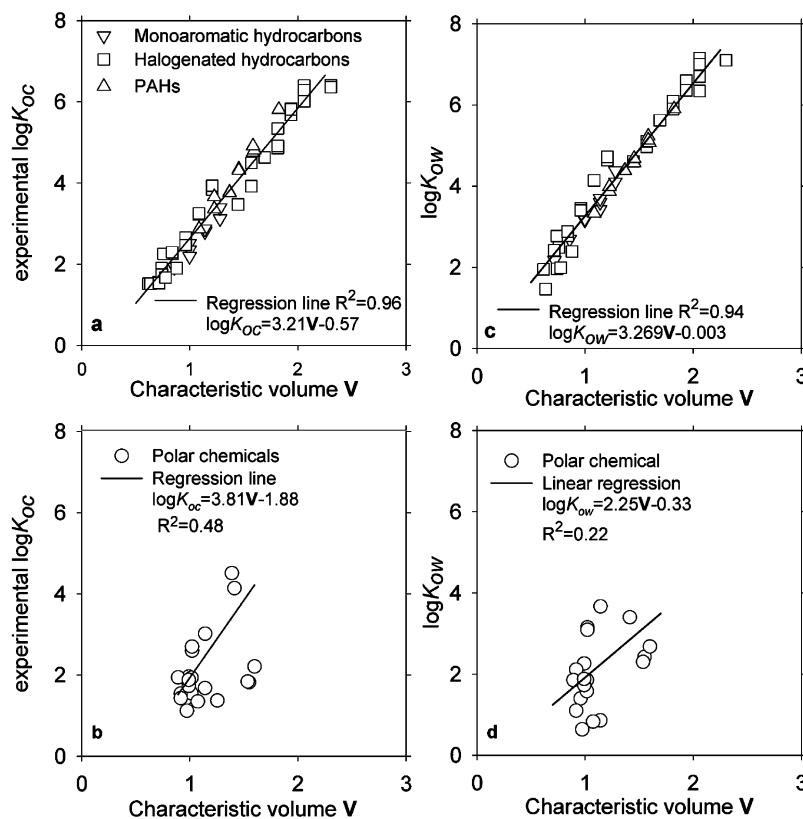
FIGURE 4. Plot of experimental log K_{oc} and log K_{ow} vs the characteristic volume (V_x) for (a and c) nonpolar chemicals and (b and d) for polar chemicals. Note that panels a and b show regressions for log K_{oc} whereas panels c and d show regression for log K_{ow}. Experimental data shown are the average values of collected data for each chemical.

Example Applications of the pp-LFER Approach. For purposes of example application of our developed pp-LFER, we chose carbaryl and 4-nonylphenol, which were not included in our data set but for which measured values of log K_{oc} are available recently (68, 69). Carbaryl is an insecticide widely used on fruits and vegetables (70). 4-Nonylphenol has been identified as a potential endocrine disruptor found in surface water and is emerging as a potential candidate for future regulation (71).

(i) For the case of carbaryl, values of log K_{ow} reported in Mackay et al. (70) are from 1.59 to 3.13. Using these values of log K_{ow}, we estimate a range of K_{oc} values that span nearly 2 orders of magnitude. Log K_{ow} values in the range of 1.93–2.31 are perhaps the most accurate, as these were measured with well-established methods. Specifically, measures based on reverse-phase HPLC retention times gave log K_{ow} values of 1.93 (72) and 1.99 (73), and a measure based on a shake flask technique gave a log K_{ow} of 2.31 (74). Using our class-specific op-LFER (log K_{oc} = 0.73 log K_{ow} + 0.52, Figure 2d), these values correspond to log K_{oc} values of 1.93, 1.97, and 2.21, respectively. The experimental values of log K_{oc} for carbaryl range from 1.80 to 2.78 (n = 33, Table 1) (69). Therefore, a critical selection of log K_{ow} and a suitable op-LFER (class-specific K_{oc}–K_{ow} correlation) would (perhaps fortuitously) lead to a reasonable estimation of log K_{oc}. In regard to the pp-LFER approach, carbaryl is a chemical for which pp-LFER descriptors have not yet appeared in peer-reviewed literature. For carbaryl and many other chemicals, however, pp-LFER descriptors have in fact been developed and are available in a database that is maintained by Abraham (75) and distributed by Pharma Algorithms (76). (At the time of this writing, such data are available for about 5000 chemicals.) For carbaryl, the following parameters are reported: **E** = 1.512; **S** = 1.68; **A** = 0.21; **B** = 0.80; **V** = 1.5414 (75). Using eqs 9a and 9b and this set of descriptors, the

values of log K_{oc} for carbaryl are 2.64 and 2.55, which are also in the range of experimental log K_{oc}.

(ii) For the case of 4-nonylphenol, Düring et al. (68) have recently reported linear isotherms for 51 soils. Values of log K_{oc} are in the range of 3.5–4.4. Values of log K_{ow} for 4-nonylphenol are uncertain, with experimentally measured values ranging over 2 orders of magnitude. Measures based on the shake flask method gave log K_{ow} values of 3.97 and 4.48 (68, 77), and methods based on HPLC retention time gave values of 4.2 (78) and 6.3 (77). Two frequently used computer programs based on fragment contributions—ClogP (79, 80) and SPARC (81, 82)—gave values of log K_{ow} of 5.99 and 6.2, respectively, which are at the high end of the experimentally measured values. Using the values for log K_{ow} in the range of 3.97 and 6.3 and our op-LFER (Figure 2d), we estimate log K_{oc} in the range of 3.42–5.12. Using the full range of reported K_{ow} values and the op-LFER gives Δ log K_{oc} of between −0.97 and +1.65, depending upon which experimental and estimated values of log K_{ow} are chosen. The QSAR-based PCKOCWIN software gave a log K_{oc} estimation of 4.8, which is 0.4–1.3 log units higher than the experimentally reported values.

To make a pp-LFER prediction for 4-nonylphenol, values for descriptors (**E, S, A, B**, and **V**) are required. Although descriptors for 4-nonylphenol are not yet available in the literature, they can nonetheless be estimated. For **V**, such estimation is accomplished using atomic volume contributions as previously described, and for other descriptors, the estimation can be achieved using an extrapolation of results for other alkyl phenols that have fewer carbon atoms in chain. Given the molecular formula of 4-nonylphenol ($C_{15}H_{24}O$) and knowing that the number of single and double bonds is 40, one can calculate **V** = (16.35 × 15 + 8.71 × 24 + 12.43 − 6.56 × 40)/100 = 2.043 (54). As shown in Figure 2S in the Supporting Information, other alkyl phenols with fewer

carbon atoms in chain have similar values for the descriptors E, S, and A—these are approximately 0.8, 0.9, and 0.55, respectively—and it is reasonable to assume that these descriptors will be approximately the same for 4-nonylphenol. In regard to B, we observed a linear relationship between this descriptor and the number of carbons in chain, as illustrated in Figure 2S in the Supporting Information. With this linear relationship, the value of the B parameter for 4-nonylphenols was estimated to be 0.49. Using the above-described set of estimated descriptors and eqs 9a and 9b, the predicted log K_{oc} values for 4-nonylphenol are 4.46 and 4.13, respectively, which are close to the experimentally measured log K_{oc} (3.47–4.39) (68). Thus, for this emerging contaminant, the pp-LFER outperformed both the class-specific op-LFER and QSAR-based approaches for estimation of log K_{oc}.

Overview of the pp-LFER Approach as Applied to SOM: A Promising and Practical Approach. To date, well over 90 equations for op-LFER log K_{oc}–log K_{ow} have been published in the literature (5, 9, 14, 15). Although, many of these op-LFERs can give reasonably accurate estimations of log K_{oc} for nonpolar chemicals, they do not provide accurate K_{oc} estimation for polar chemicals. More than 20 equations using MCI have also been developed, but these share many of the same difficulties as the other op-LFERs for predicting the K_{oc} of polar chemicals (15). In this work, we have shown that a single pp-LFER (i.e., either eq 9a or eq 9b) is able to estimate log K_{oc} to within 0.6 order of magnitude for all compounds evaluated. Moreover, both polar and nonpolar chemicals could be estimated with one equation—that is, a single set of parameters could be used to represent SOM in a large variety of soils and sediments.

The pp-LFER approach is slowly gaining acceptance for use in the context of environmental chemistry and contaminant fate modeling (36, 38, 83–85). One of the perceived disadvantages of a pp-LFER approach, however, has been that the necessary chemical descriptors are unavailable and difficult to obtain. Such parameters are becoming increasingly available as the method gains acceptance and their determination or estimation is not always difficult (see the Supporting Information for details). Moreover, many emerging environmental contaminants are pharmaceutical drugs for which extensive research on the applicability of pp-LFERs can be found in the literature from medicinal chemistry. In fact, published descriptors for more than 200 pharmaceutical drugs are available in Zhao and Yang (86) and Abraham and Chadham (35), and data for thousands of additional chemicals are commercially available (76). Many of these chemicals have been found in the environment and are currently the subject of active research (71, 87).

As a final note, we remind readers that log K_{oc} may not be a sufficiently comprehensive descriptor for sorption in many cases. Examples include cases where adsorption contributes substantially to sorption and/or where the average SOM quality for absorption is "unusual". Adsorption can be of concern for apolar chemicals when the sediment or soil contains substantial quantities and quality of black carbon surfaces and for many categories of strongly polar organic chemicals, most of which can compete with water for adsorption on polar surfaces of certain inorganic solids (clays and metal oxides). In such cases, sorption is not fully accounted by linear absorption in SOM, and more comprehensive modeling approaches will be required (5, 88–90). Even for such cases, however, absorption to "typical" SOM is still important to quantify, and this contribution should be well-estimated through a pp-LFER approach. For polar chemicals, the resulting estimates of log K_{oc} are likely to be much more accurate than those obtained from op-LFER methods.

Supporting Information Available

Description of methods used for the determination of chemical descriptors; one-parameter class-specific LFERs between log K_{oc} and log K_{ow} for all collected K_{oc} data with sediments and soils (Figure 1S); relationship between the descriptors for alkyl phenol and the number of carbon atoms in chain (Figure 2S); log K_{ow} data and solute descriptors for the 75 sorbates studied (Table 1S); log K_{oc} data for soils and sediments and predicted log K_{oc} data using op-LFERs (Figures 1Sa–d) and pp-LFER (eq 9a) (Table 2S); averaged log K_{oc} data for soils and sediments and calculated log K_{oc} using op-LFERs (Figure 2) and pp-LFER (eq 9b) (Table 3S), regression data for one-parameter LFERs for four chemical classes (Table 4S); regression data for pp-LFERs (Table 5S); fractional contributions from each term in the eqs 9a (Table 6S) and 9b (Table 7S). This material is available free of charge via the Internet at http://pubs.acs.org.

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