

ESTIMATING SOIL/SEDIMENT PARTITION COEFFICIENTS FOR ORGANIC COMPOUNDS BY HIGH PERFORMANCE REVERSE PHASE LIQUID CHROMATOGRAPHY

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Abstract—High performance reverse phase liquid chromatography (HPRPLC) retention parameters were correlated to organic-carbon-normalized partition coefficient (K_{oc}) values for sorption of various uncharged organic substances onto sediments and soils in an attempt to devise a model for predicting sorption behavior. The results reveal a relationship between the logarithm of HPRPLC retention time and $\log K_{oc}$ that appears to provide a reasonable means for estimating partitioning properties from HPRPLC data. The technique was compared to methods which utilize octanol/water partition coefficients (K_{ow}) and aqueous solubilities as surrogate predictors of sorption behavior and was found to yield superior correlations in all cases tested.

Key words—sorption, partitioning, sediment, soil, reverse phase liquid chromatography, aqueous solubility, octanol/water partition coefficient

INTRODUCTION

Sorption phenomena exert important influences on diagenetic processes and the environmental fate of biogenic and anthropogenic organic substances in aqueous systems. Through sorption/desorption and sedimentation/resuspension phenomena natural soils and sediments can act as both aquatic sources and sinks for a host of organic compounds. The extent to which a particular organic species undergoes partitioning between sediments/soils and the aqueous phase is significantly affected by the physicochemical properties of that species. This suggests the possibility of developing means for estimation of the specific sorptive properties of particular organic substances from known properties and characteristic parameters, a highly desirable objective in terms of facilitating environmental fate and transport projections.

The sorption of uncharged organic species onto sediments and soils frequently has been observed to be linearly or quasi-linearly dependent upon solution phase concentration, particularly at very low concentration levels, and usually dependent upon the organic carbon content of the solid (Karickhoff, 1981, 1984; Chiou *et al.*, 1983; Gschwend and Wu, 1985; Brownawell, 1986; Brownawell and Farrington, 1986). This behavior is not unexpected, given the relatively low aqueous solubilities of such substances and their greater affinity for the organic phases associated with most natural solids. Many "state-of-the-art" modeling procedures for predicting sorption

phenomena in geochemical and environmental systems are predicated upon either the octanol/water partition coefficient (K_{ow}) or the aqueous solubility (S_i^w) of sorbing species (Karickhoff *et al.*, 1979; Karickhoff, 1981, 1984; Chiou *et al.*, 1979, 1983; Means *et al.*, 1980, 1982; Brown and Flagg, 1981; Voice *et al.*, 1983). Observed correlations between these two physicochemical parameters are attributable largely to their mutual dependence on the aqueous activity coefficient of a solute (Chiou *et al.*, 1979, 1982, 1983; Miller *et al.*, 1985). This has resulted in an extensive compilation of both K_{ow} (Leo and Hansch, 1979) and S_i^w values (Yalkowsky and Valvani, 1980; Yalkowsky *et al.*, 1983), both of which can be either determined experimentally (Haque and Schmedding, 1975; Karickhoff and Brown, 1979; Sutton and Calder, 1974; Miller *et al.*, 1985) or estimated from empirical models based on additive free energy concepts (AFECs) (Fujita *et al.*, 1964; Rekker, 1977; Arbuckle, 1983).

Efforts to model the sorption of hydrophobic non-electrolytic organic substances using octanol/water partition coefficients or aqueous solubilities have proven reasonably successful (Karickhoff, 1981), but are still problematic. With respect to the octanol/water partition coefficient approach, Chiou *et al.* (1982) observed that the mutual saturation of octanol and water may alter the activity coefficient of an organic solute in each phase, particularly for very hydrophobic compounds. Voice and Weber (1985) suggested that K_{ow} values may tend to underpredict the partitioning of hydrophobic compounds between

water and particulate organic carbon because of mutual saturation effects. Moreover, experimental determinations of K_{ow} are time consuming, and may lack analytical precision and accuracy, while estimates of these surrogate parameters derived from AFEC models cannot take into account steric effects or special molecular configurations.

Predictions of sorptive processes using aqueous solubility are even less satisfactory than those using octanol/water partition coefficients (Karickhoff *et al.*, 1979). The predictive capabilities of aqueous solubility sorption models are greatly enhanced if one takes into account the crystal energy contribution of solutes that are solids at room temperature (Tsonopoulos and Prausnitz, 1971; Karickhoff, 1981; Weber *et al.*, 1986; Yalkowsky and Valvani, 1980). Nonetheless, the application of aqueous solubility as a "predictor" of sorption offers no real advantage over the octanol/water partition coefficient approach, and experimental determinations can be exceedingly difficult to perform and reproduce.

High performance liquid chromatography has been utilized in organic geochemical and environmental applications to study the diagenesis of polynuclear hydrocarbons in lacustrine sediments (Wakeham *et al.*, 1979), and quantify and separate complex mixtures of pollutants in water (Sorrell *et al.*, 1977). In addition, high performance reverse phase liquid chromatography (HPRPLC) solute retention data has been utilized to rapidly estimate octanol/water partition coefficients (McCall, 1975; Vieth *et al.*, 1979; Eadsforth and Moser, 1983; D'Amboise and Hanai, 1982; McDuffie, 1980; Rapaport and Eisenreich, 1984; Burkhard *et al.*, 1985; Chin *et al.*, 1986) and aqueous solubilities (Hakfenschied and Tomlinson, 1981; Chin *et al.*, 1986). Predictive modeling of the sediment/soil sorption behavior of uncharged organic solutes would seem a logical extension of this technique, in that the analysis would potentially be fast, accurate, and not require the use of such information as solute melting points and entropies of fusion. Rapaport and Eisenreich (1984) have in fact suggested that the partitioning behavior of an organic solute between the reverse phase, stationary phase and the mobile phase in a HPRPLC system is analogous to that involved in soil/sediment sorptive processes, and is therefore potentially a more accurate predictor of sorption than either aqueous solubility or octanol/water partition coefficients. This method, coupled with other qualitative techniques (e.g. mass spectrometry) might be particularly attractive for rapidly identifying and assessing the sorptive properties of diagenetically altered organic pollutants in marine and freshwater sediments (Burkhard *et al.*, 1985). This paper investigates the feasibility of applying HPRPLC as a technique for estimating sediment partition coefficients, and compares the results with those obtained using octanol/water and aqueous solubility sorption models.

THEORETICAL

The distribution of a hydrophobic organic compound between water and a natural solid can be quantified through the use of several models. Weber *et al.* (1983) found that the Freundlich equation is particularly useful for analyzing sorption equilibrium data over large concentration ranges

$$q_c = K_F C_c^n \quad (1)$$

where q_c and C_c are the concentrations of the sorbate in the solid and aqueous phases, and K_F and n are empirical coefficients relating to the adsorption capacity and energy or intensity of adsorption respectively. If the value n approaches unity, sorption can be quantified using a simple linear model

$$K_p = \frac{q_c}{C_c} \quad (2)$$

where K_p is the equilibrium partition coefficient. It should be emphasized that equation (2) applies rigorously only to true absorption partitioning processes, or to adsorption phenomena in systems in which the equilibrium solution phase concentration is exceedingly low for any given solute (generally $< 100 \mu\text{g l}^{-1}$); i.e. the "Henry's" sorption domain (Weber *et al.*, 1983). Several investigators (Lambert *et al.*, 1965; Karickhoff *et al.*, 1979; Means *et al.*, 1980; Brownawell and Farrington, 1986) observed that the sorption of uncharged hydrophobic organic compounds can be correlated to the organic carbon content of the sorbent. For such cases partition coefficient values for a variety of soils and sediments can be normalized in terms of the fraction of organic carbon associated with the sorbent to yield an organic-carbon-partition coefficient, K_{oc} ,

$$K_{oc} = K_p / f_{oc} \quad (3)$$

Karickhoff *et al.* (1979) observed a generally good relationship between K_p and K_{oc} , but noted deviations for sandy soils having low organic carbon content ($f_{oc} < 0.001$). The K_{oc} values in the latter cases were lower by approximately a factor of two than those determined for high organic content silty sediments. Miller and Weber (1986) found a similar effect for the relative sorption of lindane onto a moderately high organic carbon soil and a sandy low organic carbon aquifer material. Equation (3) thus seems most appropriate for sediments and soils of moderately high organic carbon content.

The carbon normalized partition coefficient can be expressed in terms of the respective aqueous and organic carbon phase activity coefficients for a target compound γ_i^w , and γ_i^o , and the respective molar volumes of the water and organic matter phases, V_w and V_o , (Chiou *et al.*, 1983; Karickhoff, 1984) as

$$K_{oc} = \frac{\gamma_i^w}{\gamma_i^o} \left[\frac{V_w}{V_o} \right] \quad (4)$$

or, in logarithmic form,

$$\log(K_{oc}) = \log(\gamma_i^w) + A \quad (5)$$

where $A = \log(V_w/V_o) - \log(\gamma_i^o)$. The values V_o and γ_i^o cannot be reliably determined *a priori*, and must therefore be evaluated empirically.

Weber *et al.* (1986) demonstrated that the elution order of uncharged organic solutes in HPRPLC systems can be correlated to their mobile phase activity coefficients. They also observed that the logarithm of the activity coefficient of a target substance varied linearly with the amount of organic modifier present in the mobile phase, and were able to derive a correlation between aqueous phase solute activity coefficients and retention times of uncharged hydrophobic compounds

$$\log(\gamma_i^w) = \alpha \log(t_c) + \beta \quad (6)$$

where α and β are empirically determined constants, and t_c is the solute retention time corrected to the retention

time of an internal standard. Chin *et al.* (1986) observed an excellent correlation between the aqueous activity coefficients of several uncharged aromatic compounds and their respective HPRPLC retention times.

Combination of equations (5) and (6) yields

$$\log(K_{oc}) = \alpha \log(t_r) + C \quad (7)$$

where $C = A + \beta$. Equation (4) assumes that the aqueous activity coefficient exerts primary control on sorptive processes that can be directly determined with HPRPLC retention data and equation (6). Karickhoff (1981, 1984) also suggested that sorption is largely controlled by the aqueous phase solute activity coefficient. In addition, the partitioning behavior of organic compounds between a polar mobile phase and reverse phase packings is analogous to soil/sediment sorption phenomena. This paper examines the validity of the assumptions used to derive the above equations, and compares the suitability of the HPRPLC- K_{oc} equation as a predictor of sorption behavior with the suitability of sorption models based on aqueous solubility and octanol/water partition coefficients.

MATERIALS AND METHODS

Soil and sediment isotherms

The sediment used for this study was obtained from Lake Michigan, offshore from South Haven, Mich. It was wet-sieved to $<60 \mu\text{m}$, freeze-dried, and stored in a sealed container at -20°C . The soil was collected from Michawye, Mich. It has a sandy character with a mean grain dia 0.432 mm. This particular soil, chosen for its low and uniform organic carbon content, closely resembles sands in many aquifers, and thus provides a useful basis for measurement of sorption of organic compounds in subsurface systems. The sediment and soil were analyzed for organic carbon content using a persulfate oxidation technique, which yielded an organic content of 1.42% for the sediment and 0.13% for the soil.

The compounds included both aromatic and aliphatic chlorinated hydrocarbons; specifically, carbon tetrachloride (Kodak Co.), *cis*-chlordane (EPA, Research Triangle, N.C.), 1,2,4-trichlorobenzene (Aldrich Chemicals), 4,4-PCB, 2,5,2'-PCB and 2,2',4,5-PCB (Analabs/Foxboro Corp.). These compounds were chosen in part because their relative stability in the environment allows them to be used as tracers of environmental and geochemical fate and transport processes (Bopp *et al.*, 1982; Wakeham and Farrington, 1980; Schwarzenbach and Westall, 1981; Brownawell, 1986; Brownawell and Farrington, 1986), in part because their toxicity poses as an environmental hazard, and in part because they are also relatively easy to assay.

Sorption equilibrium isotherm experiments using the offshore South Haven (OSH) lacustrine sediments and the nonvolatile organic compounds (PCBs, chlordane) were carried out using 150 ml-Hypo-Vials (C.P. Pierce Co.) as individual completely mixed batch reactors (CMBRs) in so-called "bottle-point" experiments. In this type of measurement each point on the adsorption isotherm is determined in an individual CMBR by equilibrating a given solution of solute with a given quantity of sorbent. A 100 ml aliquot of deionized distilled water was added to each vial, and the target compound introduced to this water by direct injection in an acetone carrier to give solute concentrations ranging from 0 (blank) to approx. $50 \mu\text{g l}^{-1}$ (or $100 \mu\text{g l}^{-1}$ in the case of 1,2,4-trichlorobenzene) in the several CMBRs run for each compound. One hundred milligrams of sediment was then added to each reactor and the bottles sealed with aluminum crimp seals lined with Tuff-Bond teflon discs. Controls containing no sorbent solids were run alongside the isotherm CMBRs to determine whether any significant losses of solute to the reactor surfaces were incurred. Generally the amount of solute mass recovered exceeded 95%. The sealed CMBRs were sonicated to break up any large aggregates of sorbent solids and then

placed on a rotary tumbler for a time sufficient to allow solution/sorbent equilibration.

Bottle-point CMBR rate studies were conducted to determine the time required to attain equilibrium in the isotherm tests. The same amount of sorbent was added to each of a series of CMBRs. A $10\text{-}\mu\text{g l}^{-1}$ working solution of the target compound was then added to each reactor and the reactors were agitated on a rotary tumbler. At regular intervals a different CMBR was removed from the tumbler, and its solids separated from the liquid phase by passing the suspension through two 25-mm glass fiber filters housed in a stainless steel holder (Anspec Inc.). Controls indicated that losses to the filters were $<5\%$. The aliquots were then extracted with hexane and assayed for residual concentration of solute. It was observed from these rate studies that no significant change in solute concentration occurred after approx. 100–120 h. An equilibration period of 120 h was thus selected for use in all isotherm tests.

Following equilibration, the isotherm CMBRs were centrifuged at 2000 rpm for 1 h to separate the solid and liquid phases. A portion of the supernatant was pipetted out and extracted with pesticide-grade hexane for approx. 30 min. The phases were allowed to separate, and the hexane was assayed on a Hewlett-Packard 5880 gas chromatograph equipped with a ^{63}Ni electron capture detector and a glass column packed with a stationary phase suited to the particular compound being analysed. The instrument was operated isothermally using a methane-argon mobile phase.

All isotherm experiments involving volatile organic compounds were performed using a no-headspace technique. Either 2 g of soil or 0.04 g of sediment were placed into each of a number of 40-ml centrifuge tubes. A known amount of target solute in an acetone carrier was injected into 100 ml of water, and this working solution was quickly added to the centrifuge tubes. The bottles were then sealed with Teflon-lined screw caps and gently tapped to remove any air bubbles. The caps were removed, more solution was added to completely fill the vials, and the reactors were then sealed again. The remainder of the experimental procedure was carried out in the manner prescribed for the isotherm tests with nonvolatile compounds.

High performance liquid chromatography

The high performance liquid chromatography instrument used in this study was comprised of a solvent delivery system (Waters Assoc. M45 pump), a variable wavelength detector (Waters Assoc. Lambda Max detector), a rotary injector fitted with a $20 \mu\text{l}$ sample loop (Rheodyne Co.), and a $5\mu\text{-C18}$ reverse phase Econosphere cartridge column system (Alltech Assoc.). The HPLC was interfaced to a Hewlett-Packard 3390A integrator, which recorded solute retention times.

This solutes examined in this phase of the study included those investigated in the sorption isotherm experiments plus several other pesticides and polynuclear aromatic hydrocarbons (PAHs). The target compounds were made up in acetone, which also served as the internal standard, and eluted isocratically with a methanol:water mix (80:20 v/v). The mobile phase comprised of HPLC grade Millipore Norganic water and HPLC grade methanol (Fisher Co.), and was degassed prior to use to eliminate potential interferences. Solute samples were run in duplicate at a flow rate of 1 ml min^{-1} , and at a wavelength of either 254 or 221 nm, depending upon the particular compound being analyzed.

RESULTS AND DISCUSSION

Partitioning of hydrophobic compounds onto soils and sediments

Representative sediment isotherms for 2,5,2'-PCB, chlordane, and 1,2,4-trichlorobenzene are illustrated

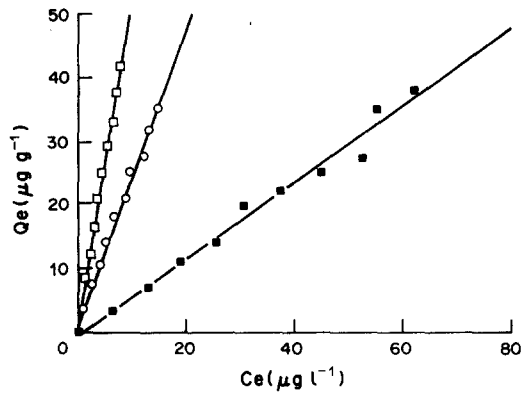


Fig. 1. Sorption of three HOCs on OSH sediment. □, Chlordane; ○, 2,5,2'-PCB; ■, 1,2,4-TCB.

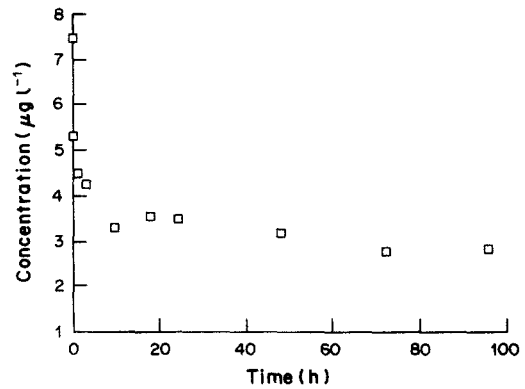


Fig. 2. 2,5,2'-PCB bottle point rate study. □, 2,5,2'-PCB.

in Fig. 1. These are typical of the results obtained for both solids studied. The isotherm data for the seven target compounds was fitted to both the linear-partitioning and the Freundlich isotherm models. Data which exhibits truly linear trends should yield n coefficient values approaching unity. The partition coefficients, Freundlich parameters and respective correlation coefficients resulting from the fitting of these two models to the experimental data are presented in Table 1. Judging from the correlation coefficients, both models appear to fit the data quite well. The majority of the slope values (n) for the fitted Freundlich isotherms were reasonably close to unity, falling in a range from 0.85 to 1.07. For purposes of comparing sorption isotherm data with HPRPLC data, the isotherm trends were sufficiently close to linear to allow approximate characterization in terms of the linear partition model.

The results of the sorption rate study described earlier indicated that the time required to attain equilibrium can be significant. It has long been assumed and often observed that sorption of hydrophobic organic compounds onto natural solids occurs within a rather small frame (hours). The rate profile illustrated in Fig. 2 for sorption of 2,5,2'-PCB onto OSH lacustrine sediments is representative of rate profiles generated for all systems studied in this work. It is readily apparent from Fig. 2 that a significant

uptake of target compound occurs quickly, but that sorption subsequently continues slowly over an extended period. Miller and Weber (1986) observed similar behavior for sorption of lindane onto several different types of soil. Karickhoff (1980, 1984) suggested that such sorptive processes can be described by a two-component model involving: (1) a rapid component in which the solute quickly sorbs onto a readily available fraction of the sorbent; and (2) a slower component in which solute sorbs at the less accessible remaining sites. Miller and Weber (1984, 1986) suggested an alternative model predicated on a dual-resistance mass transfer concept, and demonstrated an increased resistance to mass transfer and thus lower rates of sorption as solute hydrophobicity increased. Wu and Gschwend (1986) employed a simple, single resistance diffusion model to fit sorption data, and also speculated that the rate of diffusion of a solute is dependent upon its relative hydrophobicity. The slow sorption process observed in the current work and by others may extend over periods of days or even weeks. Experimental partition coefficients and predictive models based on assumptions of rapid kinetics may therefore not sufficiently represent actual sorption conditions for hydrophobic compounds. As noted earlier, equilibrium isotherms determined in this work were allowed to run for 120 h, after which

Table 1. Linear partition coefficients, Freundlich parameters and correlation coefficients for sorption of target compounds onto a lacustrine sediment and a sandy soil

Compound	K_p	r	$\log K_F$	n	r
<i>On OSH lacustrine sediments</i>					
2,2',4,5-PCB	6193	0.994	0.90	0.87	0.996
2,5,2'-PCB	2295	0.996	0.51	0.88	0.997
4,4'-PCB	2668	0.988	0.52	0.92	0.992
Chlordane*	5216	0.999	0.71	1.00	0.997
1,2,4-TCB†	587	0.996	0.14	0.94	0.997
<i>On Michawye soil (cm g⁻¹)</i>					
CCL4	0.542	0.996	-3.08	0.96	0.988
1,2,4-TCB*	12.45	0.998	-1.71	0.94	0.997
2,5,2'-PCB	37.70	0.994	-1.21	0.85	0.994
Chlordane	182.7	0.990	-0.78	1.07	0.991

**cis* isomer.

†Trichlorobenzene.

Table 2. Logarithm of normalized carbon partition coefficients and retention times for the target compounds

Compound	$\log(K_{oc})$	$\log(t_c)$
2,2',4,5'-PCB(OSH)	5.64	1.22
2,5,2'-PCB(OSH)	5.21	1.06
4,4'-PCB(OSH)	5.27	1.13
Chlordane(OSH)	5.57	1.25
Trichlorobenzene(OSH)	4.61	0.89
CCL4 (Michawye)	2.62	0.39
Lindane (Michawye)*	3.42	0.67
1,2,4-TCB (Michawye)	3.98	0.89
2,5,2'-PCB (Michawye)	4.46	1.06
Chlordane	5.15	1.25

*Lindane K_p value from Miller and Weber (1986). The sorption isotherms were done in a similar fashion, and K_{oc} determined from the organic fraction of the sorbent.

no noticeable further decrease in solution phase concentration occurred. It cannot necessarily be assumed, however, that the experimental systems were at true thermodynamic equilibrium after 120 h. The condition is therefore characterized as an "apparent" equilibrium.

Correlations between partition coefficients and HPRPLC retention times

Experimentally determined partition coefficients and corresponding HPRPLC corrected retention times, t_c , for the six target compounds and the two sorbents studied are listed in Table 2. The K_{oc} value for sorption of lindane by Michawye soil was taken from the work of Miller and Weber (1986), in which the isotherm was measured under conditions similar to those described in this paper. Corrected retention times (the difference between a solute and a relatively unretained internal standard retention time) are used in lieu of capacity factors because unretained tracers commonly utilized to determine the reverse phase column void volumes yield different retention times (Krstulovic *et al.*, 1982; Chin *et al.*, 1986). Acetone was selected as the internal standard to which all target compounds were referenced; it was found to be relatively unretained, innocuous to the system, and easily detected.

The soil K_{oc} values for chlordane, trichlorobenzene, and 2,5,2'-PCB differ from their respective OSH K_{oc} values by approximately one-half order of magnitude. This may be due in part to the low organic carbon content of the soil relative to the sediment. Karickhoff *et al.* (1979) observed that the normalization of partition coefficients to sorbent organic matter is applicable only to solids having organic carbon contents greater than 0.1%. They noted that $\log(K_{oc})$ values for sandy materials ($f_{oc} < 0.01$) were consistently lower than those determined for organic-rich sediments.

The so-called "solids effect" may also account in part for the lower effective soil K_{oc} value because the solids levels employed in experiments with the soils were approximately two orders of magnitude greater than those employed in the tests on the lacustrine sediments. Several investigators (O'Conner

and Connolly, 1980; Voice *et al.*, 1983) have observed that the apparent partition coefficient for a hydrophobic compound can sometimes decrease with increasing solids to water ratios. Several explanations have been proposed (Curl and Keolian, 1983; Gschwend and Wu, 1985; Voice and Weber, 1985), and there is reasonably general agreement that natural solids may release organic constituents (dissolved and/or colloidal) which may potentially interact with a target compound to change its sorption characteristics. Gschwend and Wu (1985) and Voice *et al.* (1983) observed that the amounts of dissolved organic carbon and colloidal material released were dependent upon the amount of solids present. It is apparent in any event that the normalizing of soil/sediment partition coefficients to organic carbon content of the solid phase may be limited in validity by system-specific factors.

Correlations relating K_{oc} and t_{oc} for the solutes listed in Table 2 are plotted in Fig. 3. The linear regression analyses of the OSH and Michawye K_{oc} - t_c data give relationships of the form

$$\log(K_{oc})_{OSH} = 2.78 \log(t_c) + 2.17; \quad r = 0.982, \quad n = 5 \quad (8)$$

and

$$\log(K_{oc})_{MICH.} = 2.88 \log(t_c) + 1.47; \quad r = 0.998, \quad n = 5. \quad (9)$$

It is evident from the coefficients of determination that a good correlation exists between $\log(K_{oc})$ and HPRPLC retention times for the systems tested. This is significant because any relationship associating the sorptive behavior of an uncharged compound to its chromatographic behavior in a reverse phase column allows K_{oc} values to be estimated quickly from a measurement of the target compound's retention time. In addition, the ratio of the coefficient (slope of the generated lines) for the two equations is approximately unity, which seems to indicate that the sorptive process is dominated in both systems by the solute aqueous phase activity coefficient. The different y-intercept values seem to indicate that

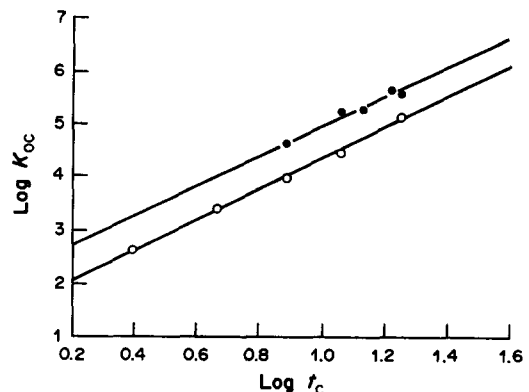


Fig. 3. Correlation between K_{oc} and t_c . ●, OSH; ○, Michawye.

Table 3. Correlation between K_{oc} , the octanol/water partition coefficients, and the mole fraction aqueous solubilities of the target substances

Compound	$\log(K_{oc})$	$T_m(^{\circ}C)$	$\log(K_{ow})$	$-\log(X_i^*)$
2,2',4,5-PCB(OSH)	5.64	47§	6.67*	8.57§
2,5,2'-PCB(OSH)	5.21	44*	6.00*	7.83*
4,4'-PCB(OSH)	5.27	149*	5.32*	7.07*
1,2,4-TCB(OSH)	4.61	17*	3.98¶	5.46*
Chlordane (OSH)	5.57	107†	6.00	7.78†
CCL4 (Michawye)	2.62	-23†	2.64†	4.03†
Lindane (Michawye)	3.42	112.9†	3.72†	5.46‡
1,2,4-TCB (Michawye)	3.98	17	3.98	5.46
2,5,2'-PCB (Michawye)	4.46	44	6.00	7.83
Chlordane Michawye	5.15	107	6.00	7.78

*From Yalkowsky *et al.* (1983); †Callahan (1979); ‡Karickhoff (1981); §Miller *et al.* (1985); ¶Chin *et al.* (1986); ||MacKay (1982).

the solute interaction with the sorbent-associated organic phase is different for the two solids studied. This observation reinforces the hypothesis that sorption onto natural solids is highly system-specific, and that the normalization of partition coefficients to sorbent target cannot be applied universally. It should also be stressed that retention times for any given set of organic solutes vary with different HPRPLC instruments, because they are dependent upon column design; i.e. column dimensions and the composition, particle size and configuration of the stationary phase. The correlation of t_c to K_{oc} values for a system of interest must first be established for a particular instrument and column. Reverse phase columns deteriorate over time, and retention times must be periodically checked to determine potential changes in resolution and precision. In addition, retention times and partition coefficients are sensitive to temperature fluctuations. An increase in temperature will tend to decrease both the retention time of an organic solute, and possibly K_{oc} . Thus it is important to maintain a constant temperature for the duration of the experiment that is reflective of natural waters.

K_{oc} values for the solutes studied were also correlated to corresponding octanol/water partition coefficients and mole fraction solubilities. Values for the latter are presented in Table 3. The regression plot

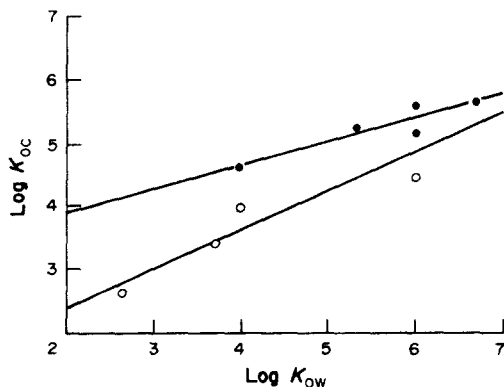


Fig. 4. Correlation between K_{ow} and K_{oc} . ●, OSH; ○, Michawye.

of K_{oc} and K_{ow} values is given in Fig. 4. Regression analyses of the OSH and Michawye data yields

$$\log(K_{oc})_{OSH} = 0.374 \log(K_{ow}) + 3.16;$$

$$r = 0.94, \quad n = 5 \quad (10)$$

and

$$\log(K_{oc})_{MICH} = 0.615 \log(K_{ow}) + 1.18;$$

$$r = 0.94, \quad n = 5. \quad (11)$$

The slope and intercept values for both regression analysis agree reasonably well with those determined by Kenaga and Goring (1980), who measured a K_{oc} - K_{ow} relationship of the form

$$\log(K_{oc}) = 0.544 \log(K_{ow}) + 1.377 \quad (12)$$

for soils and sediments.

Although it is evident that a reasonably good relationship exists between K_{oc} and the octanol/water partition coefficient, the correlation is less satisfactory than that between K_{oc} and HPRPLC corrected retention time, t_c . This is true for both the soil and sediment studied. The fact that the observed correlation between $\log(K_{oc})$ and $\log(K_{ow})$ is poorer could be due, in part, to the effect of mutual saturation and/or, in part, to inaccurate literature values for K_{oc} , which vary by as much as an order of magnitude for certain compounds. The effects of water in octanol and octanol in water on the partition characteristics of an uncharged hydrophobic compound has been observed to alter the solute activity coefficient in both phases (Chiou *et al.*, 1983; Miller *et al.*, 1985; Chin *et al.*, 1986). Further, it cannot be assumed that the behavior of a solute with respect to octanol will be similar to its association with heterogeneous organic geopolymer phases associated with solid sorbents, while solute interactions with the reverse phase resin may be more realistic. The octanol/water partitioning coefficient can provide a "first approximation" of the partitioning tendencies for a particular organic solute, while the HPRPLC model can be used to more accurately describe and quantify solute sorption in soil/sediment systems.

A plot of $\log(K_{oc})$ and mole fraction solubility, X_i^* is given in Fig. 5. Linear regression fitting of the OSH

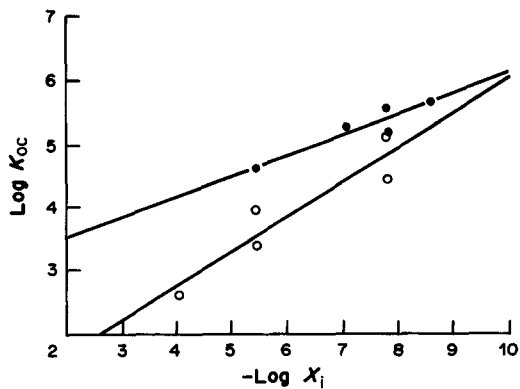


Fig. 5. Correlation between K_{oc} and solubility. ●, OSH; ○, Michawye.

and Michawye data yields

$$\log(K_{oc})_{OSH} = \frac{-\Delta S_f(T_m - T)}{2.3RT} - 0.324 \log(X_i^*) + 2.88;$$

$$r = 0.94, \quad n = 5 \quad (13)$$

and

$$\log(K_{oc})_{MICH.} = \frac{-\Delta S_f(T_m - T)}{2.3RT} - 0.547 \log(X_i^*) + 0.58;$$

$$r = 0.93, \quad n = 5. \quad (14)$$

It is apparent that this correlation between K_{oc} and aqueous solubility are less satisfactory than those between K_{oc} and t_c , even when the activity of the solute is corrected to its supercooled liquid phase. This is probably due in large measure to the wide discrepancies commonly observed in reported solubility values. Experimental determination of aqueous solubility can be exceedingly difficult for a number of reasons, including compound instability, the presence of impurities, and slow rates of approach to equilibrium. These problems are especially prominent for very hydrophobic organic substances (Chin *et al.*, 1986). Reported values for the solubility of *p,p'*-DDT, for example, range over two orders of magnitude (Hakfenschied and Tomlinson, 1981). The accuracy of a K_{oc} estimate based on aqueous solubility is highly dependent upon the accuracy of the measured value, as well as on that of other parameters required in performing the estimate (e.g.

the solute melting point, and entropy of fusion if the compounds are nonrigid) (Karickhoff, 1981).

Carbon normalized partition coefficient estimates derived from equations (8) and (9) are presented in Table 4. The predicted $\log(K_{oc}s)$ are compared in this table to experimental values from similar natural sorbent/water systems. The agreement between HPRPLC-estimated and observed $\log(K_{oc})$ values is good, with an average absolute deviation of 0.18 log units for the high-solids system and 0.25 log units for the low solids system. Larger deviations do occur for the low-solids data because the determination of linear distribution coefficients is analytically more difficult and subject to greater error. It appears from both the measured and predicted K_{oc} values that sorption behavior is specific to the type and amount of solid present. The HPRPLC approach thus requires calibration of solute retention time to a particular system if reliable estimates are to be expected.

CONCLUSIONS

Investigation of the sorption and HPRPLC retention characteristics of several hydrophobic organic solutes with respect to different solids indicates that HPRPLC corrected retention time provides a reasonable basis for estimation of linear partitioning behavior. A HPRPLC retention time- $\log(K_{oc})$ model has been derived using a thermodynamic approach, and experimental data obtained to evaluate the coefficients of that model. Absolute average deviations between K_{oc} values estimated by the model are well below a half order of magnitude. Correlations between K_{oc} , K_{ow} and aqueous solubility have also been established, but these in general provide a poorer characterization of K_{oc} . The HPRPLC retention time technique has potential as a means for elucidating the sorptive properties of geochemically and environmentally significant substances, and, when coupled with a qualitative analytical instrument (e.g. mass spectroscopy), can also be used to quickly identify and determine the sorptive properties of diagenetically altered organic compounds.

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Table 4. HPRPLC-estimated and observed K_{oc} values

Compound	$\log(t_c)$	$\log(K_{oc})_p^*$	$\log(K_{oc})_o$	$\log(K_{oc})_p^\dagger$	$\log(K_{oc})_o$
Phenanthrene	0.95	4.81	5.10‡	4.20	4.08§
Naphthalene	0.62	3.89	3.52††	3.25	3.11
Pyrene	1.16	5.40	5.40‡	4.81	4.88§
<i>p,p</i> -DDT	1.30	5.78	6.25¶	5.21	5.14
<i>p</i> -DCB	0.63	3.92	4.04**	3.28	2.78

*Low solids to water ratio. †High solids to water ratio. ‡B. J. Eadie, unpublished data; §Karickhoff *et al.* (1979) and Karickhoff (1981); ¶Pierce *et al.* (1974); ||Schwarzenbach and Westall (1981); **Measured for OSH for this paper; ††Voice and Weber (1985).

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