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# SEDIMENT-WATER PARTITION COEFFICIENTS AND HPLC RETENTION FACTORS OF AROMATIC HYDROCARBONS

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ABSTRACT Sediment to water partition coefficients have been measured for fourteen alkylbenzene and polyaromatic hydrocarbons together with their HPLC capacity factors. The partition coefficients vary between $10^{0.2}$ and $10^{3.7}$, and different homologous series of hydrocarbons separately correlate both the octanol-water partition coefficients and octadecylisilane capacity factors. All partition coefficients correlate well with the alkylcyano capacity factors, and it is suggested that this mildly polar phase mimics better the sorption onto sediment than either octanol or octadecylsilane phases.

## INTRODUCTION

The sediment or soil-water partition coefficient ($K_p$) is an important parameter in describing the environmental fate of lipophilic organic compounds (1). Values for $K_p$ may be obtained by direct measurement or may be estimated by indirect techniques. Karickhoff, Means and Schwarzenbach and their co-workers (1-5) have shown that the partition coefficient may be estimated from the octanol-water partition coefficient, Kow, using the equation:

$$\log K_p = a \log K_{ow} + \log f_{oc} + b \qquad (1)$$

where $f_{oc}$ is the fractional organic content of the particulates and a and b are constants. For a wide variety of substrates, partition is determined by the lipophilicity of the solute and the organic carbon content of the substrate, so that Equation (1) can be simplified to:

$$\log K_{oc} = a \log K_{ow} + b \qquad (2)$$

where $K_{oc}$ is the notional organic carbon-water partition coefficient.

The difficulty with such empirical relationships is twofold. Firstly, there is uncertainty in the $K_{ow}$ values particularly for the more lipophilic compounds (6) and, secondly, there does not appear to be a unique equation for all substrate or compound types (5). In view of this, it seemed worthwhile to investigate the relation between sediment partition coefficients and



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retention on reverse-phase high performance liquid chromatography (R-P HPLC). Both the surface chemistries and the theory of partition suggest close parallels between adsorption onto natural particulates and retention by lipophilic HPLC phases (7-9). A group of alkylbenzene and polyaromatic hydrocarbons were chosen as solutes for this study as they span a wide range of properties associated with the hydrocarbons that are toxic constituents of oil.

## EXPERIMENTAL

Surface sediment (2-10 cm) was collected from the central Tamar estuary in February 1984, wet sieved (<60 µm), aerated for 24 hr, and reseparated by centrifuge. The solid was freeze dried and disintegrated in an end-over-end shaker. This material had >75% of the particle size evenly distributed in the range 2.7 - 37.6 µm (Malvern 2200/3300 Particle Sizer) and an organic carbon content of 4.02 ± 0.06% according to the oxidative method of Amoto (10).

Hydrocarbons were LR grade or better and used without further purification. Water was adjusted to 0.2% with synthetic sea salt (Tropic Marin). All equilibrations and separations were carried out at 18.5°C.

For most partition experiments, weighed mixtures of water (~ 11 mL) and sediment (0.05-2g) were placed in 10 mL screw-cap glass vials with minimum headspace. Spikes (2-20 µL) of hydrocarbon in acetone solution (0.2-0.5mg/mL) were added and the mixtures stirred for 2 hours.

After centrifuging, a weighed portion of the supernatent was extracted with dichloromethane containing 1-chloro-n-octane and 1-chloro-n-decane as internal standards. Extracts were assayed using a Carlo-Erba HRGC gas chromatograph equipped with an SE-54 capillary column.

For 1-ethylnaphthalene and pyrene, extraction was into dichloromethane containing naphthalene as internal standard followed by quantitation by HPLC using methanol-water (75-25), a Varian CH-10 MicroPak column and detection at 285nm.

Time sequence experiments showed that partition was sensibly complete after 1 hour. There was insignificant (<2%) hydrocarbon contributed by the sediment, and recoveries from water were efficient (>96%) except for n-butylbenzene (90%) for which a correction was made. The concentration of sorbed hydrocarbon was calculated by difference, and the partition coefficient calculated according to the formula:

$$Kp = \frac{\%(w/w) \text{ in sediment} \times \text{mass of water}}{\%(w/w) \text{ in water} \times \text{mass of sediment}} \qquad (3)$$

Retention data on HPLC were obtained using either a Varian CH-10 MicroPak column and 75-25 methanol-water (1 mL/min) with detection at 283nm or a Varian CN-10 MicroPak column and 55-45 methanol-water and detection at 255 nm. Methanol was the unretained compound used in calculating capacity factors.

## RESULTS AND DISCUSSION

The sediment-water partition coefficients and HPLC capacity factors (k') are in given in Table 1. For the range of sediment loads (7-200 mg/mL) and initial hydrocarbon concentration (0.1-1.5 μg/mL), there is no systematic change in $K_p$ values and thus there is simple partitioning according to Equation 3.

Table 1: Partition, retention and solubility data for aromatic hydrocarbons.

| Compound | Log $K_p$ | n[a] | Log $k'_{ODS}$ | Log $k'_{CN}$ | Log $K_{ow}$ [b] | Log S [b,c] |
|---|---|---|---|---|---|---|
| Benzene | 0.020 ± 0.16 | 6 | -0.0515 | -0.369 | 2.13 | -1.64 |
| Methylbenzene | 0.60 ± 0.12 | 11 | 0.124 | -0.186 | 2.65 | -2.20 |
| Ethylbenzene | 1.01 ± 0.08 | 16 | 0.280 | -0.035 | 3.13 | -2.75 |
| n-Propylbenzene | 1.47 ± 0.05 | 16 | 0.466 | 0.177 | 3.69 | -3.36 |
| n-Butylbenzene | 2.00 ± 0.04 | 16 | 0.626 | 0.438 | 4.28 | -3.99 |
| *o*-Xylene | 0.95 ± 0.07 | 17 | 0.268 | -0.017 | 3.13 | -2.68 |
| *p*-Xylene | 1.02 ± 0.08 | 17 | 0.298 | 0.000 | 3.18 | -2.69 |
| Naphthalene | 1.53 ± 0.04 | 19 | 0.210 | 0.080 | 3.35 | -3.09 |
| 1-Methylnaphthalene | 1.96 ± 0.03 | 17 | 0.384 | 0.272 | 3.87 | -3.70 |
| 2-Methylnaphthalene | 2.00 ± 0.03 | 15 | 0.386 | 0.283 | 3.86 | -3.65 |
| 1-Ethylnaphthalene | 2.37 ± 0.04 | 3 | 0.519 | 0.432 | 4.39 | -4.16 |
| 2-Ethylnaphthalene | 2.36 ± 0.04 | 14 | 0.520 | 0.460 | 4.43[c] | -4.32[d] |
| Phenanthrene | 2.88 ± 0.04 | 6 | 0.485 | 0.535 | 4.57 | -4.60 |
| Pyrene | 3.73 ± 0.06 | 4 | 0.629 | 0.810 | 5.18 | -4.88 |

a Number of measurements

b Data from ref 18

c Solubility, S, in mole/L for liquids or supercooled liquids

d Data from ref 23

Figure 1 shows the correlation between $K_p$ and $K_{ow}$, with regression for all 14 hydrocarbons giving:

$$\log K_p = 1.15 \log K_{ow} - 2.53 \quad r^2 = 0.961 \qquad (4)$$

Accommodating on organic carbon content of 4.0% gives:

$$\log K_{oc} = 1.15 \log K_{ow} - 1.13 \qquad (5)$$

The slope parameter "a" in equation 2 is a measure of the change in free energy of solute transfer from water to sediment organic matter compared to the change in free energy on solute transfer from water to octanol. A value a=1 implies that these changes are the same, that is, both octanol and sediment organic matter are behaving similarly towards the variations in solute characteristics (11).

Slope parameters a=1.0 have been reported by Karickhoff (1,2) and Means (3,4) and their co-workers for various natural substrates and solutes. However, not all compounds fit these correlations (12), and other studies have yielded different slope parameters of a=0.904 (8) and a=0.72 (5). This led Schwazenbach & Westall (5) to suggest that, rather than real differences in substrate lipophilicity, the variation in slopes could reflect only the total number and types of solutes for which the correlations were made and the non-uniqueness of the correlation.

It would be fortuitous for different classes of solutes to have similar affinities for octanol and natural organic matter. Indeed, as shown in Figure 1, the present data are more sensibly correlated if the hydrocarbons are placed into homologous groups. The sequence benzene-naphthalene-phenanthrene-pyrene gives:

$$\log K_{oc} = 1.20 \log K_{ow} - 1.13 \quad r^2=0.998 \qquad (6)$$

while the alkylbenzenes and alkylnaphthalenes give, respectively:

$$\log K_{oc} = 0.904 \log K_{ow} - 0.46 \quad r^2=0.996 \qquad (7)$$

$$\log K_{oc} = 0.774 \log K_{ow} + 0.37 \quad r^2=0.992 \qquad (8)$$

The separation between homologous series is clearer in the correlation between $K_p$ and HPLC capacity factors on octadecylsilane phase, $k'_{ODS}$, as shown in Figure 2. Here the polyaromatic sequence yields:

$$\log K_p = 5.406 \log k'_{ODS} + 0.315 \quad r^2=0.998 \qquad (9)$$

while alkylbenzenes and alkylnaphthalenes yield regressions of substantially smaller slopes:

$$\log K_p = 2.845 \log k'_{ODS} + 0.193 \quad r^2=0.996 \qquad (10)$$

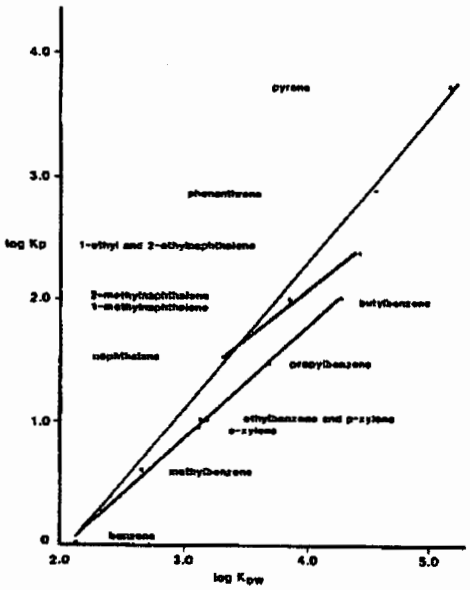


Figure 1: Relationship between sediment-water partition coefficient and octanol-water partition coefficient.

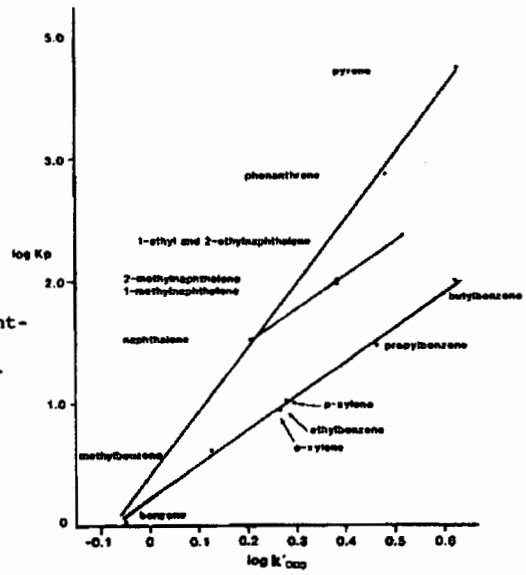


Figure 2: The relationship between sediment-water partition coefficient and octadecylsilane capacity factor.

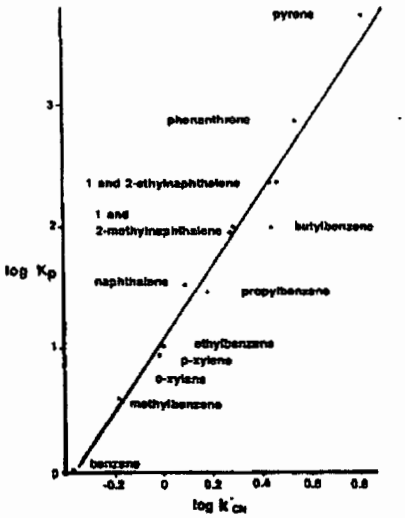


Figure 3: Relationship between sediment-water partition coefficient and alkylcyano capacity factor.

$$\log K_p = 2.71 \log k'_{ODS} + 0.95 \quad r^2=0.998 \quad (11)$$

Changing the chromatographic phase to alkylcyano largely collapses these differences (Figure 3), and all 14 hydrocarbons can be regressed to give:

$$\log K_p = 3.023 \log k'_{CN} + 1.085 \quad r^2=0.972$$

Rather than focus on the absolute magnitude of the slope values "a", these patterns are better understood in terms of the divergence of the aromatic and aliphatic sequences. The divergence is small for the alkylcyano phase suggesting that it is behaving as a similar sorbent to sediment organic matter for all 14 hydrocarbons. Octanol and octadecylsilane show progressively larger divergences, and an order may be generated: organic matter ~ alkyl CN > octanol > ODS. This is about the order we expect for the polarity of the sorbent phase. Octadecylsilane should be the least polar in view of its hydrocarbon-like structure and chromatographic properties (13), while sediment organic matter should be the most polar due to the presence of groups such as carboxyl, phenol and amine in humic materials (14). Both octanol and alkylcyano should be intermediate. Octanol, for example, dissolves less water than soil organic matter and is the superior partition phase for lipophilic compounds (8). The functionality of the MicroPak CN column is cyanopropyl, and this phase is described as 'moderately polar' with retentive properties that allow it to absorb polar as well as lipophilic materials (13).

These polarity differences may then explain why the Kp values are more sensitive than either $K_{ow}$ and $k'_{ODS}$ to changes in solute aromatic structure (Figures 1 and 2). Aromatic hydrocarbons are more polar (polarizable) than aliphatic hydrocarbons, as evidenced, for example, by the higher solvent strengths (15) and water solubility (16) of aromatics for molecules of similar carbon number. Modification of the aromatic structure may then cause greater change in partition to a similar phase (organic matter) than to one that is not (octanol or ODS). The same would hold for changes in aliphatic structure except that here the more compatable phase is either octanol or ODS.

For weakly-polar compounds, hydrophobic interactions or water insolubility has been advanced as the major driving force for sorption or solvent partition (8,17). Thus log Kp should correlate -log SV, where S is the liquid or supercooled liquid solubility and V is the molar volume of hydrocarbon (18). Figure 4 shows that all 14 hydrocarbons yield:

$$\log K_p = -1.142 \log SV - 3.132 \quad r^2=0.955$$

Again, however, alkylbenzenes are more closely correlated ($r^2$=0.994) with the PAH's lying above the line indicating enhanced sorption. We note that the polyfunctional nature of humic materials (14) may provide several modes of sorbate-sorbent interaction, so that different classes of compounds may have different strengths of sorption. This does not appear to be the case for partition into octanol, where hydrophobic interactions appear to dominate (17). In our case also, log SV closely correlates log $K_{ow}$ ($r^2$=990), with the exception of pyrene. Pyrene appears to have an anomalously high solubility in relation to its Kow, Kp, $k'_{ODS}$ and $k'_{CN}$.

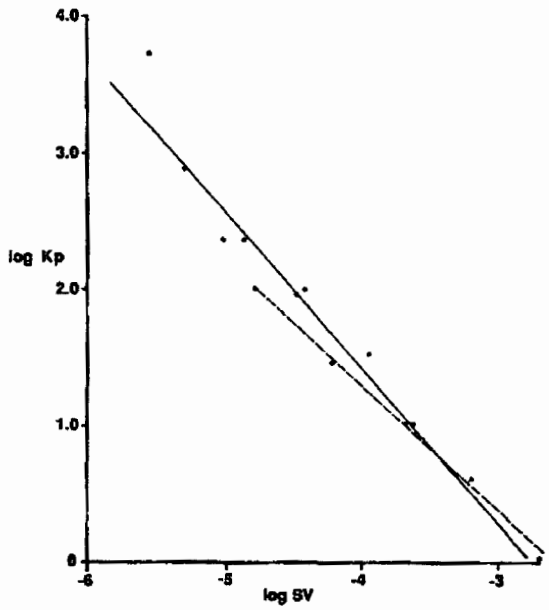


Figure 4: Relationship between sediment-water partition coefficient and water solubility, S in mole/L and V in litre/mole. The interrupted line is the regression for alkylbenzenes only.

Two further points can be made. Firstly, reverse-phase chromatography on the mildly polar alkylcyano media may be a rapid way of estimating unknown $K_p$ values. The choice of sorbent phase similar to sediment organic matter may also compress any partition differences between different classes of compounds. It would be interesting to see if these differences extend to other homologous series. We note that despite the very large number of investigations into the solubility and partition behaviour of hydrophobic solutes, only polychlorinated biphenyls (7), chlorinated hydrocarbons (5, 8, 19), and alkylated hydrocarbons (20,21) have formed closely related series of compounds.

Secondly, the systematic way in which $K_p$ (or $K_{oc}$) varies along a homologous series suggests that a substituent constant may be generated in much the same way as proposed for soil organic matter (1) and $K_{OW}$ (22). The change in partition coefficient for the addition of a methylene group (alkyl substituents), $\Delta \log K_{oc}$, is 0.48 for alkylbenzenes and 0.41 for alkylnaphthalenes. A comparable figure of 0.39 ± 0.10 is obtained from soil sorption of alkylbenzenes reported by Schwarzenbach and Westall (5). For fused ring fragments, $\Delta \log K_{oc}$ is 1.4 for α-substitution (benzene-naphthalene-phenanthrene), 0.8 for β substitution (pyrene), or 1.2 overall. Values for α-substituted PAH[B] sorbed onto soil are 1.16-1.20 (1,2) while the sorption data for colloidal organic substrates reported by Wijayaratne and Means (4) yield an average figure of 1.5.

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