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# Sorption of Polynuclear Aromatic Hydrocarbons by Sediments and Soils†

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■ The sorption of pyrene, 7,12-dimethylbenz[*a*]anthracene, 3-methylcholanthrene, and dibenzanthracene on 14 soil and sediment samples exhibiting a wide range of physicochemical properties was studied. The equilibrium Freundlich constants ($K_d$) and linear partition coefficients ($K_p$) for each compound were found to be highly correlated with the organic carbon content of the soils/sediments tested. No other significant correlations with soil/sediment properties were observed. The sorption constants ($K_p$) when normalized to organic carbon content of the substrate ($K_{oc}$) were predictive of the octanol–water partition coefficients for the compounds tested. A highly significant negative correlation was observed between log $K_{oc}$ and log (water solubility) for these compounds. Experimental values of the water solubility and octanol–water partition coefficients for the four compounds are reported.

## *Introduction*

Polynuclear aromatic hydrocarbons (PAHs) are ubiquitous products of the combustion of carbon-based materials. As a class these compounds are important environmentally because many individual PAHs have been demonstrated to cause mutations and certain types of cancer (*1, 2*).

The PAHs are a diverse chemical class, and member compounds have been found widely distributed in atmospheric particulates (*3*), freshwater and various sediments (*4, 5*), soils (*6*), and leachates (*7*). The environmental sources of the PAHs include both anthropogenic inputs such as energy production (*8*) and the transportation, storage, and refining of fuels (*9*) and natural inputs such as combustion (e.g., forest fires) (*10*), sediment diagenesis (*11, 12*), geologic phenomena (e.g., volcanos, tar pits, seepage from rock formations) (*13*), and biological conversion of biogenic precursors (*14*).

Although the sources and distribution of PAHs in soils and sediments have been studied fairly extensively, the transport and fate of PAHs on soil/sediment surfaces are poorly understood. In addition, the physical and chemical properties which govern the interaction of the PAHs and substrates have not been characterized or quantitated. Sorption is known to be an important factor in the determination of the fate of hydrophobic molecules in a water/sediment or water/soil system (*15, 16*). Karickhoff et al. (*17*) have described the sorption behavior of a number of hydrophobic molecules including some PAHs on sediments. They suggested that the sorption of such molecules appears to be determined by the organic carbon content of the substrate. They further suggested that the sorption constant $K_{oc}$, which is derived from the linear partition coefficient $K_p$ and the organic content of the sorptive substrate (fractionated sediment fines), could be related to the solubility of the compound and to the solvent partitioning of the compound (e.g., octanol–water partition coefficient, $K_{ow}$). In preliminary studies on two PAHs, we were able to demonstrate that these observations were true for sorption of hydrophobic molecules on whole sediments and soils of differing geologic origin (*18*). In addition, we have shown that the sorption of nitrogen heterocyclic (*19*) and sulfur heterocyclic (*20*) PAH is determined by the organic carbon content of the soil/sediment and is independent of substrate pH, cation exchange capacity, textural composition, or clay mineralogy. We concluded that soil/sediment $K_{oc}$ values could be fairly reliably predicted from the $K_{ow}$ of the sorbing compound and the organic carbon content of the individual soil/sediment.

In the present study, we have investigated the detailed sorptive behavior of four PAH compounds with varying chemical and structural characteristics on a group of 14 sediments and soils. Linear partition coefficients ($K_p$) and $K_{oc}$ values for each compound on each sediment/soil are reported. The water solubility and octanol–water partition coefficients of the four compounds were determined experimentally. The relative influence of the chemical and physical properties of the compounds and substrates on the sorptive process is discussed. The value and reliability of the $K_{ow}$ and water solubility parameters for predicting sorption of PAH is evaluated.

## *Experimental Section*

**Collection of Samples.** The soil and sediment samples used in this study were collected from sites along the Missouri, Ohio, Wabash, Illinois, and Mississippi Rivers (Figure 1). These sites were selected because (1) they are already associated with numerous energy-generating facilities and are likely sites for the construction of additional coal or oil-fired power plants and advanced coal conversion facilities (*21*) and (2) they provide a wide range of soil/sediment types which exhibit properties that have been shown to affect the degree of adsorption of organic compounds. A total of 28 samples were collected. Fourteen samples were selected for the sorption studies following the detailed characterization described below.

**Sample Characterization.** Each soil/sediment sample was analyzed for a number of physical and chemical properties including reaction pH, cation exchange capacity, percent total nitrogen, percent organic carbon, and texture (i.e., sand, silt, and clay fraction). In addition, clay mineral analysis and determinations of amorphous aluminum, iron, and silicon were performed. The methods for each of these determinations have been outlined by Means et al. (*18*).

**Water Solubilities and Octanol–Water Partition Coefficients of Selected PAHs.** The water solubilities and octanol–water partition coefficients of pyrene, 7,12-dimethylbenz[*a*]anthracene (DMBA), 3-methylcholanthrene (3-MC), and 1,2;5,6-dibenzanthracene (DBA) were determined by using the procedures outlined by Means et al. (*18*). In each determination, the final data were corrected for trace impurities by using methods outlined by Wood and Means (*22*).

† This paper is Contribution No. 1026 of the Center for Environmental and Estuarine Studies of the University of Maryland and a contribution of the Institute for Environmental Studies and the Department of Agronomy of the University of Illinois at Champaign-Urbana.



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**Figure 1.** Sampling sites for the 14 sediments and soils.

**Reagents and Chemicals.** Three of the PAHs studied were obtained in radiolabeled form from New England Nuclear. The compounds 7,12-di[$^{14}$C]methylbenz[*a*]anthracene (98+% pure, specific activity, 114.6 mCi/mmol), 3-methyl[6-$^{14}$C]-cholanthrene (97+% pure, specific activity, 60.2 mCi/mmol), and 1,2;5,6-[G-$^{3}$H]dibenzanthracene (96+% pure, specific activity, 35.1 Ci/mmol) were further purified by preparative thin-layer chromatography. All materials used for these studies were 99+% pure.

Pure pyrene (99+%, Aldrich) was tritiated by using the $BF_3$–$^{3}H_3PO_4$ procedure described by Hilton and O'Brien (*23*). The radiolabeled pyrene was purified by microdistillation followed by preparative thin-layer chromatography. The final material had a purity of 99+% and a specific activity of 300 mCi/mmol as determined by liquid scintillation counting and gas chromatography.

All reagents used in these experiments were reagent grade and certain solvents (e.g., 1-octanol, methanol) were redistilled in glass. The water used in all experiments was generated by a Milli-Q purifying system (Millipore).

**Sorption Isotherms.** Batch equilibrium sorption isotherms were determined for five concentrations of each compound on each soil/sediment sample. The sorption isotherms were measured in triplicate on mixtures of soil/sediment and water in the proportions of 2 g to 40 mL for 3-MC and DBA, and 4 g to 40 mL for pyrene and DMBA in stainless steel centrifuge tubes. In the case of pyrene, 40 mL of aqueous solution of the compound were added to the substrate in each tube. In the other three cases, the compound was plated onto the walls of the tubes from acetone solution by evaporating the acetone under nitrogen. The substrate and water were added to the tubes. The tubes were sealed with Teflon-lined caps and placed in a temperature-controlled shaking water bath at 25 °C for 24 h. Kinetic studies on each compound/substrate combination indicated that equilibrium was achieved in 20 h or less.

After equilibration, the tubes were centrifuged in a temperature-controlled (25 °C) centrifuge at 12 000*g* for 10 min. Following centrifugation, the aqueous phase was sampled (1 mL) for liquid scintillation counting. The initial and final solution concentrations of the compound were determined by liquid scintillation counting, and the amount sorbed was calculated by difference. A mass balance for the $^{14}$C or $^{3}$H label was performed for each set of isotherms to verify that there were no losses of labeled material during the isotherm experiments. Techniques for these mass balance determinations are discussed by Means et al. (*18*) and Hassett et al. (*24*).

It should be noted that studies of this type require handling of relatively large quantities of radioactive substances and compounds which are known or suspected carcinogens. Investigators are cautioned that experiments of this type should only be conducted in approved laboratory facilities with stringent supervision by personnel who have been specifically trained in the safe use of radioactive and toxic compounds.

## *Results and Discussion*

The physicochemical characterization of the 11 sediments and 3 watershed soils selected for this study revealed that the samples possessed a broad range of values for all parameters tested including clay mineralogy (Tables I–III). The pHs of 1:1 (water:substrate) slurries of the substrates ranged from 4.54 to 8.34. Cation exchange capacities (CEC) ranged from 3.72 to 33.01 mequiv/100 g, and percent nitrogen and percent organic carbon ranged from 0.010 to 0.195% and from 0.11 to 2.38%, respectively. The clay content of the samples ranged from 6.8% (EPA-8) to 69.1% (EPA-23). Matrix correlation of the major substrate characteristics (Table I) associated with sorption indicated that the 14 substrates were random with respect to all characteristics except for the percent organic carbon/percent nitrogen interaction and the percent clay/CEC interaction.

**Table I. Characteristics of Soils and Sediments**

| Sample | pH (1:1) [b] | pH (1:2) [b] | CEC, mequiv/100 g | total N, % | organic carbon, % | sand, % | clay, % | silt % |
|---|---|---|---|---|---|---|---|---|
| EPA-B2 | 6.35 | 6.50 | 3.72 | 0.073 | 1.21 | 67.5 | 18.6 | 13.9 |
| EPA-4 | 7.79 | 8.22 | 23.72 | 0.190 | 2.07 | 3.0 | 55.2 | 41.8 |
| EPA-5 | 7.44 | 7.20 | 19.00 | 0.192 | 2.28 | 33.6 | 31.0 | 35.4 |
| EPA-6 | 7.83 | 8.23 | 33.01 | 0.097 | 0.72 | 0.2 | 68.6 | 31.2 |
| EPA-8 | 8.32 | 8.56 | 3.72 | 0.010 | 0.15 | 82.4 | 6.8 | 10.7 |
| EPA-9 [a] | 8.34 | 8.55 | 12.40 | 0.015 | 0.11 | 7.1 | 17.4 | 75.6 |
| EPA-14 [a] | 4.54 | 4.30 | 18.86 | 0.064 | 0.48 | 2.1 | 63.6 | 34.4 |
| EPA-15 | 7.79 | 7.80 | 11.30 | 0.092 | 0.95 | 15.6 | 35.7 | 48.7 |
| EPA-18 | 7.76 | 7.79 | 15.43 | 0.062 | 0.66 | 34.6 | 39.5 | 25.8 |
| EPA-20 [a] | 5.50 | 5.16 | 8.50 | 0.126 | 1.30 | 0.0 | 28.6 | 71.4 |
| EPA-21 | 7.60 | 7.95 | 8.33 | 0.157 | 1.88 | 50.2 | 7.1 | 42.7 |
| EPA-22 | 7.55 | 7.90 | 8.53 | 0.128 | 1.67 | 26.1 | 21.2 | 52.7 |
| EPA-23 | 6.70 | 7.10 | 31.15 | 0.195 | 2.38 | 17.3 | 69.1 | 13.6 |
| EPA-26 | 7.75 | 8.10 | 20.86 | 0.152 | 1.48 | 1.6 | 42.9 | 55.4 |

[a] Soils; all others are sediments. [b] Equilibrium pH of 1:1 and 1:2 (water:substrate) slurries.

**Table II. Semiquantitative Determination of Clay Minerals in the <2 μm Fraction of Sediments and Soils by X-ray Diffraction**

| sample | montmorillonite (M) or vermiculite (V), % | illite, % | kaolinite, % |
|---|---|---|---|
| EPA-B2 | 2.0 (V) | 2.7 | 13.9 |
| EPA-4 | 40.1 (M) | 5.7 | 9.4 |
| EPA-5 | 25.7 (M) | 1.8 | 3.5 |
| EPA-6 | 60.8 (M) | 4.6 | 3.2 |
| EPA-8 | 6.1 (M) | 0.2 | 0.5 |
| EPA-9[a] | 16.3 (M) | 0.4 | 0.7 |
| EPA-14[a] | 13.8 (V and M) | 12.8 | 37.0 |
| EPA-15 | 10.1 (V and M) | 10.4 | 15.2 |
| EPA-18 | 29.7 (M) | 2.8 | 7.0 |
| EPA-20[a] | 21.9 (M) | 2.1 | 4.6 |
| EPA-21 | 2.8 (M) | 1.6 | 2.7 |
| EPA-22 | 14.8 (M) | 2.1 | 4.3 |
| EPA-23 | 57.6 (M) | 4.2 | 7.3 |
| EPA-26 | 37.1 (M) | 1.7 | 4.1 |

[a] Soils; all others are sediments.

**Table III. Sodium Hydroxide-Extractable Si and Al and Citrate-Dithionate-Extractable Fe in the Sediment and Soil Samples**

| sample | Si, % | Al, % | Fe, % |
|---|---|---|---|
| EPA-B2 | 0.12 | 0.25 | 0.88 |
| EPA-4 | 0.18 | 0.07 | 0.71 |
| EPA-5 | 0.12 | 0.03 | 0.49 |
| EPA-6 | 0.44 | 0.03 | 0.59 |
| EPA-8 | 0.08 | 0.01 | 0.22 |
| EPA-9[a] | 0.26 | 0.02 | 0.59 |
| EPA-14[a] | 0.10 | 0.20 | 1.38 |
| EPA-15 | 0.09 | 0.10 | 1.27 |
| EPA-18 | 0.10 | 0.05 | 0.74 |
| EPA-20[a] | 0.16 | 0.14 | 0.61 |
| EPA-21 | 0.12 | 0.05 | 0.60 |
| EPA-22 | 0.09 | 0.05 | 0.61 |
| EPA-23 | 0.21 | 0.12 | 0.73 |
| EPA-26 | 0.29 | 0.13 | 0.63 |

[a] Soils; all others are sediments.

The clay mineralogy of the 14 samples also indicated a wide range of both swelling and nonswelling clay types (Table II). Both predominantly montmorillonitic and predominantly kaolinitic types coupled with high and low organic carbon contents are represented among the substrates. This is important because the clay type and clay/organic matter content ratio of the sorbent have been shown to be significant in determining the degree of sorption of certain classes of organic compounds (25–27). Amorphous silica, iron, and aluminum contents (Table III) of the 14 substrates ranged from 0.08 to 0.44, from 0.22 to 1.38, and from 0.01 to 0.25%, respectively.

The water solubilities and octanol–water partition coefficients of the four PAH compounds used in these studies are presented in Table IV. The four compounds span a range of approximately two orders of magnitude for water solubility (2.5–135 ppb) and an order of magnitude for $K_{ow}$ ($1.2 \times 10^5$–$3.2 \times 10^6$). The water solubilities compare well with data obtained by Mackay and Shiu (28) on several PAHs. The octanol–water partition coefficients determined in this study

**Table IV. Water Solubilities and Octanol–Water Partition Coefficients for Selected PAHs**

| compd | water solubility, μg/L | octanol–water partition coeff, $K_{ow}$ |
|---|---|---|
| pyrene | 135 ± 13 | 124 000 ± 11 000 |
| 7,12-dimethylbenz-anthracene | 24.4 ± 4.2 | 953 000 ± 59 000 |
| 3-methylcholanthrene | 3.23 ± 0.17 | 2 632 000 ± 701 000 |
| 1,2;5,6-dibenzanthracene | 2.49 ± 0.81 | 3 170 000 ± 883 000 |

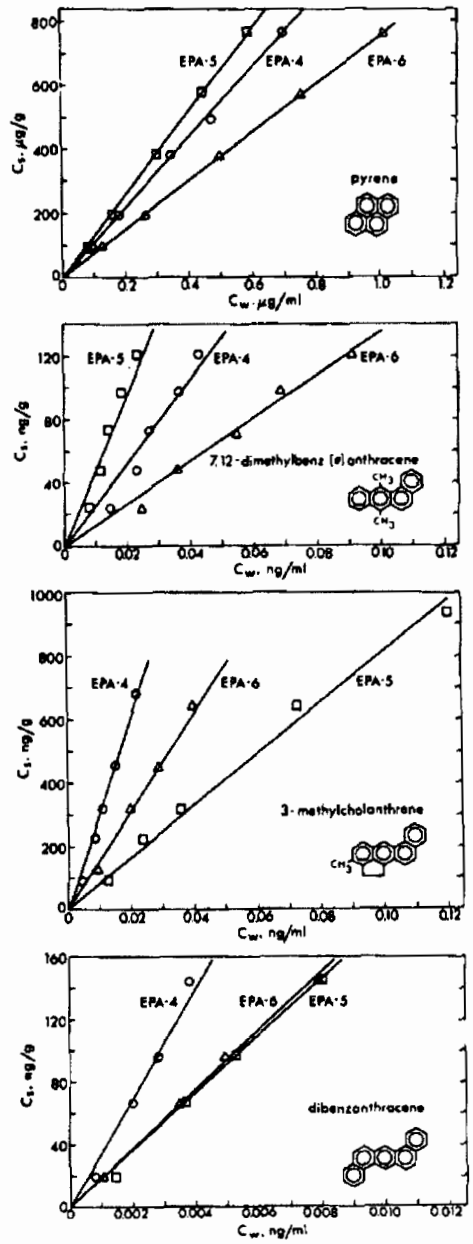


**Figure 2.** Representative sorption isotherms for pyrene, 7,12-dimethylbenz[a]anthracene, 3-methylcholanthrene, and dibenzanthracene.

**Table V. Equilibrium Sorption Constants for Selected PAHs on 14 Soil/Sediment Samples**

| | | pyrene | | | 7,12-dimethylbenzanthracene | | | 3-methylcholanthrene | | | 1,2;5,6-dibenzanthracene | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| soil/sed | % OC | $K_p$ | $r^2$ | $K_{oc}$ | $K_p$ | $r^2$ | $K_{oc}$ | $K_p$ | $r^2$ | $K_{oc}$ | $K_p$ | $r^2$ | $K_{oc}$ |
| EPA-B2 | 1.21 | 760 | 0.988 | 62 860 | 2371 | 0.896 | 195 998 | 15 140 | 0.935 | 1 251 210 | 20 461 | 0.955 | 1 690 971 |
| EPA-4 | 2.07 | 1065 | 0.995 | 51 469 | 2646 | 0.978 | 127 812 | 30 085 | 0.965 | 1 453 404 | 34 929 | 0.947 | 1 687 404 |
| EPA-5 | 2.28 | 1155 | 0.981 | 50 650 | 5210 | 0.971 | 228 499 | 8 273 | 0.995 | 362 845 | 18 361 | 0.975 | 805 292 |
| EPA-6 | 0.72 | 614 | 0.964 | 85 256 | 1346 | 0.954 | 186 986 | 15 820 | 0.974 | 2 197 250 | 18 882 | 0.979 | 2 622 453 |
| EPA-8 | 0.15 | 101 | 0.989 | 67 467 | 611 | 0.975 | 407 496 | 2 257 | 0.970 | 1 504 538 | 1 759 | 0.931 | 1 172 847 |
| EPA-9[a] | 0.11 | 71 | 0.979 | 64 706 | 1028 | 0.992 | 934 225 | 2 694 | 0.995 | 2 449 190 | 2 506 | 0.957 | 2 277 875 |
| EPA-14[a] | 0.48 | 277 | 0.979 | 57 763 | 562 | 0.981 | 117 161 | 30 627 | 0.975 | 6 380 703 | 14 497 | 0.959 | 3 020 262 |
| EPA-15 | 0.95 | 783 | 0.994 | 82 421 | 3742 | 0.981 | 393 907 | 23 080 | 0.993 | 2 429 456 | 25 302 | 0.973 | 2 663 317 |
| EPA-18 | 0.66 | 504 | 0.994 | 76 316 | 1895 | 0.988 | 287 196 | 20 642 | 0.995 | 3 127 521 | 20 192 | 0.951 | 3 059 425 |
| EPA-20[a] | 1.30 | 723 | 0.986 | 59 646 | 1617 | 0.969 | 124 347 | 16 231 | 0.961 | 1 248 534 | 7 345 | 0.967 | 565 014 |
| EPA-21 | 1.88 | 1119 | 0.990 | 59 515 | 5576 | 0.987 | 296 580 | 24 506 | 0.983 | 1 303 532 | 55 697 | 0.956 | 2 962 603 |
| EPA-22 | 1.67 | 806 | 0.977 | 48 236 | 2679 | 0.984 | 160 391 | 20 972 | 0.943 | 1 255 821 | 39 809 | 0.976 | 2 383 765 |
| EPA-23 | 2.38 | 1043 | 0.942 | 43 807 | 6777 | 0.981 | 284 743 | 17 127 | 0.973 | 719 633 | 19 254 | 0.963 | 808 991 |
| EPA-26 | 1.48 | 994 | 0.994 | 67 189 | 3740 | 0.984 | 252 735 | 37 364 | 0.974 | 2 524 581 | 39 840 | 0.855 | 2 691 870 |
| | | mean $K_{oc}$ = 62700 ± 12000 | | | mean $K_{oc}$ (w/o 9) = 235700 ± 92800 | | | mean $K_{oc}$ (w/o 5 and 14) = 1789000 ± 694000 | | | mean $K_{oc}$ = 2029000 ± 862000 | | |

[a] Soils; all others are sediments.

for DMBA, 3-MC, and DBA are the first experimental values to be reported.

The data obtained from the batch equilibrium sorption experiments for the four PAH compounds on the sediments and soils are presented in Table V. The Freundlich equilibrium constants ($K_d$) were obtained by first fitting the averages of the triplicate values determined for five concentration points in each isotherm to eq 1,

$$C_s = K_d C_w^{1/n} \quad (1)$$

where $C_s$ is equal to the equilibrium concentration of the compound sorbed to the solid phase calculated on a dry weight basis, $C_w$ is equal to the concentration of the compound remaining in the aqueous phase at equilibrium, $K_d$ is the partition coefficient (constant), and $1/n$ is a constant related to the surface adsorption capacity of the solid phase. For all cases, the best fit was a linear isotherm with the $1/n$ value varying near unity. Examples of representative isotherms for the four compounds are given in Figure 2. Since the isotherms were linear, the data were fit to a simplified partition equation:

$$C_s = K_p C_w \quad (2)$$

where $1/n$ from eq 1 was held at unity. The resulting partition constants ($K_p$) and corresponding coefficients of determination ($r^2$) for all compound/substrate combinations are contained in Table V.

For pyrene, the $K_p$ values ranged from 71 to 1155 on the 14 substrates. The $K_p$ values were regressed against the values of each of the substrate properties reported in Tables I–III. The only significant relationship found was that between $K_p$ and percent organic carbon. The $K_{oc}$ thus derived was 63 400 ($r^2$ = 0.965). Individual $K_{oc}$ values for pyrene on each soil/sediment are presented in Table V. The $K_{oc}$ has been shown to be a unique constant for nonpolar compounds which is dependent on the properties of the compound being sorbed and on the organic carbon content of the sorbent but independent of the other sorbent properties (*17–20*).

Karickhoff et al. (*17*) demonstrated that there is a significant relationship between the octanol–water partition coefficient ($K_{ow}$) and the $K_{oc}$ value for a compound. In other studies, we have demonstrated that this relationship holds for a variety of nonpolar compounds (*18–20, 27*). Equation 3, based on a study of the sorption of 22 compounds by various soils and sediments, describes the relationship between $K_{oc}$ and $K_{ow}$.

$$\log K_{oc} = \log K_{ow} - 0.317 \qquad r^2 = 0.980 \quad (3)$$

The calculated $K_{oc}$ for pyrene (59 762) obtained by using eq 3 agrees quite well with the regressed $K_{oc}$ (63 400) and falls within one standard deviation of the experimental average (62 700).

The sorption of 7,12-dimethylbenzanthracene (DMBA) yielded $K_p$ values ranging from 562 to 6777, indicating much stronger sorption than was observed with pyrene. The $K_p$ values were highly correlated with organic carbon content. No other significant correlations were observed. The $K_{oc}$ values calculated for the individual substrates tended to converge on an average of 235 700 when the $K_{oc}$ value for soil no. 9 was omitted. This value was dropped because it was more than two standard deviations from the mean. Regression of $K_p$ vs. percent organic carbon for all 14 samples yielded a $K_{oc}$ value of 225 308 ($r^2$ = 0.908).

The $K_p$ values for 3-methylcholanthrene (3-MC) ranged from 2257 to 37 364 for the 14 substrates. This compound was much more strongly sorbed to all sediments and soils than either pyrene or DMBA. Regression of the $K_p$ values against substrate property values yielded a single significant correlation with percent organic carbon ($K_{oc}$ = 1 244 046; $r^2$ = 0.705). The $K_{oc}$ values calculated for the 14 samples (Table V) tended to converge on an average value of 1 789 000 when the extreme values obtained on EPA-5 and 14 were omitted. The regressed $K_{oc}$ value (1 244 046) compares well with the calculated $K_{oc}$ (1 268 487) obtained with eq 3.

It is interesting to note that although the empirical formulas and molecular weights of DMBA and 3-MC differ by one carbon and 12 amu, respectively, the sorption constants for 3-MC exceed those of DMBA by as much as an order of magnitude. We would suggest that one possible explanation for this observation is that the methyl group and closed ring moieties on the 3-MC contribute more to the effective chain length of the molecule than do the two methyl groups on DMBA.

The sorption of dibenzanthracene (DBA) on the 14 samples

yielded equilibrium $K_p$ values which ranged from 1759 to 55 697. These values represent the strongest sorption constants observed for any of the compounds tested. Regression of the individual $K_p$ values against substrate property values yielded a single significant correlation with percent organic carbon ($K_{oc}$ = 1 668 800; $r^2$ = 0.783). This value agrees well with both the average $K_{oc}$ determined for each of the 14 substrates ($K_{oc}$ = 2 029 000) and the calculated $K_{oc}$ (1 527 775) obtained by using eq 3.

The increase in sorption observed for 3-MC vs. DBA (1 244 046 to 1 668 800) results from the addition of one carbon and 10 amu to the unit structure in a slightly different configuration. When this increase is contrasted with the increase in sorption noted earlier between DMBA and 3-MC (225 300 to 1 244 000) for approximately the same increase in mass but in a very different configuration, it suggests that addition of molecular weight alone does not control the sorptive properties of neutral molecules. This is consistent with our hypothesis that effective chain length may be more important in determining sorption than absolute increases in molecular weight.

Chiou and co-investigators suggested that the solubility of a hydrophobic organic molecule is a good estimator of the organic–water partitioning coefficients (*29*). By inference, we concluded that the log solubilities ($S$) should be a reliable means of estimating log $K_{oc}$. Regression of the water solubilities ($\mu$g/mL) and $K_{oc}$ values (Tables IV and V) for pyrene, DMBA, 3-MC, and DBA yielded the following linear relationship:

$$\log K_{oc} = -0.82 \log S + 4.070 \qquad r^2 = 1.000 \qquad (4)$$

This equation agrees with that recently published by Chiou et al. (*30*) and also agrees well with the overall relationship

$$\log K_{oc} = -0.686 \log S + 4.273 \qquad r^2 = 0.933 \qquad (5)$$

which has now been observed for a total of 22 compounds (*17, 24*).

## Summary and Conclusions

The sorption of pyrene, 7,12-dimethylbenz[*a*]anthracene, 3-methylcholanthrene, and dibenzanthracene has been studied on 14 sediment and soil substrates which exhibit a wide range of physicochemical properties. In all cases, the equilibrium isotherms were linear, and the resulting partition constants ($K_p$) for each compound were found to be significantly correlated with the organic carbon content of the 14 substrates. The $K_p$ values were independent of all other substrate properties. The increase in sorption of hydrophobic compounds appears to be more closely related to increases in the effective chain length of the molecule rather than increases in mass alone.

Water solubilities and octanol–water partition coefficients were determined experimentally for each compound. It was demonstrated that significant linear relationships exist between log values of both of these compound properties and the corresponding sorption constants ($K_p$) for the compound on each substrate tested when the $K_p$ values were normalized for organic carbon. The equations derived from the experimental data were shown to be predictive of the sorption of other hydrophobic compounds studied in our laboratory and in two other laboratories. The reliability of these relationships suggests that they may be very useful in estimating the sorption of other hydrophobic substances on a given substrate.


## Acknowledgment

We thank John Ameel, Sandra Dick, Kathleen Brinkman, David Ellis, David Zierath, Elsa Tong, Carolyn Hanson, Syed Ali, and Adam Khan for their assistance in the laboratory.


## Literature Cited


(1) Pitts, J. N., Jr.; Grosjean D.; Mischke, T. M. *Toxicol. Lett.* **1977**, *1*, 65.
(2) TRW Systems and Energy, Inc. "Carcinogens Relating to Coal Conversion Processes"; U. S. Energy Research and Development Administration: Oak Ridge, TN 1976.
(3) Sharkey, A. G.; Schultz, J. L.; White, C.; Lett, R. Washington, D.C., 1976, U.S. Environmental Protection Agency Report No. EPA-600/2-76-075.
(4) Suess, M. J. *Sci. Total Environ.* **1976**, *6*, 239.
(5) La Flamme, R. E.; Hites, R. A. *Geochim. Cosmochim. Acta* **1976**, *42*, 289.
(6) Blumer, M.; Youngblood, W. W. Washington, D.C., 1976, Office of Naval Research Report, NTIS NO. AD AO23637.
(7) Forney, A. J.; Haynes, W. P.; Gasior, S. J.; Johnson, G. E.; Strakey, J. P., Jr. Washington, D.C., 1974, Bureau of Mines, U.S. Department of the Interior Progress Report 76.
(8) Hase, A.; Hites, R. A. In "Identification and Analysis of Organic Pollutants in Water"; Kieth, L. H., Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1976; p. 205.
(9) Pancirov, R. J.; Brown, R. A. *Proc. Conf. Prev. Control Oil Pollut.* **1973**, 103.
(10) Youngblood, W. W.; Blumer, M. *Geochim. Cosmochim. Acta* **1975**, *39*, 1303.
(11) La Flamne, R. E.; Hites, R. A. *Geochim. Cosmochim. Acta* **1979**, *43*, 1687.
(12) Wakeham, S. G.; Schaffner, C.; Giger, W. *Geochim. Cosmochim. Acta* **1980**, *44*, 415.
(13) Greiner, A. C.; Spyckerelle, C.; Albrecht, P.; Ourisson, G. *J. Chem. Res., Miniprint* **1977**, 3829.
(14) Aizenshtat, A. *Geochim. Cosmochim. Acta* **1973**, *37*, 559.
(15) Stumm, W.; Morgan, J. J. "Aquatic Chemistry"; Wiley-Interscience: New York, 1970.
(16) Kipling, J. J. "Adsorption from Solution of Non-electrolytes"; Academic Press: New York, 1965.
(17) Karickhoff, S. W.; Brown, D. S.; Scott, T. A. *Water Res.* **1979**, *13*, 241.
(18) Means, J. C.; Hassett, J. J.; Wood, S. G.; Banwart, W. L. In "Polynuclear Aromatic Hydrocarbons"; Jones, P. W., Leber, P., Eds.; Ann Arbor Science Publishers: Ann Arbor, MI, 1979; p. 327.
(19) Means, J. C.; Hassett, J. J.; Wood, S. G.; Banwart, W. L.; Ali, S.; Khan, A. In "Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects"; Bjørseth, A., Dennis, A. J., Eds.; Battelle Press: Columbus, OH, 1980; p 395.
(20) Hassett, J. J.; Means, J. C.; Banwart, W. L.; Wood, S. G.; Ali, S.; Khan, A. *J. Environ. Qual.* **1980**, *9*, 184.
(21) Lindquist, A. E. Washington, D.C., 1977, U.S. Department of the Interior, Bureau of Mines Circular 8735.
(22) Wood, S. G.; Means, J. C., submitted for publication in *Anal. Chem.*
(23) Hilton, B. D.; O'Brien, R. D. *J. Agric. Food Chem.* **1964**, *12*, 236.
(24) Hassett, J. J.; Means, J. C.; Banwart, W. L.; Wood, S. G. Athens, GA, 1980, U.S. Environmental Protection Agency Final Report No. EPA 600/3-80/041.
(25) Bailey, G. W.; White, J. L. *J. Agric. Food Chem.*, **1964**, *12*, 324.
(26) Zierath, D.; Hassett, J. J.; Banwart, W. L.; Wood, S. G.; Means, J. C. *Soil Sci.* **1980**, 129, 277.
(27) Khan, A.; Hassett, J. J.; Banwart, W. L.; Means, J. C.; Wood, S. G. *Soil Sci.* **1979**, *128*, 297.
(28) Mackay, D.; Shiu, W. Y. *J. Chem. Eng. Data* **1977**, *22*, 399.
(29) Chiou, C. T.; Freed, V. H.; Schmedding, D. W.; Kohnert, R. L. *Environ. Sci. Technol.* **1977**, *11*, 475.
(30) Chiou, C. T.; Peters, L. J.; Freed, V. H. *Science* **1979**, *206*, 831.



*Received for review May 19, 1980. Accepted September 2, 1980. Support for this work was obtained from the U.S. Environmental Protection Agency Contract No. 68-03-2555.*