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# Partition Characteristics of Polycyclic Aromatic Hydrocarbons on Soils and Sediments

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The partition behavior was determined for three polycyclic aromatic hydrocarbons (PAHs), i.e., naphthalene, phenanthrene, and pyrene, from water to a range of soil and sediment samples. The measured partition coefficients of the individual PAHs between soil/sediment organic matter (SOM) and water (i.e.,  $K_{oc}$  values) are relatively invariant either for the "clean" (uncontaminated) soils or for the clean sediments; however, the mean  $K_{oc}$  values on the sediments are about twice the values on the soils. This disparity is similar to the earlier observation for other nonpolar solutes and reflects the compositional differences between soil and sediment organic matters. No significant differences in  $K_{oc}$  are observed between a clean coastal marine sediment and freshwater sediments. The coastal sediments that are significantly impacted by organic contaminants exhibit higher  $K_{oc}$  values. At given  $K_{ow}$  values (octanol–water), the PAHs exhibit much higher  $K_{oc}$  values than other relatively nonpolar solutes (e.g., chlorinated hydrocarbons). This effect is shown to result from the enhanced partition of PAHs to SOM rather than from lower  $K_{ow}$  values of PAHs at given supercooled liquid solute solubilities in water. The enhanced partition of PAHs over other nonpolar solutes in SOM provides an account of the markedly different correlations between  $\log K_{oc}$  and  $\log K_{ow}$  for PAHs and for other nonpolar solutes. The improved partition of PAHs in SOM stems apparently from the enhanced compatibility of their cohesive energy densities with those of the aromatic components in SOM. The approximate aromatic fraction in soil/sediment organic matter has been assessed by solid-state  $^{13}\text{C}$ -NMR spectroscopy.

## Introduction

The extent of sorption of an organic contaminant to soil (sediment) has a major influence on its transport and fate in the environment. In soil/sediment–water systems, where the soil/sediment organic matter (SOM) content is significant, the sorption of relatively nonpolar contaminants (solute) occurs largely by partition (dissolution) into SOM (1, 2) because of the concomitant suppression by water of adsorption onto mineral matter (3–6), especially for the solutes at significant relative concentrations (7). Accordingly, the soil/sediment–water distribution coefficient ( $K_d$ ) of a nonpolar contaminant (solute) is strongly dependent on the soil/

sediment organic matter content ( $f_{om}$ ) or, alternatively, on the soil/sediment organic carbon content ( $f_{oc}$ ), unless either is extremely low. In an earlier study (8), the  $K_{oc}$  values (where  $K_{oc} = K_d/f_{oc}$ ) of two relatively nonpolar solutes, carbon tetrachloride (CT) and 1,2-dichlorobenzene (DCB), measured at significant relative concentrations were about the same on a large set of soils and similarly on a large set of bed sediments, the samples being from dispersed locations in the United States and People's Republic of China. The  $K_{oc}$  values for the sediments were about twice those for the soils (8). This finding suggests that the SOM compositions for a wide range of soils (or of sediments) are relatively comparable and that the sediment organic matter has a somewhat lower overall polarity than the soil organic matter.

Although the  $K_{oc}$  values of many nonpolar contaminants can often be estimated with sufficient accuracy from their related physical parameters, such as the octanol–water partition coefficients ( $K_{ow}$ ) or the solute water solubilities ( $S_w$ ) (1–3, 8–10), the selection of a proper correlation for estimation may be complicated by inconsistency between published correlations for different types of nonpolar compounds on soils and sediments. A particular case in point is the inconsistency of the correlations for relatively nonpolar polycyclic aromatic hydrocarbons (PAHs) and for other nonpolar substituted aromatic compounds. For instance, the relation between  $\log K_{oc}$  and  $\log K_{ow}$  established by Chiou et al. (3) for substituted aromatic compounds (primarily, chlorinated benzenes and PCBs) on soil gives

$$\log K_{oc} = 0.904 \log K_{ow} - 0.543 \quad (1)$$

with  $n = 12$  and  $r^2 = 0.996$  for solutes with  $\log K_{ow}$  ranging from 2.11 to 5.62. By contrast, the correlation presented by Karickhoff et al. (2) for mainly PAHs and their derivatives over a comparable range of  $\log K_{ow}$  (2.11–6.34) on river sediment gives

$$\log K_{oc} = 1.00 \log K_{ow} - 0.21 \quad (2)$$

with  $n = 10$  and  $r^2 = 1.00$ . As noted, eq 2 gives higher  $K_{oc}$  than eq 1 at a given  $K_{ow}$ ; moreover, the difference between the calculated  $K_{oc}$  values becomes greater with increasing  $K_{ow}$ . In the range of  $\log K_{ow} = 3$ –6, the ratio of the  $K_{oc}$  from eq 2 for PAHs on sediment to that from eq 1 for chlorinated benzenes and PCBs on soil increases from 4 to 8.

From the two  $\log K_{oc}$ – $\log K_{ow}$  correlations illustrated, it appears either that PAHs on sediments exhibit much higher  $K_{oc}$  values than substituted aromatic solutes on soils or else that PAHs exhibit considerably smaller  $K_{ow}$  values than substituted aromatic solutes. As shown later, the latter effect can be largely ruled out on the basis that plots of  $\log K_{ow}$  vs  $\log S_w$  (supercooled liquid solubility in water) for different nonpolar solutes, including substituted aromatic solutes and PAHs, fall virtually onto a single line. Similarly, in view of the absence of strong polar groups in PAHs, the much higher  $K_{oc}$  values of PAHs cannot be logically attributed to specific interactions of the solutes with SOM or with soil minerals in water solution (7, 11). Therefore, the higher  $K_{oc}$  values of PAHs as exhibited by eq 2 result presumably from two effects: (i) higher partition in sediments than in soils for a wide variety of nonpolar solutes including PAHs and (ii) PAHs exhibiting higher partition coefficients with SOM than other nonpolar solutes.

The first effect, which was noted earlier for CT and DCB (8), is to be further tested for PAHs. An important goal of this work is to account for the nature and magnitude of the

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TABLE 1. Molecular Properties of Naphthalene (NAP), Phenanthrene (PHN), and Pyrene (PYP) at Room Temperature

property	NAP	PHN	PYP
molecular weight	128	178	202
melting point (°C)	80	101	156
heat of fusion (kcal/mol) <sup>a</sup>	4.61	4.45	4.20
log <i>K</i> <sub>ow</sub> (octanol–water) <sup>a</sup>	3.36	4.57	5.18
log <i>S</i> <sub>w</sub> (water solubility) for solid compound (mol/L) <sup>a</sup>	–3.61	–5.14	–6.18
log <i>S</i> <sub>w</sub> (water solubility) as supercooled liquid (mol/L) <sup>a,b</sup>	–3.08	–4.48	–5.24
solubility parameter (δ) <sup>c</sup> (cal/mL) <sup>1/2</sup>	9.9	9.8	10.6 <sup>c</sup>

<sup>a</sup> Values as cited in ref 12. <sup>b</sup> Values at 25 °C. <sup>c</sup> Values for NAP and PHN from ref 13 and for PYP from ref 14.

second suggested effect. In this study, batch sorption data were obtained for three PAHs, naphthalene (NAP), phenanthrene (PHN) and pyrene (PYP), on a series of clean soils and freshwater (FW) sediments and on some contaminated coastal marine sediments for comparison of their partition effects with SOM. The solid-state <sup>13</sup>C-NMR data of some soils and sediments have also been measured to substantiate the effect of SOM composition on the partition behavior of the PAHs.

### Experimental Section

**Materials.** Naphthalene (NAP) (99+%), phenanthrene (PHN) (98%), and pyrene (PYP) (99%) were purchased from Aldrich Chemical Co. and used as received. The molecular weights, melting points, water solubilities (*S*<sub>w</sub>), octanol–water partition coefficients (*K*<sub>ow</sub>), solubility parameters (δ), and other properties of these compounds at room temperature are listed in Table 1.

The soils used for sorption experiments are Woodburn soil from Oregon, Marlette soil from Michigan, Elliot soil from Illinois, Anoka soil from Minnesota, and Piketon soil from Ohio. All soil samples were taken from the A horizon of the soil profile; their sources were described in an earlier work (6). The sediment samples comprise three FW sediments originating from the Mississippi River in Louisiana and Arkansas and from Lake Michigan in Michigan and four coastal marine sediments near Boston, MA. The sediment samples were taken from the top 0–20 cm of the sediment. The two sediment samples from the Mississippi River were collected near St. Fransville, LA, and Helena, AR, respectively (6). The Lake Michigan sediment was collected near Frankenmuth, MI, at 44°41' N, 86°46' W. Of the four coastal marine sediments, a relatively clean sediment was collected from Massachusetts Bay in Boston. The other three coastal sediments were collected from Fort Point Channel, Spectacle Island, and Peddocks Island of Boston Harbor, MA, as described in McGroddy and Farrington (15). The latter three coastal sediments are known to be contaminated to varying degrees by anthropogenic organic wastes. Soil and sediment samples were dried at 100 °C and ground and homogenized to pass a 35-mesh sieve.

The organic carbon contents of soil and sediment samples were measured by a high-temperature oxidation method using a Leco instrument (16). The organic carbon contents (*f*<sub>oc</sub>) of the samples are listed with the sorption data of PAHs in Table 2. The precision of measured *f*<sub>oc</sub> values is within ±0.002 of the reported values.

**Sorption Experiments.** PAH sorption experiments began by suspending 1–4 g of soil or sediment in 27–170 mL of 0.005 M CaCl<sub>2</sub> water solution. PAH stock solutions in methanol were introduced to the soil/sediment slurries by syringe. The total volume of the stock PAH solutions were less than 100 μL. The presence of the carrier solvent was assumed to have little effect on solute equilibrium behavior. The soil/sediment to water ratios in sorption experiments were adjusted to allow for significant quantities of solutes to be sorbed to the soil/sediment and to provide sufficient

TABLE 2. Organic Carbon-Normalized Partition Coefficients (*K*<sub>oc</sub>) of NAP, PHN, and PYP on Studied Soils and Sediments

soil/sediment sample	sample <i>f</i> <sub>oc</sub>	log <i>K</i> <sub>oc</sub>		
		NAP	PHN	PYP
Woodburn soil	0.0126	2.61	4.27	4.99
Elliot soil	0.0290	2.63	4.27	4.98
Marlette soil	0.0180	2.68	4.12	4.96
Piketon soil	0.0149	2.77	4.27	4.97
Anoka soil	0.0108	2.76	4.10	4.97
Lake Michigan sediment	0.0402	2.91	4.38	5.14
Mississippi River sediment (St. Fransville, LA)	0.0040	2.86	4.45	5.22
Mississippi River sediment (Helena, AK)	0.0160	2.88	4.53	5.23
Massachusetts Bay sediment	0.0163	2.87	4.33	5.12
Spectacle Island sediment	0.0334	2.89	4.42	5.04
Peddocks Island sediment	0.0312	2.95	4.62	5.24
Fort Point Channel sediment	0.0519	3.07	4.64	5.45

amounts of water solution for determination of the solute. The percent of NAP sorbed to soil/sediment was in the range of 20–50%, the value for PHN was about 60–85%, and the value for PYP was about 80–95%. The slurries were continuously mixed on a shaker at room temperature (24 ± 1 °C) for 48–72 h, and the solid and aqueous phases were separated by centrifugation at 1000g.

Concentrations of PAH compounds in water after equilibration were analyzed by direct injection of water samples into a reverse-phase HPLC system with a fluorescence detector. PHN and PYP were determined using an excitation wavelength of 230 nm and an emission wavelength of 390 nm. NAP was quantified using 280 nm/329 nm (excitation/emission). The average uncertainty for the measured concentrations was about ±5–6%. The amounts sorbed to soil/sediment for PHN and PYP were determined mostly by the difference of the total mass and the determined mass in water, with selective extraction of some solid samples with acetonitrile to verify the results. The results for PHN and PYP from direct solvent extraction were found to be in good agreement with the by-difference data, which is attributable to their high sorbed fractions to the soil/sediment. The recoveries of total masses by extraction experiments were mostly at 90+%, and the deviations between solid-extraction and by-difference data were generally less than 30%. For NAP, where the sorbed fraction was relatively small, the amounts sorbed were analyzed both by solvent extraction and by mass difference. The recoveries of total masses of NAP by extraction ranged from 70% to 100%. The solid-extraction data with >90% mass recovery were used along with the by-difference data if the latter showed <30% deviations from those of the extraction data.

In blank experiments with the Fort Point Channel sediment, a noticeable level of fluorescent materials was detected in water following the equilibration of the sample with water without added PAHs. The background fluorescent levels of Spectacle Island and Peddocks Island sediments

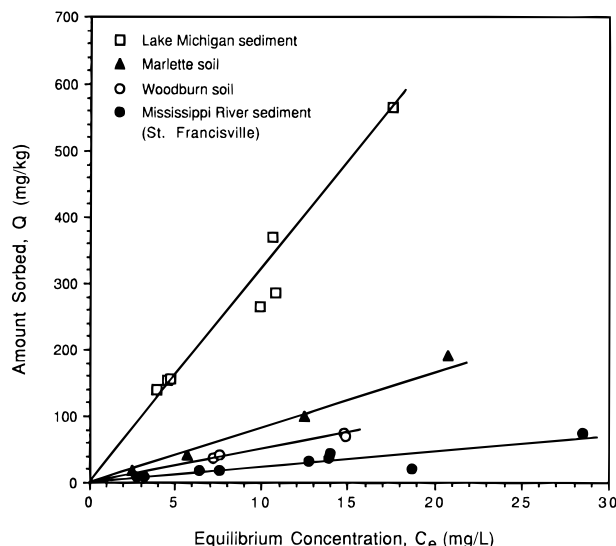


FIGURE 1. Sorption isotherms of NAP on representative soils and sediments at room temperature.

were less significant. These materials did not seriously interfere with the quantitation of PAHs in water in sorption experiments, since the amounts of added PAHs were generally much higher.

Sorption coefficients ( $K_d$ ) were determined by plotting the amount of solute sorbed per unit weight of soil (or sediment) against the equilibrium solute concentration in water. The  $K_d$  values are converted to  $K_{oc}$  values by normalizing the  $K_d$  to the organic carbon fraction of the soil or sediment ( $f_{oc}$ ).

**Solid-State  $^{13}\text{C}$ -NMR Spectrometry.** The cross polarization/magic angle spinning (CP/MAS)  $^{13}\text{C}$  spectra of dry soils and sediments were measured on a 200 MHz Chemagnetics CMX spectrometer with a 7.5 mm diameter probe. The spinning rate was 4000–4600 Hz. The acquisition parameters were contact time of 1 ms, pulse delay of 1 s, and a pulse width of 4.5  $\mu\text{s}$ . Adequate signal-to-noise response was obtained for most soil and sediment samples with 68 850–134 000 scans (run times of 19–37 h). For some samples, e.g., Woodburn soil, the signal-to-noise response was relatively poor, due presumably to the presence of paramagnetic substances. The run time was determined by the sample organic carbon content. A line broadening of 100 Hz was applied in the Fourier transformation of the free induction decay data. The chemical shifts were calibrated with hexamethylbenzene (methyl carbon at 17.35 ppm). Bands representing the chemical shifts of carbons in SOM were integrated to calculate the respective functional group contributions. The spectra were divided into four major regions: alkyl (0–45 ppm), *O*-alkyl (45–110 ppm), aromatic (110–160 ppm), and carboxyl–amide–ester (160–200 ppm) (17).

## Results and Discussion

The sorption isotherms of NAP, PHN, and PYR at room temperature from water on representative soils and sediments are presented in Figures 1–3, respectively, where the amount of PAH uptake by soil/sediment ( $Q$ ) is plotted against the equilibrium PAH concentration ( $C_e$ ). In all systems, the isotherms are essentially linear, with  $C_e$  in most cases extended to greater than half the PAH water solubility ( $S_w$ ), i.e., to more than 0.5 in relative solute concentration. The observed isotherm linearity over the range of concentrations studied is in keeping with the characteristics of solute partition in SOM (1–6). The organic carbon-normalized partition coefficients ( $\log K_{oc}$ ) for the studied soils and sediments are given in Table 2.

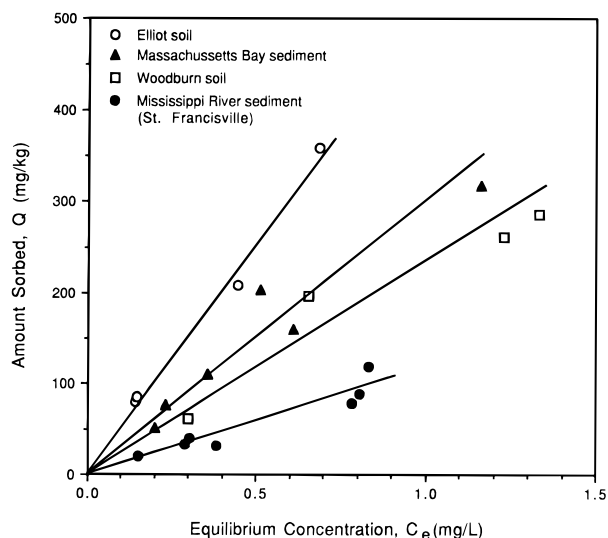


FIGURE 2. Sorption isotherms of PHN on representative soils and sediments at room temperature.

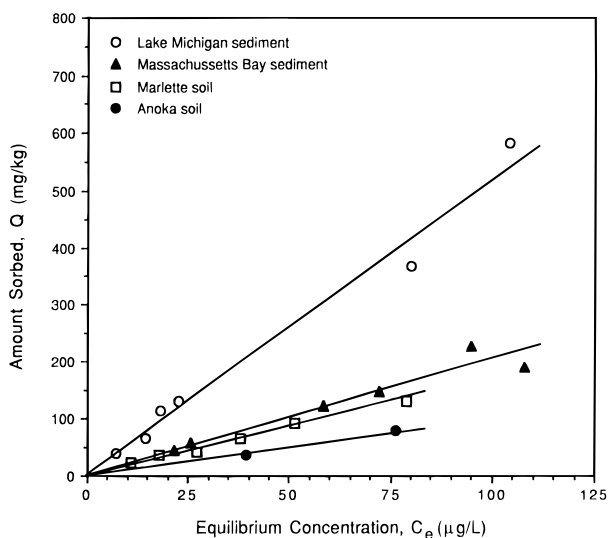


FIGURE 3. Sorption isotherms of PYR on representative soils and sediments at room temperature.

Before the sorption data of NAP, PHN, and PYR on the soils and sediments are further scrutinized, it is important to assure that the closer proximity of  $K_{oc}$  to  $K_{ow}$  for PAHs than for other nonpolar solutes is not a result of PAHs exhibiting lower  $K_{ow}$ . In Figure 4, the plot of  $\log K_{ow}$  vs  $\log S_w$  for NAP, PHN, and PYR are compared with a similar plot for some chlorinated nonpolar solutes (CT, DCB, 2-PCB, 2,4'-PCB, and 2,4,4'-PCB) with data from earlier works (3, 5). The  $S_w$  values for the solid solutes in these plots are those of the supercooled liquids after a correction for their melting point effects on solid solubilities (3). The  $\log K_{ow}$ – $\log S_w$  plot reveals no significant discrepancy between PAHs and other low-polarity chlorinated solutes. This means that, at the same (supercooled liquid)  $S_w$ , PAHs and other nonpolar solutes exhibit comparable compatibilities with octanol. In addition, for a series of nonpolar solutes, the solute exhibits a moderate decrease in compatibility with octanol with reducing  $S_w$  or with increasing molecular weight (12); for example, the Raoult's law solute activity coefficient in octanol ( $\gamma_o$ ) increases from 4.4 for NAP to 6.8 for PHN and 9.6 for PYR (12).

To evaluate the effect of SOM polarity between soil and sediment on  $K_{oc}$ , the  $\log K_{oc}$  values for the three PAHs on five studied soils and the corresponding values on four sediments (the three FW sediments and the coastal Massachusetts Bay

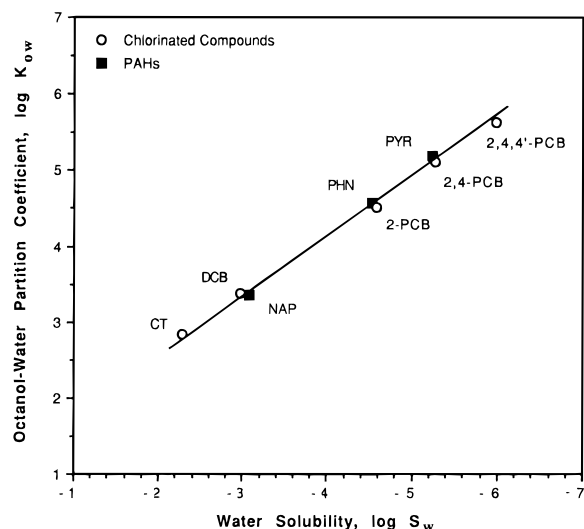


FIGURE 4. Plot of  $\log K_{ow}$  versus  $\log S_w$  (supercooled liquid) for selected PAHs and chlorinated compounds.

marine sediment) are compared. The data for other coastal sediments of Boston Harbor are excluded from this comparison because they are either known or suspected of being contaminated by organic wastes (15). As shown (Table 2), the  $K_{oc}$  values between soils or between sediments are relatively invariant, as similarly noted earlier for CT and DCB on soils and sediments. The  $K_{oc}$  values on Massachusetts Bay sediment are similar to those on FW sediments, in reflection of the likely terrestrial influence of this coastal sediment and its absence of serious organic contamination.

The mean  $\log K_{oc}$  values of NAP, PHN, and PYR on the five soils are  $2.69 (\pm 0.073 \text{ SD})$ ,  $4.21 (\pm 0.088)$ , and  $4.98 (\pm 0.009)$ , and the values on the four sediments are  $2.88 (\pm 0.022)$ ,  $4.42 (\pm 0.087)$ , and  $5.18 (\pm 0.056)$ . The sediment  $\log K_{oc}$  values of the three PAHs fit fairly closely the predictions of eq 2. From these mean  $\log K_{oc}$  values, the partition of PAHs with sediment organic matter is about 1.6 times as effective as that with soil organic matter, which is greater than the standard deviations (SD) of the mean  $K_{oc}$  values for the soils and for the sediments. The observed difference in PAH partition between the soil and the sediment (i.e., by about 1.6) is comparable in magnitude to that (by about 1.8) found for CT and DCB on a large set of soils and sediments (6). The result suggests that roughly half the difference in  $K_{oc}$  as exhibited by eq 1 for soils and eq 2 for sediments results from the unequal solute partition efficiencies with the organic contents of soils and sediments. The remaining difference results from the unequal solubilities of PAHs and substituted aromatic compounds in SOM.

The disparity in partition behavior between PAHs and substituted aromatic solutes with SOM may be demonstrated by comparing the present mean  $K_{oc}$  values of PHN ( $\log K_{oc} = 4.21$ ;  $\log K_{ow} = 4.57$ ) and PYR ( $\log K_{oc} = 4.98$ ;  $\log K_{ow} = 5.18$ ) on soils with the  $\log K_{oc}$  values of 2-PCB ( $\log K_{oc} = 3.50$ ;  $\log K_{ow} = 4.51$ ) and 2,4'-PCB ( $\log K_{oc} = 4.16$ ;  $\log K_{ow} = 5.10$ ) (3) on soils, where the two types of solutes possess comparable  $\log K_{ow}$  values. As seen, there is a sharp decline in  $K_{oc}$  for substituted aromatic solutes (PCBs) relative to that for the PAHs with increasing molecular weight (or  $K_{ow}$ ); the  $K_{oc}$  values for PHN and PYR are 5.1 and 6.6 times, respectively, those of 2-PCB and 2,4'-PCB. These differences are similar in magnitude to those based on eqs 1 and 2, when a correction is made for the soil vs sediment effect. In addition, the increased reduction in  $K_{oc}$  with increasing  $K_{ow}$  for chlorinated solutes (PCBs) relative to PAHs indicate that the partition effect of the former with SOM decreases more rapidly with increasing molecular weight.

We now consider the source of the enhanced partition of PAHs in SOM over that of other nonpolar solutes, such as chlorinated benzenes and PCBs. Since the SOM contains various polar and nonpolar moieties (17), including aromatic and aliphatic groups, it is pertinent to compare the partition behavior of PAHs in both bulk aromatic (e.g., benzene) and aliphatic (e.g., *n*-hexane) media and in a moderately polar medium (e.g., octanol). The solubilities of NAP, PHN, and PYR in benzene at room temperature are 3.26 (18), 2.27 (19), and 0.697 mol/L (20), respectively; they are about 2.5, 4.9, and 7.4 times higher than the respective values in *n*-hexane. The solubilities of the PAHs in benzene are very close to their ideal solubilities by Raoult's law, with PYR showing the greatest deviation from ideality by only about a factor of 2; i.e., the molecular size of the PAH has no strong effect on its solubility in benzene relative to its ideal solubility. The observed PAH solubilities in *n*-hexane are comparable with those in octanol (12). The increased downward deviation of PAH solubilities in benzene and *n*-hexane (or octanol) with increasing molecular size suggests some increasing incompatibility with an aliphatic phase (or a moderately polar phase) with increasing PAH molecular size. From these results, PAHs should exhibit greater partition interactions with the aromatic components of SOM (especially, those without polar substituents) than with other components or molecular segments.

The illustrated difference in PAH solubilities with aromatic and non-aromatic solvents is analogous to the noted disparity in  $K_{oc}$  between PAHs and other low-polarity solutes (e.g., chlorinated benzenes and PCBs) with increasing molecular weight (or increasing  $K_{ow}$ ). The disparity suggests that the higher  $K_{oc}$  values of PAHs with SOM result presumably from their improved partition with the aromatic components of SOM. To relate the  $K_{oc}$  data to solute partition with SOM's components, it is necessary to know the aromatic fraction and other group contents in SOM. On the basis of  $^{13}\text{C}$ -NMR data for whole soils, the organic carbon in SOM is about  $20 \pm 5\%$  aromatic,  $25 \pm 6\%$  alkyl,  $40 \pm 10\%$  *O*-alkyl (e.g., carbohydrate), and  $15 \pm 5\%$  carboxyl-amide-ester (17). The aromatic content includes hydrogen- and carbon-substituted aromatics, oxygenated aromatics (e.g., those with -OH and -COOH), and unsaturated carbons (17); the separation of these components is technically difficult. Taking the above estimated carbon fractions in SOM, if one assumes that (i) the PAHs partition to SOM's aromatic components as effectively as they do in a nonpolar aromatic solvent (as in benzene); (ii) the partition to SOM's aliphatic components is about the same as to *n*-hexane; and (iii) the partition to the remaining SOM components is not significant, the calculated  $K_{oc}$  values for NAP, PHN, and PYR by the assumed solubilities in SOM and in water should be about the same as the measured values. The calculated  $K_{oc}$  values, even if the partition to SOM's aliphatic components is excluded, are however significantly higher than the measured values for reasons to be discussed later; the partition to aliphatic components alone is not sufficient to account for the measured  $K_{oc}$  values. On the other hand, if one assumes that the SOM contains an "equivalent nonpolar aromatic carbon fraction" of about 0.10, the calculated  $\log K_{oc}$  values for NAP (3.12), PHN (4.50), and PYR (5.02) compare favorably with the presently measured values on sediments (2.88, 4.42, and 5.18, respectively) and with earlier reported values (3.11, 4.36, and 4.92, respectively) of these PAHs on sediments (2). The similarly calculated  $\log K_{oc}$  for anthracene (4.55) using its solubilities in benzene ( $8.90 \times 10^{-2}$  mol/L) (18) and in water ( $2.51 \times 10^{-7}$  mol/L) (12) also agrees well with the published  $\log K_{oc}$  of 4.41 with sediments (2).

Whereas a quantitative account of the  $K_{oc}$  values requires well-defined SOM molecular structures that are presently unavailable, the above results support the suggested influence

of aromatic components in SOM on PAH partition. That the calculated  $K_{oc}$  values based on the total aromatic content in SOM are much higher than the measured values suggests that most aromatic structures in SOM are substituted with some polar and nonpolar groups, which reduce their overall compatibilities with PAHs. In view that sediments exhibit slightly higher  $K_{oc}$  values than soils, the sediment organic matter should have either a lower polar group content or a higher aromatic content. The approximate aromatic fractions in SOM for some of the present soils and sediments will be estimated later using the solid-state  $^{13}\text{C}$ -NMR spectra of the whole samples.

The enhanced partition of PAHs with dissolved organic matter (DOM) has been attributed to their planar molecular structures that enable them to gain a closer approach to the DOM's aromatic components (21) or to enhance their mutual attractions through  $\pi$ - $\pi$  interactions (22). From the partition standpoint, the favored interaction between aromatic components seems more likely to be related to similarity in their cohesive energy densities (CEDs) (or their solubility parameters,  $\delta$  values); the CED is the energy of vaporization per unit volume of a pure (liquid) substance, and  $\delta$  is the square root of CED (13). Note, for example, that the  $\delta$  values (in  $(\text{cal/mL})^{1/2}$ ) for benzene (9.2), NAP (9.9), PHN (9.8), and anthracene (9.9) are relatively high as compared with those of other nonpolar solutes (13). The  $\delta$  value for PYR estimated from its solubilities in hydrocarbons is about 10.6 (14). Thus, on going from benzene to PYR, the  $\delta$  values for PAHs stay relatively constant with increasing molecular size. The  $\delta$  values for most short-chain halogenated compounds are in the range of 8.5–10 (e.g.,  $\delta = 8.6$  for CT), and the values for aliphatic hydrocarbons (e.g., *n*-hexane) are much lower, mainly in the range of 7–8. The  $\delta$  values for low molecular weight alkyl-substituted aromatic compounds (e.g., toluene and xylenes) are about 8.6–9.0 (13). The  $\delta$  data for halogenated aromatic compounds (e.g., chlorinated benzenes and PCBs) are essentially unavailable. The  $\delta$  for SOM is reported to range from 10.3 with relatively nonpolar solutes to 17.2 with highly polar and H-bonding solutes (23). As noted, since the aromatic compounds have similar structures and presumably comparable CEDs, the two mechanisms considered to favor the partition of PAHs with SOM are interrelated.

The higher partition of PAHs with SOM results presumably from the more compatible CEDs between PAHs and SOM. In view that the SOM is a natural "heterogeneous polymer", where the various components (or molecular segments) may be present in sizable domains, it is possible that a given class of solutes would interact more favorably with certain SOM components of comparable CEDs, such as for PAHs with SOM's aromatic regions. This consideration is consistent with the variable  $\delta$  value of SOM as stated earlier. The solubility of a compound in a polymer medium may thus depend more on the polymer's functional group content than on its overall polarity, the latter being more important for low molecular weight organic substances. Since the  $\delta$  values of PAHs are largely constant, their solubilities (as supercooled liquids) in SOM should be approximately the same and largely independent of the molecular weight; this is contrary to the significant reduction in solubility of other nonpolar solutes in SOM with increasing molecular weight. This dissimilarity provides an *a priori* account of the increased deviation between the  $K_{oc}$  values of PAHs and other nonpolar solutes with an increase in  $K_{ow}$ .

The relative amounts of different structural carbons in SOM, as revealed by the solid-state  $^{13}\text{C}$ -NMR spectra of whole soils and sediments, provide useful insights into the effect of SOM composition on solute  $K_{oc}$ . Such assignment of organic carbon types is only semiquantitative because of the overlap in chemical shift of certain functional group carbons

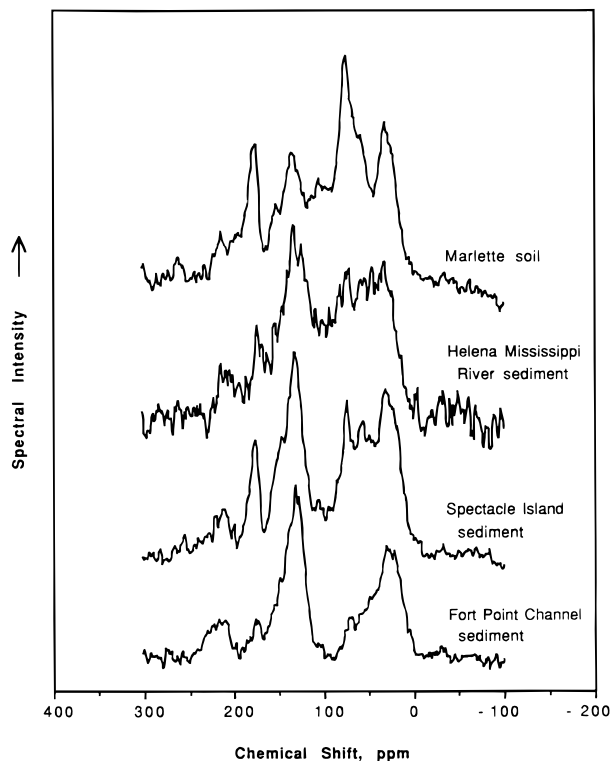


FIGURE 5. Solid-state  $^{13}\text{C}$ -NMR spectra of selected soil and sediment samples.

and of the imprecise quantitation of some functional groups (17). The  $^{13}\text{C}$ -NMR spectra of Marlette soil, Helena Mississippi River sediment, Spectacle Island sediment, and Fort Point Channel sediment are selected for comparison (Figure 5). Analyses of the spectra of a number of clean soils and FW sediments (including those not reported here) indicate that the soils generally have higher combined fractions of *O*-alkyl and carboxyl–amide–ester components than the sediments. The observed aromatic carbon fractions (110–160 ppm) fall largely into the range of  $26 \pm 8\%$  for both soils and sediments; there is no general pattern that the sediments exhibit higher aromatic fractions (unpublished results). For Marlette soil and Helena Mississippi River sediment, the aromatic carbon fractions are about 20% and 33%, respectively, which include all aromatic carbons with polar and nonpolar groups and other unsaturated carbons. The respective carbon fractions for polar *O*-alkyl (45–110 ppm) and carboxyl–amide–ester (160–200 ppm) groups, other than phenols (140–160 ppm), are 56% and 35%, respectively. The difference in alkyl carbon content between the samples is relatively minor (25% vs 33%). The higher  $K_{oc}$  of PAHs on Helena Mississippi River sediment than on Marlette soil correlates more closely with the sediment's lower polar group content. Thus, while the aromatic content in SOM may give high  $K_{oc}$  for PAHs, the difference between soil and sediment  $K_{oc}$  values is related in part to the difference of their polar group contents.

We now consider the log  $K_{oc}$  data of contaminated coastal marine sediments. The Fort Point Channel sample is known to be severely contaminated by highly aromatic organic wastes that resemble a coal tar (15), whereas Spectacle Island sediment and Peddocks Island sediment are suspected of being contaminated to lesser extents by similar organic wastes. To these samples, one notes that the  $K_{oc}$  values of the PAHs on Spectacle Island sediment are largely the same as those of clean FW sediments and Massachusetts Bay marine sediment. This suggests that the level of contamination in this sediment has not significantly affected the overall

organic composition of the sample. The carbon fractions for alkyl (29%), aromatic (32%), and *O*-alkyl and carboxyl–amide–ester components (39%) of Spectacle Island sediment are comparable with those of Helena Mississippi River sediment (Figure 5). The moderately high  $K_{oc}$  data with Peddocks Island sediment indicate that the sediment is contaminated by a significant level of organic wastes (15) that either reduce the polar group content or increase the aromatic content of the sediment (NMR spectra were not obtained). The severely contaminated Fort Point Channel sediment exhibits a high aromatic carbon content (46%); the combined carbon content of *O*-alkyl and carboxyl–amide–ester is low (21%), excluding the oxygenated aromatic carbons (e.g., the phenolic carbons at 140–160 ppm). The alkyl carbon content (33%) is the same as that of Helena Mississippi River sediment. The spectral data of this sediment correlate semiquantitatively with the much higher than average  $K_{oc}$  values of the PAHs. In an earlier study (6), anomalously high  $K_{oc}$  values are also found for CT and DCB on the same sample. A comparison of the NMR and  $K_{oc}$  data between Helena Mississippi River sediment and Fort Point Channel sediment further illustrates the point that the polar group content in SOM is also a significant factor affecting the  $K_{oc}$  values of PAHs and other solutes.

In conclusion, the considerably higher  $K_{oc}$  values of relatively nonpolar PAHs (e.g., NAP, PHN, and PYR) on sediments than those of other nonpolar solutes (e.g., chlorinated benzenes and PCBs) on soils originate essentially from (i) a somewhat higher partition of nonpolar solutes to sediment organic matter than to soil organic matter, the difference being about a factor of 1.6 for the three PAHs examined and (ii) the much higher partition of PAHs than of other nonpolar solutes into SOM. The enhanced partition of PAHs is ascribed to the preferred partition of PAHs with the aromatic components of SOM presumably because of their more compatible CEDs, as exhibited by their solubility parameters ( $\delta$ ). This hypothesis is supported by the higher solubility of PAHs in a typical aromatic solvent (benzene) than in aliphatic and weakly polar solvents and by the significant aromatic fraction in SOM as revealed by the solid-state  $^{13}\text{C}$ -NMR spectra of soils and sediments. Because the aromatic fraction in SOM derived from the  $^{13}\text{C}$ -NMR data includes all components with polar and nonpolar substituents, which are difficult to separate, the calculated  $K_{oc}$  values for PAHs from their solubilities in benzene and in water and the SOM's total aromatic content overestimate the experimental values. Thus, while the high PAH partition is likely related to the SOM's aromatic content, the polar groups in SOM (especially those with aromatic rings) should have a significant effect on PAH partition. Because of the PAH's enhanced interaction with aromatic components, PAHs should exhibit increased partition to soils or sediments that are contaminated by high levels of aromatic-rich wastes.

## Acknowledgments

The authors thank R. L. Wershaw for assistance in running and analyzing the solid-state  $^{13}\text{C}$ -NMR spectra of soils and sediments and M. Manes for discussion of and comments on the manuscript. The authors also thank Yu-Ping Chin for Lake Michigan sediment, C. E. Rostad and L. M. Bishop for Mississippi River sediments, and M. H. Bothner for Massachusetts Bay sediment. The use of trade and product names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Government.

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Received for review July 11, 1997. Revised manuscript received September 26, 1997. Accepted October 3, 1997.<sup>®</sup>

ES970614C

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, November 15, 1997.