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Organic Matter Quality and Partitioning of PCB

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Evidence suggests that K_{oc} values increase as the aromaticity of sediment organic matter increases (Paolis and Kukkonen 1997; Grathwohl, 1990; Murphy, Zachara, and Smith, 1990; Gauthier et al. 1987) although others have observed contrary results (Davis 1993). If organic matter quality differs between sediments and the differences affect partitioning, then interactions between nonpolar organic contaminants in sediments and pore waters in aquatic systems are more complex than assumed in the equilibrium partitioning approach to sediment quality criteria. This is especially important because equilibrium partitioning, used to predict pore water concentrations of nonpolar organic compounds (NPOCs) based on carbon-normalized distribution coefficients, assumes that all soil organic carbon has the same affinity for NPOCs (i.e., no regard to the source of material, polarity, etc.) (DiToro et al. 1991). This study was conducted to examine the changes in aromaticity of organic carbon in sediments and the effects of organic matter aromaticity on partitioning of PCB.

MATERIALS AND METHODS

Freshwater sediment samples were collected from Browns Lake (BL-0.963) (the number associated with the sample designation is percent organic carbon) and a farm pond (FP-0.331) in Mississippi and from two sites in the Buffalo River (NY-0.055, NY-1.28) near Buffalo, NY. The sediments were air dried, finely ground using a mortar and pestle, and analyzed for total organic carbon (TOC). TOC values were measured using a Shimadzu 5050 TOC analyzer equipped with a model SSM-500 Solids Module. Humic acids were isolated from the sediments by the methods of Davis (1993). Isolation procedures included extraction with sodium hydroxide, precipitation, and cleanup of the humic acids. A commercially available Aldrich humic acid, as well as three humic acids (Orange Heights soil, Orange Heights dissolved organic carbon (DOC), and Pine Mountain) which had been isolated in the same manner were also tested. Isolated humic acids were prepared for Fourier Transform Infrared (FTIR) analysis by dissolving (approximately 10 mg/ml) into a solution containing a fixed amount of potassium thiocyanate (KSCN) (1.97 mg/ml) at pH 4.0 in distilled deionized water (Davis 1993; Johnston, et al. 1994). The KSCN served as an internal standard to normalize the absorption at the 1600-1650 cm^{-1} region, where it is mainly due to the aromatic carbon content of the humic substances (Miikki et al. 1997; Gressel et al. 1995). The internal standard facilitates quantitative comparison of peak intensities between different humic sources. This allows FTIR spectra to be used for semi-quantitative comparisons of humic substances from different sources.

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Humic acid from each isolate sufficient to yield a nominal DOC concentration of 50 mg/L was dissolved in distilled/deionized water (pH 8). Nine 10 mL aliquots of each dissolved humic acid sample were removed and placed into 25 mL Oak Ridge glass centrifuge tubes. Each was spiked with ^{14}C-labeled PCB-52 (2,2',5,5'-tetrachlorobiphenyl, specific activity of 5.25 Bequerel/mole, purity > 98% by high performance liquid chromatography) at three concentrations (0.01, 0.007, and 0.004 mg/L) in three replicates. The highest concentration was less than 50% of the aqueous solubility of PCB-52. After mechanically shaking for 24 hrs, sufficient time for equilibrium to be reached (Gauthier et al. 1986; Backhus and Gschwend 1990), a 1-mL sub-sample was removed and assayed by liquid scintillation counting. The remaining samples were centrifuged 1 hr at 7,400 x g. A 1-mL portion of the supernatant was counted immediately; 2 mL were passed through a C-18 Sep-Pak and a 1-mL aliquot of the eluant counted. The C-18 Sep-Pak removes dissolved PCB-52, so that the PCB-52 in the eluant is associated with filterable microparticulates and DOC. The centrifugation step was taken to remove large colloidal particles that can mechanically interact with the Sep-Pak, resulting in higher apparent concentrations of freely dissolved PCB-52 (Burgess et al. 1996). Reverse-phase C-18 chromatography generates organic carbon-normalized colloidal partitioning coefficients when mechanical interactions that are reproducible are eliminated (Burgess et al. 1996).

PCB-52 bound to microparticulates and DOC was calculated by summing the ^{14}C counts that were removed between the initial counting and the counting following centrifugation with the counts from the eluant passing the C-18 Sep-Pak.

The DOC content of the humic acids in distilled water was determined using an Astro Total Organic Carbon Analyzer, Model 2100. The DOC was used to calculate the K_{DOC}.

RESULTS AND DISCUSSION

The FTIR peak heights of the humic substances normalized to the internal standard indicated significant differences in the aromaticity of the materials (Table 1). The peak height for the Aldrich humic acid was similar to the value (1.03) determined by Davis (1993). Of the sediment materials isolated and characterized in this study, FP-0.331 had the highest peak height ratio for aromatic carbon functional groups. The relative aromatic peak heights of the humics isolated by Davis ranged from 0.39-0.95 compared to the range of 2.21-5.76 for the humics isolated from sediments in this study. The materials isolated in this study showed higher relative content of aromatic carbon than either the Aldrich humic acid or the humics isolated and characterized by Davis (1993). The largest differences were between the materials from soils and river water isolated by Davis and the sediment humics isolated in this study. This suggests that sediment humic acid may be more aromatic in character than humic acids isolated from soils and water. This could explain the finding of Kile et al. (1995) that K_{oc} values for nonpolar organic contaminants in sediments are twice that of soils.

McFarland et al. (1996) studied equilibrium partitioning among environmental components including sediments, and concluded that bio-availability of PCB-52 was highly variable and not linear with sediment organic carbon content at low TOC levels. One reason for those findings may have been the differences in aromaticity of the humic acids isolated from the sediments.

Table 1. Peak height ratios for humic substance aromatic carbon (1600 cm^{-1}) functional groups. Peak heights are normalized to the response of the internal standard (KSCN) at 2050 cm^{-1} and are in units of mg KSCN/mg Humic C.

Humic Acid Source	Sediment TOC, %	Peak height ratio, 1600 cm^{-1}
Aldrich Humic Acid	NA*	0.90
Orange Heights DOC	NA	0.57**
Orange Heights soil	NA	0.60**
Pine Mountain	NA	0.39**
FP-0.331	0.331	5.76
NY-0.055	0.055	3.23
BL-0.963	0.963	2.70
NY-1.28	1.280	2.21

* NA = Not Available
** Data from Davis (1993)

Table 2. Coefficients for Regression (n = 9) of Truly Dissolved and Bound PCB in DOC.

Humic Acid Source	Slope (K_{DOC})	Standard Error of Slope	r^2
Aldrich Humic Acid	5604	2537	0.49
Orange Heights DOC	6194	918	0.90
Orange Heights soil	5682	1642	0.66
Pine Mountain	50934	19020	0.51
FP-0.331	80305	52664	0.44
NY-0.055	73426	10471	0.88
BL-0.963	22600	5410	0.85

The total organic carbon contents of the sediments were not related to the relative degree of aromaticity. For example, NY-O.055 containing 0.055 % TOC showed a higher peak height ratio than did BL-0.963 and NY-1.28. The latter two sediments contained higher levels of TOC, but had lower in peak height ratios (Table 1). These results suggest that the aromatic character of soil and sediment TOC may explain much of the variability observed during partitioning of nonpolar organic contaminants to soils and sediment containing different levels of TOC (Rutherford et al. 1992).

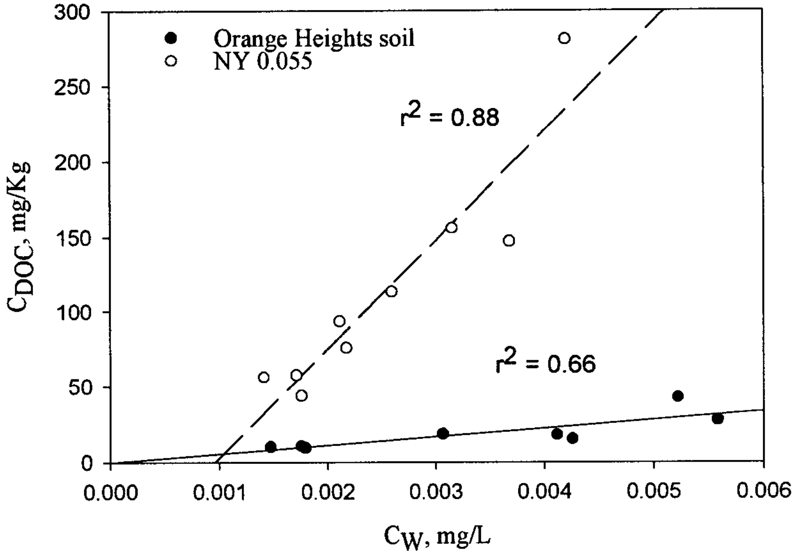

Figure 1. Best fit regression lines for adsorption isotherms (linear partitioning model).

Partitioning, or distribution of a hydrophobic organic compound between dissolved organic carbon (DOC) and water at equilibrium, is described as follows:

$$K_{DOC} = C_{DOC}/C_W \qquad (1)$$

where K_{DOC} = the distribution coefficient (L/kg), C_{DOC} = the concentration of contaminant sorbed to the dissolved organic carbon (mg/kg), and C_W = truly dissolved aqueous phase contaminant concentration (mg/L). Values of K_{DOC} were computed by regression of sorbed (normalized to DOC concentrations) versus truly dissolved PCB concentrations (Table 2). Error in estimates of the slopes averaged 33% for all humic acid solutions. Error included differences between replicates and the experimental procedure. Regression coefficients ranged from 0.44 to 0.90.

K_{Doc}s for PCB-52 varied from 5,604 L/Kg to 80,305 L/Kg. Representative adsorption isotherms for PCB-52 and isolated humic acids are shown in Figure 1. The PCB-52 K_{DOC} of materials isolated and characterized by Davis (1993) were generally lower than PCB-52 K_{DOC}s of humic material isolated from sediments, with the exception of the Pine Mountain material. However, Davis (1993) previously observed that the Pine Mountain material behaved in an anomalous manner during partitioning studies. Comparison of the K_{DOC}'s measured during this study with projected values derived from the data of Davis (1993) (who related K_{DOC} to log solubility for a series of PCBs other than PCB-52) showed good agreement except for the Pine Mountain humic material. The Pine Mountain projected value of log K_{DOC} was much lower (3.2) than the measured value in this study (4.71). Because of the anomalous behavior previously reported, the Pine Mountain K_{DOC} values were not used in further evaluations.

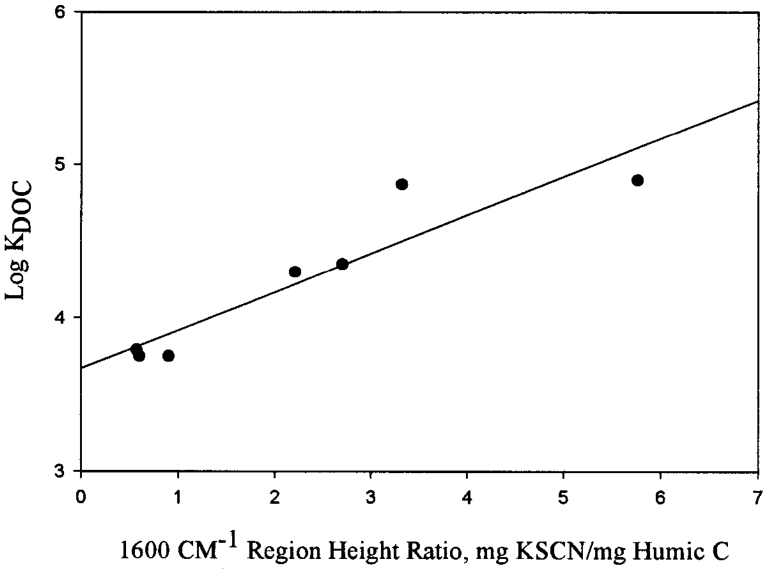

Figure 2. Plot of log K_{DOC} for PCB-52 versus aromatic peak height ratios for extracted humic materials.

Estimated values of K_{DOC} were computed by substituting the octanol/water partition coefficient log K_{ow} = 5.84 (Hawker and Connell 1988) into the equation

$$K_{OC}=0.411 \ K_{OW} \tag{2}$$

(Karickhoff 1981), or the equation

$$\log K_{OC} = 0.00028 + 0.983 \log K_{OW} \tag{3}$$

(DiToro et al. 1991). The estimated values of log K_{Doc} are 5.45 from equation (2) and 5.74 from equation (3). Both estimates are higher than measured values.

A strong linear relationship (r^2= 0.85) exists between log K_{DOC} and the FTIR peak height ratios for humic substance aromatic carbon functional groups (Figure 2). This correlation indicates that differences between measured K_{Doc} values can be caused by variations in the composition of natural organic matter, specifically variations in the aromaticity of TOC as postulated by others (Grathwohl 1990, Davis 1993, Gauthier et al. 1987). Results indicate that the relative degree of aromaticity in sediments is not constant and differs markedly from that measured in humic acids isolated from soils and river waters. Equilibrium partitioning models for predicting nonpolar organic contaminants in sediment pore water that assume all organic carbon is equal in sorptive affinity are making an erroneous assumption.

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