Correlation of Soil and Sediment Organic Matter Polarity to Aqueous Sorption of Nonionic Compounds

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Polarities of the soil/sediment organic matter (SOM) in 19 soil and 9 freshwater sediment samples were determined from solid-state ^{13}C-CP/MAS NMR spectra and compared with published partition coefficients (K_{oc}) of carbon tetrachloride (CT) from aqueous solution. Nondestructive analysis of whole samples by solid-state NMR permits a direct assessment of the polarity of SOM that is not possible by elemental analysis. The percent of organic carbon associated with polar functional groups was estimated from the combined fraction of carbohydrate and carboxyl− amide−ester carbons. A plot of the measured partition coefficients (K_{oc}) of carbon tetrachloride (CT) vs. percent polar organic carbon (POC) shows distinctly different populations of soils and sediments as well as a roughly inverse trend among the soil/sediment populations. Plots of K_{oc} values for CT against other structural group carbon fractions did not yield distinct populations. The results indicate that the polarity of SOM is a significant factor in accounting for differences in K_{oc} between the organic matter in soils and sediments. The alternate direct correlation of the sum of aliphatic and aromatic structural carbons with K_{oc} illustrates the influence of nonpolar hydrocarbon on solute partition interaction. Additional elemental analysis data of selected samples further substantiate the effect of the organic matter polarity on the partition efficiency of nonpolar solutes. The separation between soil and sediment samples based on percent POC reflects definite differences of the properties of soil and sediment organic matters that are attributable to diagenesis.

Introduction

The sorption of nonpolar, nonionic organic solutes from water to soil and sediment is predominantly controlled by partition (i.e., solubility) to soil/sediment organic matter (SOM) (*1*). Thus, the composition of the SOM can ultimately influence the extent of soil/sediment sorption. It is therefore of interest to determine the effect of SOM composition on solute partition that may potentially affect pollutant transport in hydrologic systems.

Kile et al. (*2*) observed distinct populations of soils and sediments with respect to their organic carbon-normalized

sorption coefficients (K_{oc}) for carbon tetrachloride (CT) and 1,2-dichlorobenzene (DCB). The observed K_{oc} values for sediments are generally greater than those for soils by a factor of about 2. This difference suggests that sediment organic matter may be somewhat less polar in composition than soil organic matter.

In related studies, empirical correlations between the elemental composition of natural organic matter and the extent to which various organic compounds are sorbed were investigated for a variety of natural humic materials and soils (*3−8*). Differences in the polarity of samples (as inferred from elemental analyses) have been attributed to diagenesis of organic matter (*2, 8*) that results in different degrees of enrichment of aliphatic and lignin components at the expense of cellulose and other carbohydrate components (*9, 10*). None of these studies, however, have given a direct relation between soil and sediment organic matter composition, polarity, and sorption capacity. Rice and MacCarthy (*11*) and Malcolm (*12*) found significant differences in elemental compositions and compositional characteristics of humic substances extracted from soil and aquatic samples. These studies, however, did not give a complete representation of the composition of the SOM because extractive procedures remove only a fraction of SOM from soil.

In this study, we analyzed the functional group contents of 19 soils and 9 freshwater sediments from diverse geographic sources by whole soil/sediment ^{13}C cross-polarization, magic angle spinning (CP/MAS) NMR to give a further account of differences in soil and sediment organic matter composition. Because reliable estimates of the type of organic carbon of whole soils and sediments cannot be obtained by conventional methods of elemental analysis, nondestructive analysis by ^{13}C-CP/MAS NMR becomes invaluable for a direct comparison of the composition/polarity of SOM in soils and sediments and its effect on solute partition. This is the first report relating the carbon functional group contents of whole soil and sediment samples to their sorption (partition) efficiencies.

Experimental Section

Solid-state ^{13}C-CP/MAS NMR spectra were measured with a 200 MHz (50 MHz ^{13}C) Chemagnetics CMX spectrometer with a 7.5 mm diameter probe. Acquisition parameters were 1 ms contact time, 1 s pulse delay, 4.5 μs pulse width for a 90° pulse, and a spin rate of 4600 Hz. An acceptable signal-to-noise ratio was obtained for the studied samples with scan numbers ranging from approximately 50 000 to 240 000 transients (corresponding to 14−70 h run time). Run time was dictated by the percent of sample organic carbon.

Analysis by NMR is generally limited to samples having organic carbon contents greater than about 1.5%. Spectral acquisition is further impeded by the presence of paramagnetic cations (predominantly Fe) that reduce cross-polarization efficiency and consequently signal intensity. Although treatment with dithionite has been shown to effectively remove Fe (*13, 14*), it was not done in the present study to avoid chemical modification to the organic matter (strongly magnetic minerals were however removed with a hand magnet prior to analysis). As a consequence of the reduction in signal intensities due to paramagnetic materials as well as variable NMR response factors that result from different structural groups, NMR spectroscopy of whole soils is semiquantitative. Nonetheless, it does provide a reliable means of obtaining a relative assessment of organic matter composition. In this study, spectra showing low signal-to-noise ratios were not used.

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TABLE 1. Chemical Shift Limits (ppm) and Assignments of the Four ^{13}C-CP/MAS NMR Spectral Regions from Which % POC Is Derived

spectral regions	functional group carbons
0−50	aliphatic carbons
50−105	alcoholic carbons in carbohydrates, ethers, anomeric carbons
105−160	aromatic and phenolic carbons
160−220	carboxyl, carbonyl carbons in aldehydes, amides and ketones

Integrations were carried out for spectral regions of carbon atoms associated with both polar and nonpolar structural groups to give a semiquantitative measure of their relative concentrations. The selection of these regions was based on a conventional designation of carbon structural groups (15, 16); polar and nonpolar organic carbon spectral regions used in this study are listed in Table 1. Integration was done with a calibrated polar planimeter. Percent polar organic carbon (POC) was calculated as the combined fraction of the 50−105 and 160−220 ppm regions of the NMR spectra. A detailed discussion of quantitation from ^{13}C-CP/MAS NMR as applied to whole soils is given by Baldock et al. (17) and Kinchesh et al. (18).

Soil samples from geographically diverse ecosystems and climates were obtained from localities in both the United States and the People's Republic of China. Soils were collected from the A horizon of the soil profile, except for Chinese soils from Quinghai Province and Guizhou Province, which were collected from regions about 1 m below land surface to minimize agricultural impact. Bed sediment samples were collected from the top 0−20 cm of the sediment surface. Sample locations are shown in Table 2. The peat sample, obtained as a reference sample from the International Humic Substances Society, was collected from the Belle Glade Research Station, Everglades, FL. The Houghton muck was obtained from the Michigan State University Muck Research Farm, Lainsburg, MI. All soil and sediment samples were dried and ground to pass either a 35-mesh sieve (U.S. samples) or a 200-mesh sieve (Chinese samples).

The partition coefficients (K_{oc}) of carbon tetrachloride (CT) between SOM and water are from Kile et al. (2); partition data for peat and muck are from Rutherford et al. (5). Isotherms were determined by batch sorption methods, using approximately 3 g of soil or sediment (an amount determined to be sufficient to sorb 40−60% of the measured aliquot of CT) that was equilibrated 48−72 h with 20−25 mL 0.005 M aqueous $CaCl_2$ to suppress organic matter dissolution. The aqueous solution of CT was extracted with hexane and analyzed by gas chromatography; solid-phase content of CT was determined after extraction with 4:1 hexane:acetone followed by analysis by gas chromatography. Further details are provided by Kile et al. (2). Although complete equilibrium may not have been attained in the 48−72 h time used in determination of K_{oc}, our studies (unpublished data) indicate that most of the uptake has taken place within this interval, in agreement with recent work by Xing and Pignatello (19) and by Xia and Ball (20). Given that all sorption experiments in the present study were equilibrated for the same time, it is presumed that underestimation of K_{oc}, if any, will be consistent among the samples and does not affect the

TABLE 2. Percent Polar Organic Carbon (POC), K_{oc} for Carbon Tetrachloride (CT), and Percent Organic Carbon for Soils and Sediments

	% POC	K_{oc}, CT	% OC
Soil			
Elliot, IL (IHSS reference standard)	55.6	49	2.9
Anoka, MN	56	61	1.08
Marlette soil, East Lansing, MI	51.6	45	1.8
west-central Iowa (U.S. EPA reference sample 10)	59.9	58	2.04
Columbus, KY (U.S. EPA reference sample 19)	51.1	67	1.73
Cathedral soil, Fremont Co., CO	50.6	74	3.12
Wellsboro soil, Otsego Co., NY	57.6	68	3.47
Piketon, OH	55.9	53	1.49
Pierre, SD (U.S. EPA reference soil 7)	54.9	63	2.21
Renslow soil, Kittitas Co, WA	57.5	59	2.4
Manchester, OH (U.S. EPA reference sample 12)	56.2	57	2.25
Burleigh Co., ND (U.S. EPA reference soil 2)	58.4	52	2.4
Fangshan District, Beijing, China	50.2	54	5.61
Anda, Heilongjiang, China	53.6	67	2.83
Gancha Co., Quinhai, China	54.3	62	1.12
Changshu, Jiangsu, China	54.8	55	1.77
Dushan Co., Gizhou, China	58.2	61	2.54
average	55.1	59.1	
standard deviation	2.89	7.47	
Florida peat (IHSS reference soil)	4.79	87.8[a]	50.8
Houghton muck, Michigan	53.3	59.7[a]	46.4
Sediment			
Mississippi River, Helena, AK	36.5	109	1.6
Lake Charles, adjacent to Calcasieu River, Lake Charles, LA	45.3	112	1.97
Mississippi River, St. Paul, MN (pool 2)	43.5	94	1.5
Yazoo River, Vicksburg, MS	39	119	0.58
Kaskaskia River, IL (U.S. EPA reference sediment 25)	49	90	0.99
Mississippi River, Alton, IL (pool 26)	51.7	91	1.4
Illinois River, near Lacon, IL (U.S. EPA reference sediment 22)	46.4	116	2.2
Ned Wilson Lake, Buford, CO	52.5	101	5.62
Songhuajiang River, Anda, Jiling, China	47.1	128	4.47
average	45.7	106.7	
standard deviation	5.36	13.44	

[a] Data from Rutherford et al. (5).

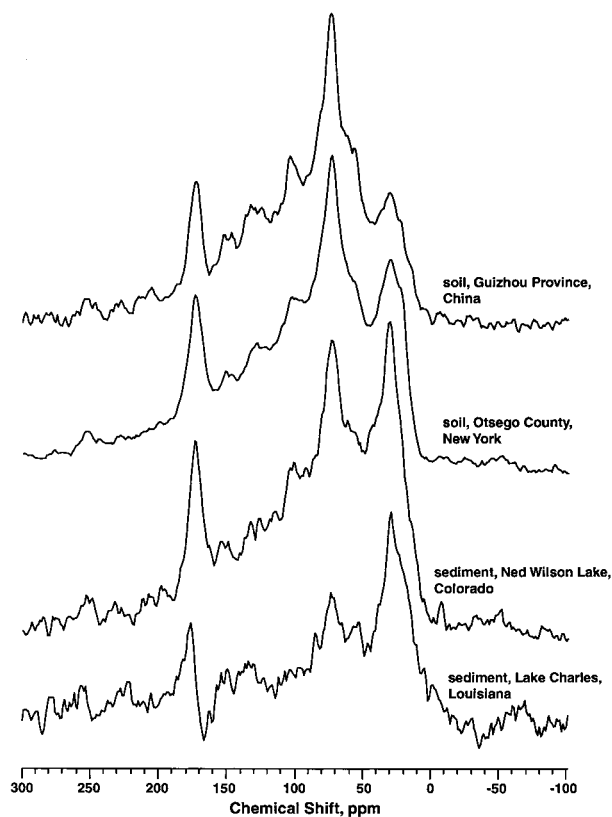FIGURE 1. NMR spectra of selected soils and sediments.

FIGURE 2. Plot of K_{oc} vs. % POC for soils and sediments.

conclusions of this paper.

The organic carbon contents of the soils and sediments were determined by a high-temperature oxidation method using a Leco instrument (21). Elemental analyses of the peat and muck samples were performed by Huffman Laboratories, Golden, CO.

Results and Discussion

Samples having an iron content (measured by Kevex, total iron expressed as FeO) exceeding about 4.5 wt % generally gave spectra showing low signal-to-noise ratios. However, a sufficiently high organic carbon content can attenuate the effects of a high FeO content. For example, the soils from Fremont County, CO, and Pierre, SD, and a sediment from the Songhuajiang River, China, all show a high FeO content but have sufficiently high total organic carbon (TOC) to yield acceptable spectra. In general, samples with a relatively high OC/FeO ratio (>0.4–0.6) gave reliable spectra, while samples showing low ratios (i.e., <0.4) gave ambiguous results. These results are similar to those reported by Arshad et al. (14), who found that the organic carbon-to-iron ratio was a critical factor, with C:Fe ratios less than 1 warranting chemical treatment to remove the iron.

Table 2 lists the soils and freshwater sediments used in this study together with their respective percents of polar organic carbon (POCs), partition coefficients (K_{oc}), and percent of total organic carbon. The K_{oc} values for soils (average K_{oc} = 59.1) are lower than those of sediments (average K_{oc} = 106.7), while the % POCs for soils are generally higher than those of sediments (averages 55.1 vs. 45.7%, respectively). Representative NMR spectra for selected soils and sediments are shown in Figure 1; the higher ratio of POC to nonpolar aliphatic and aromatic carbon is evident from the spectral intensities for soils relative to sediments.

The plot of K_{oc} for CT vs. percent POC in Figure 2 shows an inverse trend between K_{oc} and % POC, with distinct populations of soils and sediments relative to both K_{oc} and
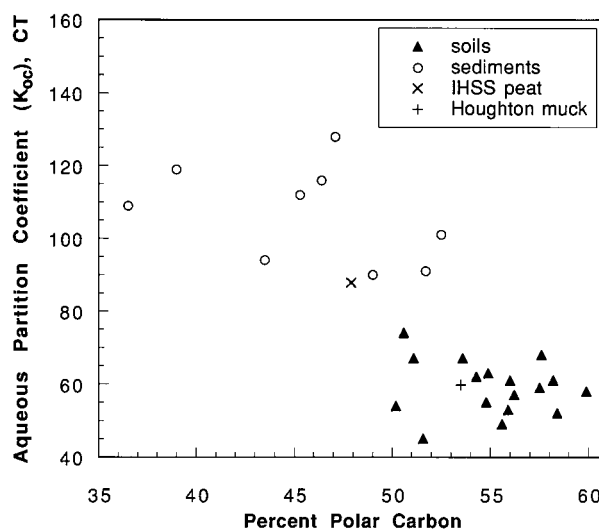
% POC. That these populations are distinct was determined with the Student's t-test (two-tailed distribution, heteroscedastic) that showed the probability of identical means to be less than 0.001.

Because sorption of nonionic organic compounds as solutes from water to soil/sediment is predominantly controlled by partition (i.e., solubility) to SOM, the extent of sorption may be expected to be governed by the polarity of the solute as well as that of the sorbent. ^{13}C NMR data for the soils and sediments studied substantiate a higher polar group content for soils relative to sediments. Furthermore, the approximate inverse trend shown in Figure 2 suggests that the polarity of SOM is a significant factor influencing the partition efficiency of nonpolar organic compounds to SOM, although additional factors such as configuration and conformation of the organic macromolecule could also affect sorption. The present data supplement and extend the earlier work of Rutherford et al. (5), where sorption was correlated to an overall polarity index described as (O + N/C). This study provides, however, a more direct account of the types and amounts of polar functional groups in soil and sediment organic matters that affect their efficiencies as partition media for nonpolar compounds.

Several recent studies have reported a correlation between the K_{oc} of polycyclic aromatic hydrocarbons (PAHs) and "aromaticity" of various humic materials (22, 23). In this study, evaluation of the contribution of aromatic carbon (the 105–160 ppm region of the NMR spectra) in SOM to the K_{oc} of CT (Figure 3) yields a poor correlation. The t-test probability of identical means for the populations of soils and sediments based on their aromatic content is approximately 0.90 (i.e., there is a 90% probability that the means are the same for these two populations), which further substantiates that the aromatic carbon content alone is subordinate to POC in governing the partition of nonpolar compounds other than PAHs (i.e., CT). Similarly, the correlation of K_{oc} with aliphatic carbon content alone or with other individual structural groups shows poor results based on the t-test. As expected, however, there is a good correlation between K_{oc} and the sum of aliphatic and aromatic structural carbons (which is inversely related to POC). This correlation is only moderate (as with POC) presumably because part of the aromatic region may be polar in nature. That the correlation of K_{oc} with individual aromatic and aliphatic groups is less than that of their sum is because nonpolar moieties occur within both groups, with individual groups containing only a part of the total nonpolar carbon in SOM.

In Figure 2, the minor degree of overlap with respect to POC is not unexpected because of a presumed continuum
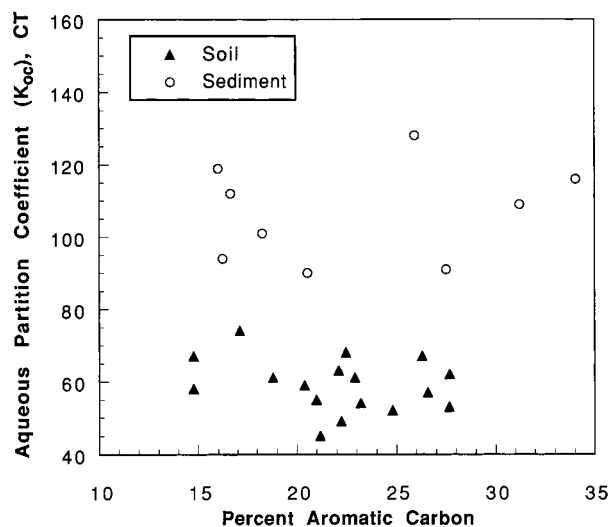
FIGURE 3. Plot of K_{oc} vs. % aromatic hydrocarbon for soils and sediments.

of diagenesis from soils to sediments. The diagenesis of eroded soils in an aquatic system may result in an increased nonpolar organic matter content at the expense of polar functional groups if the sedimentation process fractionates soil organic matter constituents such that more polar (and water-soluble) constituents are separated to form dissolved organic matter or organic colloids, or if anoxic degradation selectively consumes the more labile (or polar) components.

Florida peat and Houghton muck serve as useful models of soil organic matter. Because they are nearly pure organic materials, NMR spectroscopy yields unambiguous structural data that can be directly compared to carbon and oxygen contents of the samples. Elemental analysis (calculated on a moisture-free basis) of these materials shows that peat has organic carbon (OC) and oxygen contents of 50.8 and 30.3%, respectively; while the OC and oxygen contents for muck are 46.4 and 32.9%, respectively; POC (determined from NMR spectra, Table 2) for peat and muck are 47.9 and 53.3%, respectively. The higher oxygen content of muck correlates well with its higher POC relative to peat. The plot shown in Figure 2 indicates that while muck falls well within the range of normal soils, peat falls at the upper range of soils, within the more polar region (i.e., high % POC) of sediments. A line drawn between peat and muck (Figure 2) would coincide with the roughly inverse trend shown by soils and sediments.

In summary, the inverse relation between K_{oc} and POC values for soils and sediments indicates that natural organic matters of soils and sediments fall virtually into two populations based on their polarities and compositions, with resulting disparities on the partition of nonpolar compounds. The consistency in K_{oc} and POC among soils and among sediments also suggests relatively stable compositions for soil organic matter and sediment organic matter. These results emphasize the necessity of taking into account the different properties between soil and sediment samples in estimating the transport and fate of anthropogenic compounds in hydrologic systems.

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