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Equilibrium sorption of phenanthrene by soil humic acids

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Abstract

This study investigated the effect of chemical heterogeneity of humic acids (HAs) on the equilibrium sorption of phenanthrene by HA extracts. Six HA samples were extracted from three different soils with 0.5 M NaOH and 0.1 M $Na_4P_2O_7$ and were characterized with elemental analysis, infrared spectrometry, and solid-state ^{13}C nuclear magnetic resonance (NMR) spectrometry. The equilibrium sorption measurements were carried out with a batch technique and using the six HA solids as the sorbents and phenanthrene as the sorbate. The measured sorption isotherm data were fitted to the Freundlich equation. The results showed that, for the same soil, (i) the total HA mass extracted with $Na_4P_2O_7$ was 13.7–22.6% less than that extracted with NaOH, (ii) the $Na_4P_2O_7$-extracted HA had higher O/C atomic ratio, greater content of polar organic carbons (POC), and lower aliphatic carbon content than the NaOH-extracted HA, and (iii) the $Na_4P_2O_7$-extracted HA exhibited greater sorption isotherm linearity and but not dramatic difference in sorption capacities than the NaOH extracted HA. The differences in the HA properties resulting from the two different extraction methods may be because NaOH can hydrolyze insoluble HA fractions such as fatty acid like macromolecules bound on soils whereas $Na_4P_2O_7$ could not. As a result, the HAs extracted with the two different methods had different polarity and functionality which affected their sorption property for phenanthrene.

Keywords: Phenanthrene; Humic acid; Sorption

1. Introduction

Soil organic matter (SOM) is the predominant sorbent for sorption of hydrophobic organic chemicals (HOCs) by soils and sediments. Recent studies have treated SOM as a dual reactive domain sorbent which exhibits partitioning and adsorption behaviors for interaction with HOC molecules in aquatic systems (Xing et al., 1994; Weber and Huang, 1996; Huang et al., 1997; LeBoeuf and Weber, 1997). According to the dual reactive domain model, SOM may consist of two domains, a rubbery or “soft carbon” SOM domain exhibiting linear partitioning phenomena and a glassy or “hard carbon” SOM domain exhibiting nonlinear sorption phenomena (LeBoeuf and Weber, 1997). This model has enjoyed its success in operationally delineating chemical heterogeneity of SOM and mechanistically

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interpreting sorption of HOCs by soils and sediments (Weber et al., 1992; Young and Weber, 1995; Xing et al., 1996; Huang et al., 2003).

Humic acid (HA) is operationally defined as the fraction of SOM that is soluble in base solutions but insoluble in acids. It is ubiquitous in soils and sediments of terrestrial ecosystems and is a major fraction of SOM. It is chemically complex, structurally heterogeneous, and biologically refractory. It was shown in several recent studies that HA can change from relatively condensed and glassy states to rubbery states as temperature increases (LeBoeuf and Weber, 1997). The reported glass transition temperatures are slightly above ambient temperatures (LeBoeuf and Weber, 2000a). When at glassy states, they were also shown to exhibit nonlinear sorption isotherms for less polar HOCs (LeBoeuf and Weber, 1997, 2000b; Lu and Pignatello, 2002).

HAs are often extracted from soils and sediments with 0.5 M NaOH solution following a standard procedure recommended by the International Humic Substance Society (IHSS) (Swift, 1996). The extracted HAs were used as sorbents in several prior studies of HOC sorption (Garbarini and Lion, 1986; Rutherford et al., 1992; Huang et al., 1997; Christl and Kretzschmar, 2001; Gunasekara et al., 2003; Li et al., 2003; Terashima et al., 2003). $Na_4P_2O_7$ is a relatively weaker base with pH 10 at 0.1 M. It was also used in prior studies for extraction of HAs (Schnitzer and Schuppli, 1989). It is believed that HAs in soils and sediments are either in insoluble organic salt forms or chemically sorbed on mineral surfaces. Polyphosphate is a strong anion which can compete with HAs for bonding with divalent and polyvalent cations such as Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+}, causing HAs to dissolve in aqueous phase. Due to its weak base nature, $Na_4P_2O_7$ may not hydrolyze soil-bound HA nor dissolve fatty acid like materials from soil as does NaOH. In this study, we expected that HAs extracted from the same soil with the two different chemicals are different, and that they exhibit different sorption behavior for HOCs. The objectives of this study was to extract HAs from soils with both NaOH and $Na_4P_2O_7$, to characterize the extracted HAs with different chemical and spectral techniques, and to measure equilibrium sorption of phenanthrene on the HAs. The goal of the study was to elucidate the mechanisms of sorption by HAs by examining the effect of heterogeneous properties of HAs on the equilibrium sorption behavior of HOCs.

2. Materials and methods

2.1. Sorbents and their characterization

Three different soil samples were used in this study for extraction of HA samples. They included two soils, GZ1 (2.01 wt.% TOC) and GZ2 (3.24 wt.% TOC), collected from the top layers of the soil profile near the Lake Hongfeng, Guiyang, Guizhou Province, PR China, and a topsoil (5.23 wt.% TOC) from Chelsea, MI. Two separate HA samples were obtained from each of the three soils using the standard NaOH extraction procedure (Swift, 1996) and the $Na_4P_2O_7$ extraction method used by Schnitzer and Schuppli (1989). In brief, about 10 g of a soil sample was mixed for 24 h with 100 ml of either 0.5 M NaOH (pH 13.2) or 0.1 M $Na_4P_2O_7$ (pH 10.2) solution in a 200 ml centrifuge bottle with a headspace of N_2 gas. After mixing, the soil-solution was separated by centrifugation at 2349*g* and the supernatant was transferred to a flask and stored at 4 °C. The above procedure was repeated five to eight times with the same aqueous solution until the supernatant became visually colorless. The supernatants obtained from the repetitive extraction for a given soil were combined, acidified to pH 1 with 2 M HCl, and HA was allowed to precipitate overnight. After centrifugation, the HA precipitate was neutralized to pH 7 with 1 M NaOH, and was then dissolved in 0.1 M NaOH solution at a liquid to precipitate ratio (v/w) of 10:1. The suspension was shaken for 4 h, left overnight, and centrifuged for removal of inorganic impurity. The supernatant was transferred to another container and was acidified to pH 1 using 6 M HCl, left overnight, and centrifuged again. The HA precipitate was further purified by dissolution of HA in 0.1 M KOH (v/w = 10/1). KCl at 2.5 M was added to the solution to achieve an estimated concentration of K^+ of 0.3 M. After centrifugation at 2349*g* for 20 min, the supernatant was acidified with 6 M HCl to pH 1 and left overnight allow HA precipitate. The HA precipitate so obtained was mixed overnight with 0.1 M HCl and 0.3 M HF acids at a liquid to solid ratio (v/w) of 10:1 to remove additional silicates and polyvalent cations. The HA precipitate was washed with distilled water, freeze dried, and stored in a dessiccator until use. The above procedure was operated under an N_2 atmosphere.

The six HA samples obtained were further characterized using standard methods. The elemental composition (C, H, N, O, and S) was analyzed with a high-temperature combustion method (PE2400 SERIES II analyzer, PE, Inc.) and the ash content was determined by combustion of humic acids at 740 °C for 4 h. The infrared (IR) spectra were recorded with a Bruker Vector33 FT-IR spectrometer at a resolution of 4 cm^{-1} for pellets prepared by mixing ground HA powder (1 mg) with 60 mg KBr (FT-IR grade). The ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX-400 NMR spectrometer operated at a ^{13}C frequency of 75.4 MHz and at a magic-angle-spinning (MAS) rate of 6.0 kHz. For the ^{13}C-NMR measurement, a solid HA sample was placed in a 4-mm diameter ZrO_2 rotor with a Kel-F cap. A 1-s recycling time and a 1-ms contact time were used. Each spectrum consisted of 2400 data points and the chemical shifts were referenced externally to glycine (176.03 ppm).

2.2. Sorption experiments

Phenanthrene, a three-ring polycyclic aromatic hydrocarbon (PAH), was obtained in spectrophotometric grade from Aldrich Chemical Co., Inc. It was selected as the solute probe because it is commonly found in contaminated aquatic and subsurface environments due to petroleum- and coal-related industrial activities. This chemical is also extensively used in prior studies of HOC sorption by soils and sediments (e.g., Weber and Huang, 1996; Xiao et al., 2004).

A primary phenanthrene stock solution at 5000 mg/l was prepared by dissolving appropriate amounts of the chemical in HPLC-grade methanol. It was diluted with methanol to make a series of stock solutions of various phenanthrene concentrations. All stock solutions were stored at 4 °C in glass bottles sealed with Teflon-lined tops. A desired volume of stock solution was mixed with a background solution in a volumetric flask to make an initial aqueous solution for sorption experiments. Ten levels of initial solutions ranging from 10 to 1000 μg/l were prepared. The volumetric fraction of methanol in each initial solution was less than 0.2%, which was a level having no measurable effect of the cosolvent on sorption of organic pollutants (Wauchope and Koskinen, 1983). The aqueous background solution used in this study contained 0.005 M $CaCl_2$ as the major mineral constituent, 100 mg/l of sodium azide (NaN_3) to inhibit biological activity. In order to avoid dissolution of HA solids during sorption, the pH of the aqueous solution was adjusted to 2 using dilute HCl.

A batch technique with fixed sorbent dosages was utilized for conducting all equilibrium sorption experiments in this study. Experimental procedures described in Xiao et al. (2004) were exactly followed. In brief, 10-ml glass ampoules (flame-sealed) were used as batch reactors. According to our preliminary sorption rate and equilibrium studies, an equilibration time of 14 d was used. The initial aqueous-phase phenanthrene concentrations (C_0 in μg/l) were selected to yield a set of isotherm data for each HA that distributed evenly on a log-log scale plot and spanned approximately 2 orders of magnitude in equilibrium aqueous-phase solute concentrations (C_e in μg/l). Reactors filled with sorbent material and initial aqueous solution were flamed sealed and mixed completely by shaking at 125 rpm at room temperature (21 ± 2 °C). After 14 d, the reactors were set up-right for 2 d to allow the suspended HA solids to settle. According to Huang et al. (1997), the solid-solution separation using this settling method had no difference from the centrifugation method. After separation, an aliquot of supernatant was withdrawn from each reactor and mixed with a predetermined amount of HPLC-grade methanol in a 5-ml glass vial capped with a Teflon-lined septum.

Control reactors prepared similarly but containing no sorbent materials were run simultaneously for assessing loss of solutes to reactor components during sorption tests. Results of triplicate reactors at each C_0 level showed that the average solution phase concentrations of each solute were consistently within 98–102% of the respective initial concentration of the same solution analyzed similarly. Hence, no correction was made during reduction of the sorption data.

The mixtures of methanol-aqueous solution were analyzed for phenanthrene concentrations using a reverse-phase HPLC (ODS, 5 μm, 2.1 × 250 mm column on a Hewlett-Packard Model 1100) with a diode array UV detector for concentrations ranging from 50 to 1000 μg/l and a fluorescence detector for concentrations from approximately 0.5 to 50 μg/l. The aqueous-phase solute concentrations (C_e and C_0) were calculated by applying a dilution factor computed from the density data of the methanol–water mixture to the HPLC measurements (Weber and Huang, 1996). The solid-phase sorbate concentration (q_e in μg/g) was determined for each reactor from a solute mass balance between the two phases.

3. Results and discussion

3.1. HA characterization

Table 1 lists the elemental composition, ash content, and the O/C and H/C atomic ratio for the six HA samples. The IR spectra and the solid state ^{13}C-NMR spectra are shown in Figs. 1 and 2, respectively. The peaks on the ^{13}C NMR spectra were assigned according to Wilson (1987) and the detailed peak assignments for the ^{13}C-NMR spectra are summarized in Table 2. For better comparison, the areas of the identified ^{13}C-NMR peaks were integrated and the results are listed in Table 2. The percentage of polar organic carbon (POC) was calculated as the combined fractions of the 50–110 and 140–220 ppm regions of the NMR spectra (Kile et al., 1999), and the results are also listed in Table 2.

The results of the TOC contents analyzed for the three soils before and after extraction indicated that the $Na_4P_2O_7$ extraction method removed 23.4%, 16.8%, and 34.4% of the TOC from GZ1, GZ2, and Chelsea soil, respectively, which were 13.7–22.6% less compared respectively to 26.6%, 20.6%, and 41.6% of TOC removal by the NaOH extraction procedure. As pointed out by Schnitzer and Schuppli (1989), $Na_4P_2O_7$ is a relatively mild base compared to NaOH. At 0.1 M level, the measured pH of the $Na_4P_2O_7$ is 10.2 under N_2 atmosphere. It extracts HA that is complexed to

Table 1
Elemental composition and ash content of the extracted HA samples

HA sample	Elemental composition (wt.%)					Atomic ratio		Ash (wt.%)
	C	H	O	S	N	O/C	H/C	
GZ1-N	52.4	6.57	34.3	1.61	3.82	0.49	1.50	0.68
GZ1-P	50.5	6.29	37.5	1.28	3.48	0.56	1.49	0.78
GZ2-N	53.6	5.63	34.1	1.67	3.67	0.48	1.26	1.12
GZ2-P	50.0	5.04	39.3	1.53	3.17	0.59	1.21	0.58
Chelsea-N	51.4	5.98	31.6	1.09	3.33	0.46	1.40	5.60
Chelsea-P	48.7	5.08	36.4	1.15	3.00	0.56	1.25	4.80

The suffix "-N" and "-P" represent the HAs extracted with NaOH and $Na_4P_2O_7$, respectively. Standard deviations are within 0.5% of the values provided here.

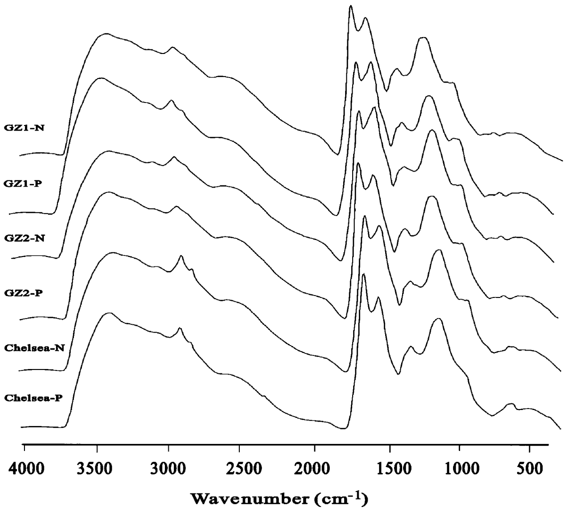

Fig. 1. Infrared spectra of the six HA samples. Compared to the $Na_4P_2O_7$ extracted HA, the NaOH extracted HA exhibits slightly greater IR absorbance at 2900–2940 cm^{-1} resulting from aliphatic carbons.

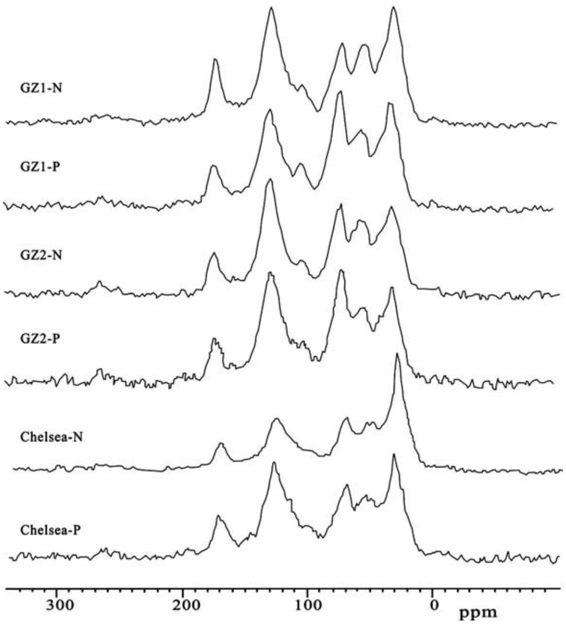

Fig. 2. CP/MAS ^{13}C NMR spectra of the six HA samples.

divalent and polyvalent metals and clays. NaOH is a strong base and its measured pH was 13.2 at 0.5 M. It can dissolve HA macromolecules that may not be soluble in relatively weaker base $Na_4P_2O_7$ solution. More importantly, strong bases such as NaOH can hydrolyze larger, less polar and insoluble HA macromolecules into smaller and more soluble HA molecules, hence possessing greater extractability for HA than weak bases. The hydrolysis reactions often result in dissolution of fatty acids, which even in a small quantity can affect the HOC sorption properties for HA materials. As shown below, each HA extracted with NaOH had relatively greater content of aliphatic C than its respective HA extracted with $Na_4P_2O_7$.

The total organic carbon contents of the six HA samples range from 48.7% to 53.6%, and their elemental compositions are consistent with typical HAs extracted from soils (Chen and Pawluk, 1995; Song et al., 2002; Li et al., 2003). A careful examination of the data summarized in Tables 1,2 indicates that the HA extracted from a given soil with $Na_4P_2O_7$ (GZ1-P, GZ2-P, or Chelsea-P) has greater oxygen content and more polar than that extracted from the same soil with NaOH (GZ1-P, GZ2-P, or Chelsea-P). The oxygen content of an $Na_4P_2O_7$ extracted HA is ~2 wt.% greater than the corresponding NaOH extracted HA and that the O/C atomic ratio of an $Na_4P_2O_7$ extracted HA is 0.07–0.11 greater than that of its corresponding NaOH extracted HA. Meanwhile, the H/C atomic ratios of the HAs extracted from the same GZ2 or Chelsea soil with the two different methods are slightly different. The NaOH extracted HA has greater H/C ratio than the $Na_4P_2O_7$

Table 2
Major functional groups of ^{13}C-NMR spectra

HA sample	Alkyl C (0–50 ppm)	O-alkyl C (50–110 ppm)	Aromatic C (110–140 ppm)	O-aryl C (140–165 ppm)	Carboxyl C (165–190 ppm)	Carbonyl C (190–220 ppm)	POC
GZ1-N	25.4	33.1	28.8	2.88	8.66	1.15	45.8
GZ1-P	24.3	40.6	25.2	2.41	6.08	1.43	50.6
GZ2-N	24.0	38.3	28.9	2.37	6.07	0.32	47.1
GZ2-P	21.6	42.4	27.2	2.04	5.84	0.94	51.2
Chelsea-N	33.5	34.2	23.0	2.12	5.73	1.48	43.5
Chelsea-P	24.0	34.9	27.7	3.16	8.88	1.45	48.4

The POC was calculated from the peak areas listed above with an equation: POC = (O-alkyl C + O-aryl C + carboxyl C + carbonyl C)/(alkyl C + O-alkyl C + aromatic C + O-aryl C + carboxyl C + carbonyl C) × 100.

extracted HA, indicating more aliphatic carbons are present in the NaOH extracted HA. As mentioned above, it is likely that NaOH can extract larger and fatty acid-containing HA macromolecules via hydrolysis reactions which are probably absent in $Na_4P_2O_7$ extraction method.

The difference between the $Na_4P_2O_7$ extracted and NaOH extracted HAs can also be found in FT-IR spectra (Fig. 1) and ^{13}C-NMR spectra (Fig. 2). According to Fig. 1, each NaOH extracted HA exhibits slightly greater IR absorbance at 2900–2940 cm^{-1} resulting from aliphatic carbons than its corresponding $Na_4P_2O_7$ extracted HA. The ^{13}C-NMR spectra shown in Fig. 2 for the six HAs have typical resonance peaks for typical soil HAs (Chen and Pawluk, 1995; Kile et al., 1999; Chefetz et al., 2000; Ahmad et al., 2001; Mao et al., 2001). The quantitative results listed in Table 3 indicate that the POC content of each NaOH extracted HA is ~4% lower than that of its corresponding $Na_4P_2O_7$ extracted HA. The peak areas of the alkyl C for the HAs extracted with NaOH from GZ1, GZ2 and Chelsea soil are respectively 4%, 10%, and 39% greater than those of the HAs extracted with $Na_4P_2O_7$. This indicates that fatty acid-containing moieties were extracted with the stronger base via hydrolysis reactions.

The content of aliphatic carbons differs among different soils. Table 2 shows that the Chelsea soil may have very high aliphatic carbon content and that two HA materials extracted from Chelsea soil had the largest difference in aliphatic carbon content. The H/C atomic ratio of the two HAs listed in Table 1 indicated that there exists the largest difference in H/C atomic ratio between Chelsea-N and Chelsea-P, suggesting the Chelsea-N may have high aliphatic carbon content. As shown below, such a difference resulted in the largest difference in sorption of phenanthrene at the low concentration range.

3.2. Phenanthrene sorption equilibria

The equilibrium sorption data measured for phenanthrene and the six HA samples were fitted to the Freundlich isotherm model having the following form:

$$q_e = K_F C_e^n \tag{1}$$

where n, the exponent of the Freundlich isotherm equation, is an indicator of the sorption isotherm linearity, and K_F [(μg/g)/(μg/l)^n] is the unit-capacity parameter of the Freundlich isotherm equation. A nonlinear regression procedure using SYSTAT software (Version 10,

Table 3
Phenanthrene sorption isotherm parameters and the calculated K_{OC} values

HA sample	K_F[a]	n	R^2	N[b]	K_{OC}[c] (l/g_{OC})		
					$C_e = 0.005S_W$	$C_e = 0.05S_W$	$C_e = 0.5S_W$
GZ1-N	54.8 (1.08)[d]	0.806 (0.019)	0.995	10	74.9 (3.8)	47.9 (2.4)	30.6 (1.6)
GZ1-P	50.5 (1.10)	0.831 (0.023)	0.995	8	74.7 (3.8)	50.7 (2.5)	34.3 (1.8)
GZ2-N	66.4 (1.08)	0.777 (0.021)	0.996	10	84.4 (4.2)	50.5 (2.5)	30.2 (1.5)
GZ2-P	52.3 (1.11)	0.839 (0.027)	0.992	10	79.3 (4.0)	54.7 (2.7)	37.8 (2.0)
Chelsea-N	43.1 (1.10)	0.828 (0.019)	0.996	9	62.4 (3.1)	42.0 (2.1)	28.2 (1.5)
Chelsea-P	33.0 (1.11)	0.874 (0.026)	0.993	10	54.5 (2.8)	40.8 (2.0)	30.5 (2.0)

[a] Units are (μg/g)/(μg/l)^n.
[b] Number of observations.
[c] Calculated based on the isotherm parameters and the organic carbon content of the HAs.
[d] Standard error (σ).

SYSTAT Inc.) was utilized for fitting Eq. (1) to the logarithmically transformed equilibrium sorption data. The resulting model parameters, along with their standard errors (σ) and the number of observations involved in their determinations, are presented in Table 3. For better comparison of the sorption properties among the six HA samples and between the $Na_4P_2O_7$ extracted and NaOH extracted HAs, a single-point organic carbon normalized distribution coefficient, K_{OC} (l/g_{OC}), was calculated based on the following equation

$$K_{OC} = K_F C_e^{n-1}/f_{OC} \tag{2}$$

where f_{OC} is the organic carbon fraction of the HA (Table 1). The calculated K_{OC} values at $C_e/S_W =$ 0.005, 0.05, and 0.5 are also listed in Table 3; S_W (1120 μg/l) is the aqueous solubility of phenanthrene at 22 °C (Gauthier et al., 1987; Grathwohl, 1990). The standard deviations of the K_{OC} values were also calculated from the standard deviations of the isotherm parameters with an error propagation procedure and with assumptions that C_e had 5% of standard deviation and TOC had no deviation. The results are listed in Table 3. The phenanthrene sorption isotherms measured for Chelsea-N and Chelsea-P are shown in Fig. 3 as examples of the sorption data and the fitting of Eq. (1) to the data.

According to Table 3, the Freundlich equation can adequately fit the sorption isotherm data obtained in this study. A major feature of the data listed in Table 3 is that the phenanthrene sorption isotherms measured for all six HA samples are nonlinear, with n values ranging from 0.777 to 0.874. This is consistent with prior studies using phenanthrene as the sorbate and HAs extracted from soils and sediments as the sorbents (Huang and Weber, 1997; Gunasekara et al., 2003; Xiao et al., 2004; Kang and Xing, 2005). It should be noted that the phenanthrene isotherms were measured at solution pH 2 in order to limit dissolution of HAs. This condition may have caused more nonlinear isotherms than at pH 7. Under the same pH condition, the difference of the isotherm nonlinearity among different HA sorbents is possibly related to the difference in the physicochemical properties of the sorbents.

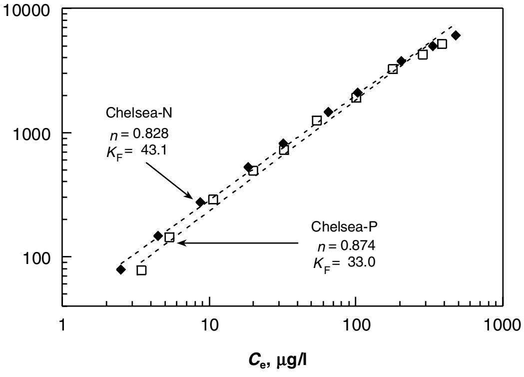

Fig. 3. Phenanthrene sorption isotherms measured for the two HA samples extracted with NaOH (Chelsea-N) and $Na_4P_2O_7$ (Chelsea-P) from Chelsea soil.

Another feature of the data summarized in Table 3 is that the HA extracted with $Na_4P_2O_7$ exhibits more linear sorption isotherm than the HA extracted from the same soil with NaOH. For instance, the n value of the isotherm measured for Chelsea-P is 0.874 ± 0.026, which is statistically greater than that (0.828 ± 0.019) for Chelsea-N. According to Tables 1 and 2, the O/C atomic ratio and POC content of Chelsea-P are 0.56% and 48.4%, respectively, which are respectively greater than 0.46% and 43.5% for Chelsea-N. Apparently, the more linear sorption isotherm exhibited by Chelsea-P is fundamentally related to its more polar matrix than Chelsea-N.

The more nonlinear sorption isotherm exhibited by the NaOH extracted HA may result from its aliphatic carbon moieties. As discussed above, the NaOH extracted HA may contain higher content of aliphatic carbon than its respective $Na_4P_2O_7$ extracted HA. The aliphatic carbon moiety could form highly hydrophobic local region within HA matrix that could not be swollen by water. Sorption of phenanthrene into this moiety could follow a complex dissolution process with a limiting site capacity. Because of its hydrophobic nature, its sites are readily saturated at relatively low C_e, resulting in a more nonlinear isotherm for the sorbent.

Among the three pairs of HA samples, the HAs extracted from GZ1 have statistically insignificant difference between the n values whereas the HAs extracted from Chelsea soil have the largest and statistically significant difference of the n values. Note that the amounts of HAs extracted from GZ1 soil with the two extraction methods were only 13.7% different whereas for Chelsea soil they were 22.6% different. This indicates that large variations in HA extractability and properties present among different soils may have varied effects on sorption isotherm nonlinearities. In fact, for the six isotherms measured for the HAs extracted from different soils, there is no clear correlation between the isotherm parameter n and the O/C atomic ratio or POC content that were observed in prior studies (e.g., Weber and Huang, 1996).

The data listed in Table 3 showed that, for the two HAs extracted from GZ1 or GZ2, there is no significant difference in the K_{OC} values at the lowest C_e/S_W (0.005). However, for the two HAs extracted from Chelsea, a statistically significant difference in the K_{OC} at C_e/S_W 0.005 exists. It is likely because the two HAs from either GZ1 or GZ2 only have very small difference in chemical compositions and functionality (especially the aliphatic carbons). As discussed above, the two HAs extracted from Chelsea had the largest difference in aliphatic carbon contents, and therefore, they exhibited the largest difference in the K_{OC} at the lowest C_e/S_W level as the sorption sites at the aliphatic moieties is likely saturated the low C_e level. We attempted to correlate the K_{OC} data at given C_e/S_W levels with the sorbent properties such as POC, aromaticity, O/H and H/C atomic ratio, but no good correlation was found. It is likely due to the fact that only three soil samples were examined in this study. A large set of soils should be studied in the future in order to establish such correlations.

According to Table 3, the calculated K_{OC} value for a given HA decreases as a function of C_e/S_W level due to isotherm nonlinearity. The K_{OC} value is approximately halved when the C_e is increased from 5.6 to 560 μg/l. It should be noted that even in recent publications (e.g., Accardi-Dey and Gschwend, 2002, 2003), sorption of PAHs on HAs has been considered as a simple partitioning process and that a single K_{OC} value was assigned for the sorption of a given HOC solute on HAs. The results of this study and others (Xing and Pignatello, 1997; LeBoeuf and Weber, 2000b) indicate that the sorption isotherms are nonlinear and that the linear model is inadequate to quantify the nonlinear sorption phenomena exhibited by HAs.

4. Conclusions

This study indicated that the HA fractions extracted from the same soil with NaOH and $Na_4P_2O_7$ were chemically different. The NaOH extracted HA had lower content of polar functional group and lower O/C atomic ratio than the $Na_4P_2O_7$ extracted HA. It is because, being a stronger base, NaOH can extract more HA from a soil than $Na_4P_2O_7$ via base-catalyzed hydrolysis reactions, resulting higher content of aliphatic carbons in the bulk HA materials.

The measured phenanthrene sorption isotherms for the six HAs were all nonlinear. Between the two HAs extracted from the same soil sample, the NaOH-extracted HA exhibited more nonlinear isotherm than the $Na_4P_2O_7$-extracted HA. The nonlinear sorption exhibited by the HAs should not be ignored in predicting the fate and transport of HOCs in the aquatic systems. Further analysis of the sorption data did not result in good correlation between sorption properties with the chemical and functional compositions of the HAs. Future studies that include a large set of samples of HAs extracted from soils are recommended for establishing such correlations.

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