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Effect of organic fractions on sorption properties of organic pollutants in sediments

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Abstract: Humic substrates are a major fraction of sediment organic matters, and the sorption of hydrophobic organic chemicals by humic substrates influences their behavior and fate in sediment. In this paper, organic matters were divided into non-humic substrates and humic substrates. Non-humic substrates include acid leaching fraction, acid extracted fraction, and lipid; humic substrates were fractionated into Ca-binding-FA (fulvic acid), Ca-binding-HA (humic acid), oxide-FA, oxide-HA, and humin. To study the effect of organic fractions on sorption properties, sorption kinetic and equilibrium sorption experiments of phenanthrene and pentachlorophenol (PCP) in five sediments were carried out. The results showed that the contents of acid leaching fraction and oxide-binding-HA were the main fractions to affect the sorption rate constant, and for the sorption capacity of phenanthrene, humin was the major fraction, followed by oxide-binding-HA, oxide-binding-FA, and so on. While for PCP, the factors of influence on sorption capacity were mainly CEC, Ca-binding-FA, and Ca-binding-HA.

Keywords: organic fraction; sediment; sorption; phenanthrene; pentachlorophenol (PCP)

Introduction

Sorption to natural solids is an underlying process affecting the transport, degradation, and biological activity of organic chemicals in the environment. Sorption equilibrium and kinetic properties are very important factors affecting natural attenuation in the water body (Pignatello, 1996). There are extensive literature related to sorption processes; however, very limited information exists on the effects of naturally occurring heterogeneous sediment organic matter on sorption properties (Karapanagioti, 1999).

Karickhoff *et al.* (Karickhoff, 1979) published one of the early and important reports on hydrophobic organic chemicals. Their research suggested instantaneous equilibrium and linear isotherms demonstrating partition-like sorption. The organic content normalized distribution coefficient (K_{oc}) was found to depend on chemical hydrophobicity as quantified via the chemical's octanol-water partition coefficient (K_{ow}) and solubility. Sorption capacity was observed to be a function of soil organic carbon content and K_{oc} (Chiou, 1998).

More recent work has revealed that in addition to the organic content the nature of the organic matter has a significant impact on sorption capacity and nonlinearity (Grathwohl, 1990; Weber, 1996; Xing, 1997). A correlation between K_{oc} and O/H ratios illustrated the importance of soil organic matter quality on sorption capacity (Grathwohl, 1990; Huang, 1997). Rügner *et al.* (Rügner, 1999) used an empirical correlation that predicts long term sorption kinetics of organic pollutants in heterogeneous aquifer materials based on intraparticle porosity and equilibrium sorption capacity of homogeneous constituents of the sample. They also used empirical correlation (i.e. Archie's Law) to determine the mechanisms in sorption experiments.

Sediment organic matter, as mentioned above, relates almost exclusively to humic substrates. Humic substrates are complex mixtures of polyelectrolytes produced by the profound biotic and abiotic alteration/degradation of plant- and animal-derived organic matter. The interaction of humic substrates with other natural, nonhumic substrates may have a significant impact upon the properties of these materials, particularly their sorption characteristics. Lipids are operationally defined as organic geochemicals that are soluble in nonpolar organic solvents such as hexane, benzene, or chloroform (Bergman, 1963).

Polycyclic aromatic hydrocarbon (PAH) is one kind of persistent organic pollutants in environment. Through air deposit and runoff, PAH was sorbed into sediments and accumulated gradually. Therefore sediment was the sink of pollutants in natural water. Especially, when outside sources were cut out, pollutants in aqueous phase may mainly come from sediments (Bremle, 1995). So the characters of transformation and transferences of pollutants in sediment and water were the key factor to control the harmful effect on biology. Pentachlorophenol (PCP), as a pesticide, herbicide, and antiseptic, was once used

worldwide. As anaerobic biodegradation of chlorophenols is relatively slow, they are preserved in sediments for a very long time. The highest concentration of PCP in aquatic environments usually has been found in river and lake sediments (Maatela, 1990; Abrahamsson, 1991). Therefore, the toxicity of PCP to aquatic organisms will remain for a very long time.

The objectives of this study were to examine the effects of heterogeneous organic matter on sorption equilibrium and kinetic parameters in five sediments. Sorption properties were explained based on organic matter characterization.

1 Materials and methods

1.1 Sediment

Five sediments sampled in the south of China were used in this study. The sediments were obtained with a clam sampler from West Lake, Yongjiang River, Dianchi Lake, Taihu Lake and Qiantang River. The sampling depth was 1—10 cm from the surface sediment. The sampled fresh sediments were air dried, crushed, mixed thoroughly and sieved through a 0.25 mm mesh, and stored in a refrigerator at 4°C. The pH of the sediments was determined with a glass combination electrode (sediment: water ratio of 1:2.5 w:v), the cation exchangeable capacity (CEC) was measured by the $\text{NH}_4\text{Cl}-\text{C}_2\text{H}_5\text{OH}$ method, and the organic matter content by the $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation method (Shore, 1995).

1.2 Organic fractions extracted and contents measured

The organic fractions of sediment were isolated and content measured by adaptations of the most popular alkaline extraction techniques (Malcolm, 1990; IHSS, 2001). The isolation procedure was briefly: the dried and sieved sediment was placed in a cellulose thimble and allowed to stand in reagent H_2O for 24 h to wet the organic matter. After wetting, the excess water was allowed to drain out of the thimble and the sediment was extracted with the mixture solvent made of benzene and ethanol (3:1, v:v) for 72 h in a Soxhlet apparatus to collect lipid organic matter. The solvent was changed after the first 24 h of extraction because of the large quantity of water removed from the sediment during the extraction. After the extraction procedure, the lipid organic content in the solvent was determined by weight upon evaporation of the mixture solvent. The residual sediment was air-dried and sieved through 0.25 mm mesh. 10 g of residual sediment was placed in glass vial and 300 ml of 0.05 mol/L H_2SO_4 were dropped into decompose carbonates and to remove alkaline-earth metals. The supernatant was collected with separating by centrifugation (10 min at 3600 r/min) to measure the organic carbon content with Apollo 9000 TOC Monitor. This fraction was called acid dissolved portion. 100 ml of 0.1 mol/L NaOH were added to the solid residue to extract humic acid (HA) and fulvic acid (FA). The suspended material was shaken intermittently at room temperature for 24 h. The FA and HA in the supernatant were separated from the solid residues by centrifugation. This procedure was repeated until the supernatant became colorless. Suspended clays were removed from the

supernatant by flocculation using 0.1 mol/L KOH. KCl was then added to make the system 0.3 mol/L with respect to potassium, and the suspended solids were removed by centrifugation after letting the solution stand for 4 h. The clear solution was acidified with concentrated HCl to pH 2, to induce the precipitation of the Ca-binding-HA, and the precipitated solid was then separated by centrifugation. The organic fraction in supernatant was Ca-binding-FA. After that, the solid sediment residues were extracted with 1 mol/L H₂SO₄ and 0.1 mol/L

NaOH alternatively till the supernatant of 0.1 mol/L NaOH extracted became colorless. The residue organic fraction in solid sediment phase was humin. The fraction extracted with 1mol/L H₂SO₄ was called acid extracted portion. The solution extracted with 0.1 mol/L NaOH was acidified with concentrated HCl to pH 2 to induce the precipitation. The organic fraction in precipitate was called oxide-binding-HA and the fraction in supernatant was called oxide-binding-FA. Abbreviations of organic fractions are presented in Table 1.

Table 1 Basic physico-chemical properties of sediment samples^a

Parameters ^b	West Lake	Yongjiang River	Dianchi Lake	Taihu Lake	Qiantang River
pH	7.35	8.15	8.08	6.50	7.90
CEC, cmol/kg	58.39 ± 0.31	14.03 ± 0.05	36.52 ± 0.09	21.40 ± 0.98	5.435 ± 0.815
OM, g/kg	365.7 ± 4.3	11.16 ± 0.25	106.8 ± 1.5	14.93 ± 0.30	5.428 ± 0.257
Lipid, g/kg	15.52 ± 0.036	4.642 ± 0.789	7.056 ± 1.028	3.606 ± 0.037	2.070 ± 0.740
AD, g/kg	2.287 ± 0.032	0.674 ± 0.012	1.408 ± 0.011	0.682 ± 0.025	0.377 ± 0.005
AE, g/kg	3.194 ± 0.261	1.027 ± 0.046	0.900 ± 0.092	0.542 ± 0.074	0.468 ± 0.198
Ca-HA, g/kg	91.15 ± 5.184	0.286 ± 0.037	18.69 ± 1.413	1.678 ± 0.916	0.053 ± 0.024
Ca-FA, g/kg	48.20 ± 3.704	1.162 ± 0.019	16.56 ± 0.961	2.758 ± 0.975	0.666 ± 0.030
O-HA, g/kg	26.27 ± 0.489	1.491 ± 0.065	11.36 ± 0.994	0.840 ± 0.404	0.500 ± 0.115
O-FA, g/kg	18.55 ± 0.864	1.125 ± 0.187	4.364 ± 0.501	0.874 ± 0.114	0.716 ± 0.055
Humin, g/kg	160.5 ± 7.375	0.748 ± 1.281	44.83 ± 2.88	3.951 ± 1.090	0.577 ± 0.648

Notes: ^a The content is given on moisture-free basis; ^b CEC = cation exchangeable capacity, OM = organic matter, AD = acid dissolved fraction, AE = acid extracted fraction, Ca-HA = Ca-binding-humic acid, Ca-FA = Ca-binding-fulvic acid, O-HA = oxide-binding-humic acid, O-FA = oxide-binding-fulvic acid

The extracted FA solution was firstly passed through a column of XAD-8 resin and eluted with 0.1 mol/L NaOH. The precipitated HA was purified by shaking for 24 h at room temperature, with 200 ml of a dilute solution of HCl-HF (0.1 mol/L HCl; 0.3 mol/L HF), and then was dissolved in 0.1 mol/L NaOH. Finally, the FA and HA dissolved in 0.1 mol/L NaOH solution passed through a H⁺-interchanged column to remove the Na⁺, and subsequently were freeze-dried to solid sample, respectively. The elemental content (C, H, N) of the HA and FA solid samples were determined using an EA-1112 elemental analyzer, and their ash contents were determined by weight after combustion at 750°C for 4 h. Oxygen content was calculated by the difference. Fourier-transform infrared (FTIR) spectra of HA and FA samples were obtained from KBr pellets (1 to 2 mg sample, 200 mg KBr) on a FTIR 8900 infrared spectrophotometer (Shimadzu, Japan).

1.3 Model chemicals

Phenanthrene and pentachlorophenol (PCP) were used as the model chemicals in this study. Phenanthrene (C₁₄H₁₀) is a three ring polycyclic aromatic hydrocarbon with (a) molecular weight: 178 g/mol, (b) solubility: 1.29 μg/ml at 25°C, (c) Henry's Law Constant: 2.6 × 10⁻⁵ (atm · m³)/mol, and (d) logK_{ow}: 4.6 (Karapanagioti, 2000). Phenanthrene was chosen because of its high hydrophobicity (K_{ow}), low volatility (Henry's Law Constant), and simplicity of analysis. PCP (C₆Cl₅OH) is a pesticide with a molecular weight of 266.5 g/mol, solubility of 3.0 μg/ml at 25°C, and logK_{ow} of 4.4 (De Paolis, 1997). Although the use of PCP has decreased during recent years, it still causes environmental problems at many locations, for instance, contaminating sediments and even groundwater. Understanding the behavior of PCP requires an assessment of the processes influencing its fate, transport and bioavailability in sediments.

In this experiment, model chemicals were dissolved in methanol to form a 100 μg/ml stock solution. Before use, the stock solution was diluted to a set concentration with an electrolyte matrix, which was composed of 1 mmol/L CaCl₂, 0.1 mmol/L MgCl₂, and 0.5 mmol/L Na₂B₄O₇ · 10H₂O. Sodium azide (NaN₃) was added at a concentration of 200 μg/ml to minimize bacterial growth and biodegradation during batch experiments. All the glass vials containing sediments and model chemical solutions were shaken in darkness until the measurement time was reached. For each batch experiment, blank samples were prepared and monitored (i.e., model chemical solutions without sediment). The blank samples did not indicate any significant degradation or sorptive losses on the glassware during the course of the experiment. Maximum phenanthrene and PCP losses in these blank samples reached 1.936% and 2.597%, respectively, within the experiment period, so the missing model chemicals from the solution phase can be considered safely sorbed into the sediment solid phase. Aqueous phase model chemical concentrations were determined with the Agilent 1100 series HPLC system. The HPLC system was equipped with a vacuum degasser,

quaternary pump, autosampler, column compartment, diode array and multiple wavelength detectors (DAD), and a hypersil reversed-phase ODS-C-18 column made by the Agilent Company, U. S. A. The conditions for measuring phenanthrene were: a mobile phase made of purified water (10%) and methanol (90%) at a flow 1.00 ml/min, signal wavelength of 250 nm with 20 nm bandwidth, and a reference wavelength of 330 nm with 50 nm bandwidth. The conditions for measuring PCP were: a mobile phase made of 1% acetic acid (10%) and methanol (90%) at a flow rate of 1.00 ml/min, signal wavelength of 220 nm with 20 nm bandwidth, and a reference wavelength of 300 nm with 50 nm bandwidth. The model chemicals concentrations were quantified with an external standard method.

1.4 Sorption kinetic experiments

All sorption kinetic experiments were conducted in triplicate in 35 ml glass vials. Sediment was taken and 30 ml model chemical solution was added into the vial. Different solid-to-water ratios were used due to the sediment samples having different sorption capacities (i.e. to achieve sufficient sorption so that it could be easily quantified while keeping the aqueous phase concentration above the detection limit). For the sediments from West Lake, Yongjiang River, Dianchi Lake, Taihu Lake, and Qiantang River, the solid-to-water ratios were 0.2:30, 1.0:30, 0.2:30, 1.0:30, 1.0:30 for phenanthrene, and 0.5:30, 2.0:30, 0.5:30, 1.0:30, 2.0:30 (wt:wt) for PCP respectively. The vials were stored at 20°C in the dark and shaken at 200 r/min. The model chemical concentration in solution phase was measured at various time intervals. Before analysis the samples were centrifuged at constant temperature of 20°C at 3000 r/min for 20 min. When the model chemical concentration in solution phase kept constant, the end point of the experiment reached.

1.5 Equilibrium sorption experiments

All equilibrium sorption experiments were conducted in triplicate in 35 ml glass vials. The sediment samples were mixed with variable model chemical concentrations and the vials were sealed and shaken for 24 h in the dark at constant temperature (20°C). An incubation period of 24 h was chosen after a preliminary kinetic experiment was conducted for 72 h. The data revealed a concentration plateau after 24 h. Different solid-to-water ratios mentioned above were used. At the end of incubation period, model chemical concentration was measured by HPLC.

1.6 Data analysis

In the sorption experiments, the mass of model chemical, which disappeared from the solution phase at the end of the sorption experiment, was assumed to adsorb onto sediment:

$$q_e = (C_0 - C_e) \frac{V_w}{W_s} \quad (1)$$

The sorption distribution coefficient K_d can be described by

$$K_d = q_e / C_e \quad (2)$$

Where q_e is the mass of solute adsorbed onto the sediment (μg/g),

C_0 is the initial concentration of solute ($\mu\text{g/ml}$), C_e is the solution-phase solute concentration at the end of the sorption experiment ($\mu\text{g/ml}$), V_w is the volume of solution (ml), and W_s is the mass of the sediment (g).

The organic carbon content normalized distribution coefficient K_{oc} is described by:

$$K_{oc} = K_d / f_{oc}, \quad (3)$$

where f_{oc} is the organic carbon content of the sediment.

To gain information about the kinetics of model chemicals in sediment solid phase, the initial concentration in water phase was set at c_{10} ($\mu\text{g/ml}$), correspondingly the initial sorbed amount in sediment phase was zero. x ($\mu\text{g/ml}$) model chemical disappeared into sediment solid phase after t min. When the equilibrium of sorption reached, i. e., $t \rightarrow \infty$, the concentration decreased from water phase was x_∞ ($\mu\text{g/ml}$), thus the equilibrium coefficient K_e was calculated by,

$$K_e = \frac{k_1}{k_{-1}} = \frac{x_\infty}{c_{10} - x_\infty}, \quad (4)$$

where k_1 is the sorption rate constant, k_{-1} is the desorption rate constant. The sorption rate was expressed by,

$$\frac{dc_w}{dt} = \frac{d(c_{10} - x)}{dt} = -k_1(c_{10} - x) + k_{-1}x. \quad (5)$$

After integrating, the sorption and desorption rate constant can be calculated based on the experiment data.

2 Results and discussion

2.1 Sediment analysis

The properties of sediment samples such as pH, cation exchangeable capacity (CEC), and content of organic fractions are presented in Table 1. It is obviously shown that the sediment properties

were different. The property values varied in a large range for different sediments, such as organic matters content of West Lake sediment was 365.7 ± 4.3 g/kg, while that of Qiantang sediment was 5.428 ± 0.257 g/kg.

The elemental composition and atomic ratio of humic fractions are shown in Table 2. The H/C-ratios and O/C-ratios of O-FA were higher than the other fractions. This indicated a high content of carboxylic groups and carbohydrates in O-FA (Christensen, 1998). The carbon content of Ca-HA was lower than that of Ca-FA, and O-FA lower than O-HA for West Lake, Yongjiang River, and Taihu Lake sediment, respectively. As for the atomic ratio, the H/C-ratio of Ca-HA was higher than that of Ca-FA, and O-FA higher than O-HA for sediment in West Lake and Yongjiang River, respectively, while in Taihu Lake sediment, the H/C-ratio of the four fractions has low difference. The trend of O/C-ratio was Ca-HA higher than Ca-FA, O-FA higher than O-HA, for all the three sediments. That suggested the property of Ca-HA was similar to O-FA, Ca-FA to O-HA.

FTIR spectra of all fractions are shown in Fig. 1. The interpretation of the absorption bands was the same as described in the literature (Kaiser, 1997). In all spectra the absorbance peaks at 3500–3300, 2940–2850, 1650–1600, 1540 and 1100–1040 cm^{-1} appeared. The strong absorbance peaks of HA at 3300, 2900, 1650 and 1030 cm^{-1} indicated that $-\text{CH}_3$, $-\text{CH}_2$, $-\text{COOH}$, $-\text{C}=\text{O}$, $-\text{C}=\text{C}$ (Morrison, 1983; Kaiser, 1997) in fatty acids were the main functional structures. The strong absorbance peaks of FA were at 3420, 2900, 1650, 1540, and 1120 cm^{-1} . In addition, the absorbance peaks at 3420, 1650, and 1120 cm^{-1} were very strong, indicating that there was more $-\text{COOH}$ content in FA (Candler, 1988).

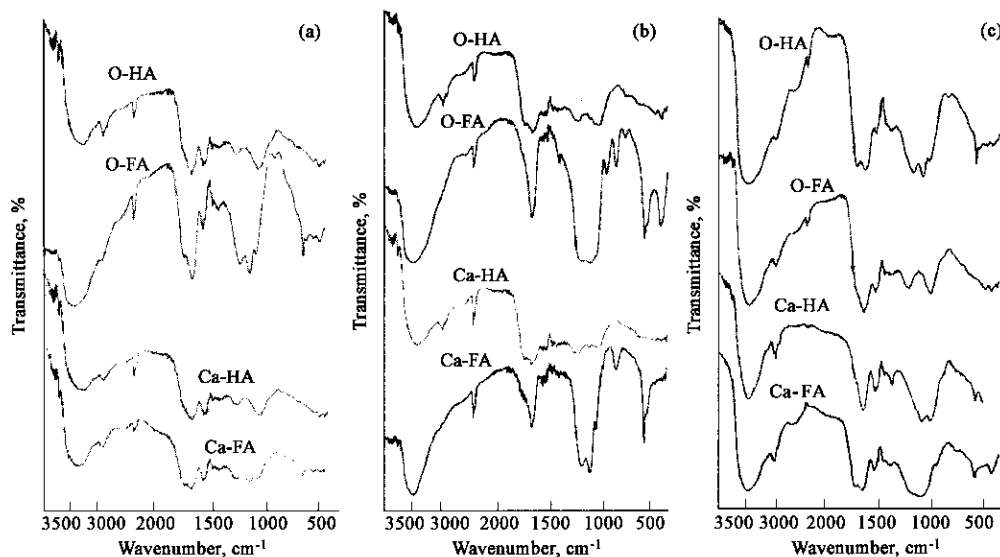


Fig. 1 The FTIR spectra of humic substances from sediments
a. Taihu Lake; b. West Lake; c. Yongjiang River; abbreviations of fractions are explained in Table 1

Table 2 Elemental compositions of fractions of humic substrates from sediments^a

Humic fraction ^b	Elemental composition, wt%				Atomic ratio		
	C	H	N	O	H/C	O/C	
West Lake	Ca-HA	48.89	6.38	3.57	41.15	1.57	0.63
	Ca-FA	55.52	4.81	4.06	35.61	1.04	0.48
	O-HA	51.66	5.24	3.88	39.22	1.21	0.57
	O-FA	45.13	5.27	7.17	42.43	1.40	0.70
Yongjiang River	Ca-HA	54.37	7.00	8.66	29.97	1.54	0.41
	Ca-FA	56.74	6.29	6.36	30.61	1.33	0.40
	O-HA	56.54	5.03	6.59	31.84	1.07	0.42
	O-FA	50.00	4.59	4.68	40.72	1.10	0.61
Taihu Lake	Ca-HA	53.05	5.19	7.96	33.80	1.18	0.48
	Ca-FA	61.67	6.30	8.43	23.59	1.23	0.29
	O-HA	61.43	7.29	8.64	22.63	1.42	0.28
	O-FA	45.03	4.95	5.37	44.65	1.32	0.74

Notes: ^a Elemental composition is given on ash- and moisture-free basis;

^b abbreviations of organic fractions are presented in Table 1

Combining the elemental composition with the FTIR spectra, the conclusion can be drawn that there was more $-\text{COOH}$ and $-\text{OH}$ in Ca-HA and O-FA, and more unsaturated fatty acids and phenyls in Ca-FA and O-HA.

2.2 Sorption rate of model chemicals in sediments

Fig. 2 is the results of sorption capacity versus sorption time of phenanthrene and PCP in five sediments. Model chemical concentration in aqueous phase decreased rapidly versus sorption time. After 4 h, aqueous phase concentration almost reached equilibrium. After 24 h sorption, the aqueous phase concentration reached constant. So the sorption capacity after 24 h was taken as total capacity during the sorption course. Most sediment can get to 95% of total sorption capacity within 2 h, and 98% within 4 h.

The calculated sorption rate constants based on Eq. (5) are presented in Table 3. For each sediment, the sorption rate constant of phenanthrene is bigger than that of PCP, suggesting that it was easier for phenanthrene to reach sorption equilibrium than PCP. That was caused by the different hydrophobic between phenanthrene and PCP. Phenanthrene had lower solubility ($1.29 \mu\text{g/ml}$) than PCP ($3.0 \mu\text{g/ml}$) at 25°C .

Table 3 Kinetic sorption properties of phenanthrene and PCP on sediments

Sediment		West Lake	Yongjiang River	Dianchi Lake	Taihu Lake	Qiantang River
Phenanthrene	k_1^a, min^{-1}	0.0517	0.0146	0.0361	0.0174	0.0050
	$k_{-1}^b, \text{min}^{-1}$	0.0016	0.0092	0.0047	0.0116	0.0050
	K_e^c	32.17	1.578	7.651	1.500	1.000
	$K_d^d, \text{ml/g}$	2252	78.88	535.6	105.0	30.02
	$\log K_{oc}^e$	4.02	4.08	3.94	4.08	3.98
PCP	k_1, min^{-1}	0.0288	0.0039	0.01544	0.006051	0.000876
	k_{-1}, min^{-1}	0.01479	0.01364	0.01870	0.01440	0.003934
	K_e	1.9448	0.2892	0.8256	0.4202	0.2225
	$K_d, \text{ml/g}$	136.1	8.676	57.79	12.60	4.45
	$\log K_{oc}$	2.81	3.12	2.97	3.16	3.15

Notes: ^a Sorption rate constant; ^b desorption rate constant; ^c sorption equilibrium coefficient; ^d sorption distribution coefficient; ^e distribution coefficient normalized to organic carbon content

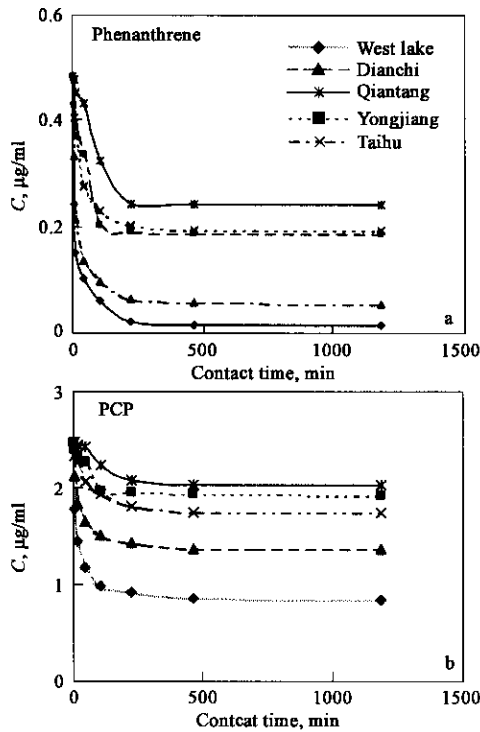


Fig.2 Sorption rate curves of phenanthrene and PCP on five sediments

2.3 Equilibrium sorption isotherms

Fig.3 is the results of phenanthrene and PCP equilibrium sorption on five sediments. The results showed the difference of sorption characters and sorption capacity of five sediments. The results of modeling sorption isotherms of phenanthrene and PCP (Table 4) showed the sediments in Yongjiang River, Dianchi Lake, Taihu Lake and Qiantang River were fit the linear equation very well while the sediment in West Lake could be modeling with Freundlich Equation as $q_e = 10^{3.7011} C_e^{1.2644}$, $r^2 = 0.9537$ ($n = 7$). The trend of sorption capacity of sediment (K_d) was that: West Lake > Dianchi Lake > Taihu Lake > Yongjiang River > Qiantang River. While the K_{oc} values for different sediments varied in a small range ($\log K_{oc}$ for phenanthrene in 3.94—4.08, for PCP in 2.81—3.16). That showed the sorption capacity of phenanthrene and PCP on sediments markedly depended on organic matters content.

2.4 Effect of properties of sediment on sorption rate

The results of correlation analysis between sorption rate constants and organic fractions contents are presented in Table 5. The results showed that the sorption rate constant was positive correlated to organic fractions content significantly at 0.05 level. The contents of acid dissolved fraction (AD) and oxide-binding-HA (O-HA) were the main fractions to affect the sorption rate constants of phenanthrene and PCP, while O-FA and acid extraction(AE) fractions had less effect on the rate constants. The sorption rate reflected the affinity of chemical with sediment, the stronger affinity, the bigger rate constant. That suggested the AD and O-HA fractions have more affinity for phenanthrene and PCP than the other fractions. CEC was a major portion to affect the sorption rate of PCP, because high CEC reflected the sediment had more activated functional groups. Ionized PCP molecular can be adsorbed through chemical interactions with sediment particle.

Table 4 Modeling equation of sorption isotherms of phenanthrene and PCP in sediments

Sediment	PCP		Phenanthrene	
	Modeling equation	r^2	Modeling equation	r^2
West Lake	$q = 163.3 C_e + 6.287$	0.9128	$q = 10^{3.7011} C_e^{1.2644}$	0.9537
Yongjiang River	$q = 15.38 C_e + 0.7284$	0.9899	$q = 92.64 C_e + 0.2425$	0.9967
Dianchi Lake	$q = 64.63 C_e + 1.326$	0.9518	$q = 1896 C_e + 4.200$	0.9701
Taihu Lake	$q = 10.89 C_e + 0.7625$	0.9692	$q = 155.4 C_e + 1.581$	0.9913
Qiantang River	$q = 20.65 C_e - 0.3218$	0.9764	$q = 30.89 C_e + 0.4519$	0.9777

Table 5 The relationships between the sorption rate and the properties of sediments

Fraction ^a	Phenanthrene		PCP	
	r	P	r	P
AD	0.989**	0.001	0.998**	0.000
Ca-FA	0.940**	0.009	0.981**	0.002
Ca-HA	0.895*	0.020	0.952**	0.006
AE	0.847*	0.035	0.903*	0.018
O-FA	0.894*	0.021	0.950**	0.007
O-HA	0.957**	0.005	0.987**	0.001
Humin	0.921*	0.013	0.969**	0.003
Lipid	0.947**	0.007	0.976**	0.002
CEC	0.994**	0.000	0.993**	0.000

Notes: * Significant at 0.05 level (1-tailed); ** significant at 0.01 level; ^a abbreviations of organic fractions are presented in Table 1

2.5 Effect of properties of sediment on sorption distribution coefficient

The results of correlation analysis between sorption distribution coefficient (K_d) and organic fractions content are presented in Table 6. The results showed that the correlation coefficients of all fractions except for AD and AE fractions were bigger, significant at 0.01 level. The sorption distribution coefficient was determined by organic carbon content in sediment, so the high correlation coefficient was found between distribution coefficient (K_d) and organic fractions content. It suggested that partition process was the main way for phenanthrene and PCP adsorbed into sediments (Chiou, 1998). For phenanthrene sorption, the contents of humin, oxide-binding-HA, and oxide-binding-FA were the major fractions; for PCP sorption, CEC, Ca-binding-FA, and Ca-binding-HA were the major fractions, which was caused by the different interaction force between phenanthrene and PCP with sediment. For

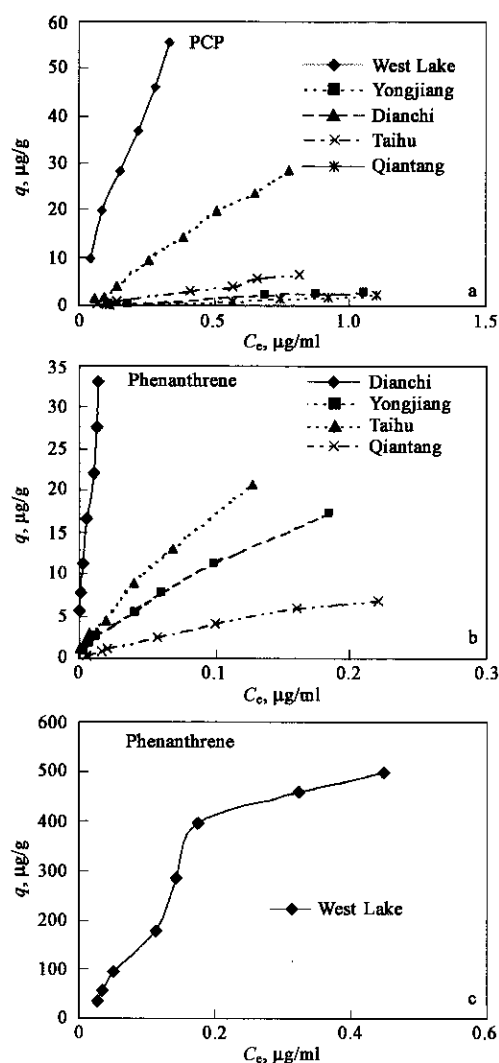


Fig.3 Sorption isotherms of phenanthrene and PCP on sediments. q is the amount of phenanthrene or PCP sorbed per amount of sediment, C_e is the equilibrium phenanthrene or PCP concentration. The symbols denote experimental data points

phenanthrene sorption, partitioning was the main course, while for PCP, in addition to partitioning, chemical adsorption was an important course, too (Pignatello, 1996).

Table 6 The relationships between the sorption distribution coefficient (K_d) and the properties of sediments

Fraction ^a	Phenanthrene		PCP	
	r	P	r	P
AD	0.836**	0.005	0.592	0.061
Ca-FA	0.951**	0.000	0.935**	0.000
Ca-HA	0.779*	0.011	0.916**	0.001
AE	0.892**	0.001	0.679*	0.032
O-FA	0.972**	0.000	0.853**	0.004
O-HA	0.965**	0.000	0.903**	0.001
Humins	0.986**	0.000	0.881**	0.002
Lipid	0.964**	0.000	0.874**	0.002
CEC	0.868**	0.003	0.937**	0.000
OM	0.972**	0.000	0.933**	0.000

Notes: * Significant at 0.05 level(1-tailed); ** significant at 0.01 level;
^a abbreviations of organic fractions are presented in Table 1

3 Conclusions

Our results showed that it was a fast course for phenanthrene and

PCP sorption into sediments. Sorption could reach equilibrium in 24 h for the both chemicals. Among the fractions in sediment, acid dissolved fraction, Ca-binding-FA, and Oxide-binding-HA were the main fractions to affect the sorption rate for phenanthrene, and cation exchangeable capacity(CEC) and acid dissolved fractions were the main fractions for PCP. The sorption isotherms of PCP on the five sediments were linear, and the sorption isotherms of phenanthrene on four sediments except for West Lake were linear. The isotherm on West Lake sediment can be described with Freundlich equation. The average sorption distribution coefficient($\log K_{oc}$) of phenanthrene was 4.02, and PCP was 3.04, respectively. The humin and CEC were the main factors affecting the adsorption processes, the former for phenanthrene as the interaction, and the later for PCP as its chemical adsorption.

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