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Sorption of PAHs to Colloid Dispersions of Humic Substances in Water

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Humic substances (HSs) make up a large portion of the organic matter found in natural environments with a typical concentration in natural waters ranging from 0.1 to 200 mg L^{-1} organic carbon (Kinniburgh et al., 1996). HSs can complicate many environmental pollutants, such as polycyclic aromatic hydrocarbons (PAHs) (LeBoeuf and Weber, 2000; Yang et al., 2001; Sabbah et al., 2004; Bercaru et al., 2006; Mashayekhi et al., 2006; Ping et al., 2006). PAHs were selected because of their planar configuration as opposed to other bulky, three-dimensional molecules (for instance, different pesticides). PAHs are expected to be less sterically hindered in their partition interaction with humic materials, but also more efficient at interacting with the π electrons associated with the humic material's aromatic moieties. In the present work, we present the adsorption behavior of eight PAHs on HSs: benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene, indeno[1,2,3-cd]pyrene, benzo[jk]fluorene (fluoranthene), benzo[a]anthracene, and dibenzo [ah]anthracene. It is important to know the distribution of PAHs in the aqueous environment (free and bound to HSs), which affects their stability and persistence. PAHs are a concern because some of them can cause cancers in humans and are harmful to fish and other aquatic life (U.S. Public Health Service, 1990). The objective of this study was to evaluate the sorption of PAHs to colloid dispersion of humic substances (HSs) in water.

Materials and Methods

HSs used in this study were isolated from soil (Swift, 1996). Briefly, 1 kg of 2 mm (sieved), air dried soil was reacted with 10 L of 0.1 M HCl for 1 h. Approximately 1 L of H_2O was added to the soil mass and the resulting slurry was allowed to incubate for 30 min, after which the pH of the slurry was adjusted to 7 with the addition of 1 M NaOH. This was followed by the addition of a sufficient quantity of 0.1 M NaOH (done under N_2) to bring the total volume of the solution phase to 10 L; the resulting slurry was stirred under N_2. After 24 h, the alkaline slurry was filtered through glass wool, and the particle-free filtrate was acidified to a pH value of 1, with the addition of 6 M HCl. This solution was then allowed to settle, was centrifuged, and the supernatant was discarded. The sediment was washed with distilled water, was repeatedly centrifuged, and the supernatant was discarded.

The solid residue after centrifugation was then suspended in a mixture of 0.1 M HCl and 0.3 M HF, to remove mineral particles. This treatment was repeated until the ash content was reduced < 2%. Afterward, humic acid dispersion in distilled water was dialyzed against water to remove chlorides, and resulting humic acids were lyophilized. The composition of the HSs used was determined by CNH

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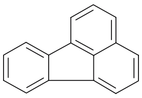
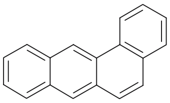
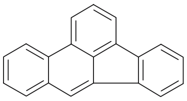
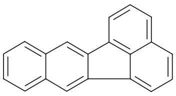
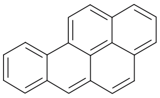
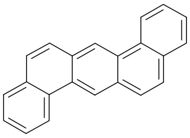
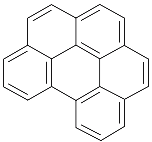
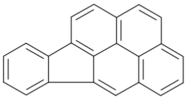
Table 1 Freundlich constants, soliubility, and log P for studied PAHs

PAH	pm g mol^{-L}	S mol L^{-1}	Log P	[PAHs] ng L^{-1}	[HSs] mg L^{-1}	Log K	N	R^2
 benzo[jk]fluorene	202	6.3 x 10^{-7}	5.2 ± 0.2	10–40	58	–1.27	1.11	0.8965
					115	–0.98	1.1	0.9102
					174	–0.92	1.01	0.9202
					232	-	-	-
					463	-	-	-
 benzo[a]anthracene	228	6.4 x 10^{-8}	5.9 ± 0.2	2–12	58	–1.16	1.35	0.9141
					115	–0.8	1.27	0.9953
					174	–0.63	1.25	0.9899
					232	–0.59	1.23	0.9976
					463	–0.52	1.25	0.9482
 benzo[b]fluoranthene	252	2.0 x 10^{-8}	6.4 ± 0.2	10–50	58	–0.54	1.27	0.9899
					115	–0.3	1.15	0.9963
					174	–0.11	1.14	0.9909
					232	0.01	1.15	0.993
					463	0.22	0.92	0.9829
 benzo[k]fluoranthene	252	1.3 x 10^{-8}	6.4 ± 0.2	2–11	58	–0.97	1.52	0.9459
					115	–0.67	1.45	0.9954
					174	–0.42	1.35	0.9912
					232	–0.3	1.49	0.9938
					463	–0.24	1.28	0.804
 benzo[a]pyrene	252	7.4 x 10^{-9}	6.4 ± 0.2	4–22	58	–0.64	1.43	0.9849
					115	–0.18	1.25	0.9888
					174	–0.04	1.23	0.994
					232	0.05	1.22	0.9979
					463	0.3	1.16	0.9877
 dibenzo[ah]anthracene	276	2.5 x 10^{-9}	7.1 ± 0.2	9–44	58	–0.24	1.39	0.9952
					115	0.12	1.27	0.9879
					174	-	-	-
					232	0.2	1.2	0.988
					463	0.67	1.1	0.9838
 benzo[ghi]perylene	278	5.9 x 10^{-9}	6.9 ± 0.2	30–130	58	0.38	1.3	0.9956
					115	0.65	1.23	0.988
					174	0.67	1.25	0.9422
					232	0.83	1.22	0.9975
					463	1.51	0.99	0.989
 Indeno[1,2,3-cd]pyrene	278	6.8 x 10^{-9}	6.9 ± 0.2	30–160	58	1.29	1.32	0.9988
					115	1.7	1.2	0.9948
					174	1.83	1.19	0.9972
					232	1.82	1.2	0.9941
					463	1.82	1.25	0.9797

elemental analysis using a Fisons EA-1108 elemental analyzer (518 g kg^{-1} C, 40 g kg^{-1} N, and 40 g kg^{-1} H). Its ash content was 61 g kg^{-1}. The functional group distribution (Swift, 1996) was: total acidity 5.99 mol kg^{-1}, COOH groups 3.30 mol kg^{-1}, and total OH groups 2.91 mol kg^{-1}.

Determination of PAHs in different media has been extensively reported in the literature (García-Falcón et al., 2004a, b; Rey-Salgueiro et al., 2004; García-Falcón et al., 2005; García-Falcón et al., 2006). The quantity of PAHs adsorbed was determined by difference between the initial

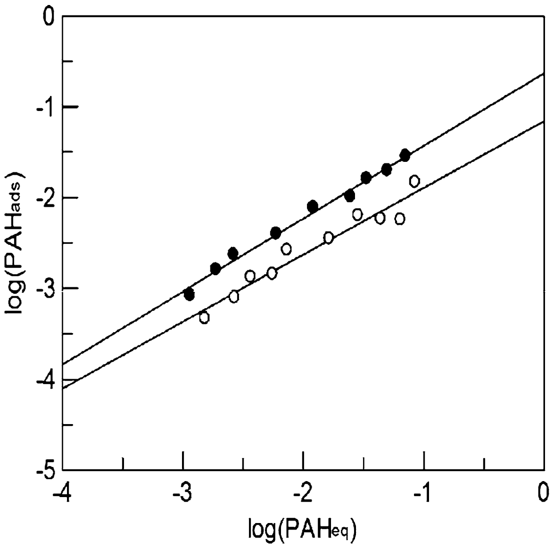


Fig. 1 Linearized Freundlich isotherm of (o) Benzo [ghi] perylene and (•) Benzo [a] pyrene to HSs ([HSs]=58 mg L^{-1})

concentration added to the humic substance-water mix and the final equilibrium concentration in the aqueous phase (free PAHs). Stir bar sorptive extraction (SBSE) was used for the extraction of free PAHs from the aqueous phase (García-Falcón et al., 2004c). PAHs concentrations were measured by fluorescence spectroscopy with a Jasco, Tokyo FP 750 spectrophotometer.

Sorption kinetics of PAHs to HSs were monitored to know whether the time necessary for equilibrium or constant sorption could be lower than 24 h. Kinetics were measured by duplicate in water at a low (58 mg L^{-1}) and a high (464 mg L^{-1}) concentration of HSs. After the addition of different amounts of PAHs to HSs dispersions in water, samples were stirred at 25°C, and free PAHs were determined after 15 min, 1, 6, and 24 h following the extraction procedure proposed in the literature (García-Falcón et al., 2004c).

PAHs adsorption was determined by the use of a batch equilibrium technique. Different quantities of PAHs (shown in Table 1) were added to 40 ml of water containing 58, 116, 174, 232, and 464 mg L^{-1} of HSs, respectively. The mixture was shaken at 25°C throughout the equilibration period, after which it was used to measure the free PAHs, as described previously (García-Falcón et al., 2004c).

Experimental data were fitted tno the Freundlich's equation (Eq. 1):

$$(PAH_{ads}) = K_F \times \left(PAH_{eq}\right)^{1/n} \tag{1}$$

where PAH_{ads} is the PAHs amount adsorbed per mass unit, K_F and n are the Freundlich's coefficients, and PAH_{eq} is the PAHs amount in equilibrium per volume unit.

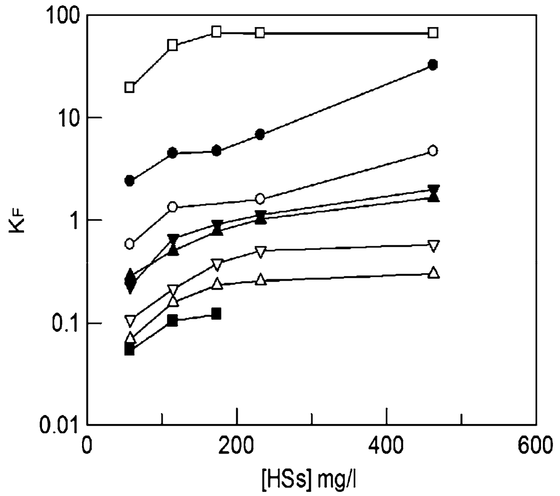


Fig. 2 Influence of HSs concentration upon Freundlich's constant, K$_F$. (○) benzo [jk] fluorine, (●) benzo [a] anthracene, (□) benzo [b] fluoranthene (■) benzo [k] fluoranthene, (△) benzo [a] pyrene (▲) dibenzo [ah] anthracene, (▽) benzo [ghi] perylene, and (▼) indeno [1,2,3-cd] pyrene

Equation 1 can be linearized as:

$$\log\left(PAH_{ads}\right) = \log K_F + \frac{1}{n}\log\left(PAH_{eq}\right) \tag{2}$$

Results and Discussion

At low HSs concentrations (58 mg L^{-1}), the lower molecular weight PAHs, with three to four benzenic rings, reach sorption equilibrium in just 15 min, whereas those of higher molecular weight, with five or more benzenic rings, need at least 6 h (already equivalent at the data obtained after 24 h). At high concentration of HSs (464 mg L^{-1}), the equilibrium is reached at 15 min for all PAHs.

The adsorption isotherms have been obtained for five HSs concentrations ([HS]=58 mg L^{-1}, 115 mg L^{-1}, 174 mg L^{-1}, 232 mg L^{-1} and 463 mg L^{-1} respectively) at five different quantities of PAHs (ranges are given in Table 1).

Figure 1 shows, as example the satisfactory fit of linearized Freundlich equation (Eq. 2) for two different PAH (Benzo[ghi]perylene and Benzo[a]pyrene) at [HSs]=58 mg L^{-1}. Freundlich's coefficients are listed in Table 1.

The value of K$_F$ increases on increasing the concentration of HSs (Fig. 2). A leveling-off was found in the dependence of K$_F$ with HSs, and at high HSs concentration, the value remains constant. The value of n decreases slightly on increasing organic matter concentration. This fact implies that no saturation of HSs surface by PAHs was found. The driving forces for PAHs adsorption would be (1) hydrophobic interactions and (2) solubility. This assumption is proved by taking into account the relation-

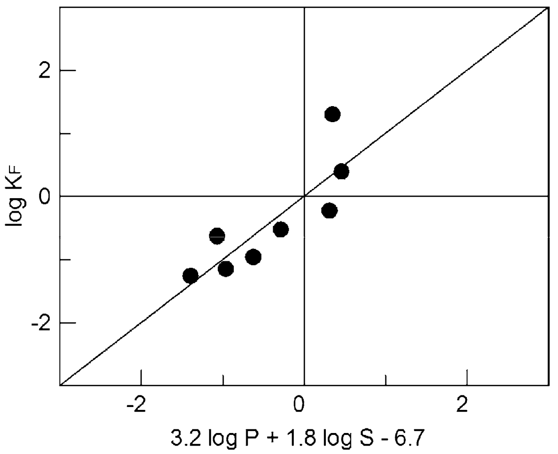


Fig. 3 Multiparametric relationship between log K_F, log P, and log S

ship among K_F and log P and log S. A multiparametric relationship has been obtained with the following equation:

$$\log K_F = \alpha \log P + \beta \log S + \gamma \quad (3)$$

The values for α, β, and γ were $\alpha = 3.2$, $\beta = 1.8$, and $\gamma = -6.7$ (r = 0.8831). Multiparametric fit is shown in Figure 3. Equation 3 can be used to estimate PAHs adsorption to HSs from PAHs octanol-water partition coefficients and water solubilities, which can be measured by conventional methods. Such a multiparametric relationship among Freundlich's constant, logP, and solubility of PAHs suggest that the physicochemical properties of both humic materials and organic solutes are important in controlling the speciation of nonpolar and planar aromatic contaminants in water.

To summarize, the parameters controlling sorption of polycyclic aromatic hydrocarbons (PAHs) to humic substances (HSs) in water were estimated based on the Freundlich equation. Both steric hindrance and molecular interactions between the PAHs and the HSs' aromatic structures may play an important role in their binding reactions. These hydrophobic PAHs will partition into the hydrophobic interiors of the humic micelle-like aggregates. The key factors controlling the distribution of PAHs in colloidal dispersions of HSs in water, and therefore their stability-persistence and possible bioavailability in the natural aqueous environments, were proved to be the hydrophobicity and the water solubility of PAHs. Adsorption of the different PAHs to HSs can be modeled in terms of both of these driving factors.

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