

PARTITION OF POLYCYCLIC AROMATIC HYDROCARBONS IN WATER-SEDIMENT SYSTEM CONTAINING HUMIC ACID

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ABSTRACT

Natural dissolved organic matter (DOM) in the water environment has the potential to enhance the solubility of PAHs into the water phase, resulting in strong influence on their environmental fate. In this study, Nordic aquatic humic acid (HA) was used as a DOM. The effect of HA on the partition behaviour of PAHs in the sediment water system was examined by comparing the partition of three PAHs: Phenanthrene (Phe), Pyrene (Pyr), and Benzo[a]pyrene (BaP) in the water sediment system. An isotherm partition of PAHs between water and sediment was studied. The presence of HA in the sediment water system shifted the sediment water partition of PAHs to the water phase. The more hydrophobic the PAH was, the stronger the effect of HA on K_d was. Observed K_{DOM} fitted well the linear free energy relationship. A three-phase partitioning model was established and successfully described the partition behavior of PAHs in water-sediment system.

Keywords: PAHs, DOM, three-phase partitioning model.

1. INTRODUCTION

The partition of hydrophobic organic contaminants in the environment is of fundamental

importance in predicting their fate and transport. Several studies showed that the affinity of a contaminant to sediment is well correlated both with hydrophobicity of the contaminant and with the organic content of the sediment. Another potentially important, but less obvious, sorbent for organic contaminants is naturally occurred dissolved organic matter (DOM). DOM and sedimentary organic matter in natural environments consist of a large variety of organic molecules which are often referred to humic substances. Humic substances have amphiphilic characteristics because they contain both hydrophilic and hydrophobic moieties in their structures [1]. As a result, humic substances have been shown to form stable complexes with several hydrophobic contaminants such as PAHs.

Many studies have revealed that hydrophobic contaminants such as PAHs have strong affinity to organic matter in soil or sediments [2, 3] and to DOM [4]. Recently, the binding of contaminants to DOM has been measured quantitatively. The binding of PAHs to dissolved humic substances has also been shown to greatly reduce the availability of the PAHs for uptake and bioaccumulation by aquatic organisms. Partition of PAHs between water and DOM has been investigated by several researchers [4, 5]. However, not so much work has focused on the partition of PAHs in the water-sediment system with the presence of humic substances as the DOM. In this study, the effect of humic substances on the partition behavior of PAHs in the sediment water system is elucidated by investigating the partition of Phenanthrene (Phe), Pyrene (Pyr), and Benzo[a]pyrene (BaP) between water and sediment in the presence of the humic acid.

2. EXPERIMENT AND METHODS

Material: Nordic Aquatic humic acid (HA) was purchased from the International Humic Substances Society, Phenanthrene, Pyrene and Benzo[a]Pyrene were purchased from Wako Pure Chemicals. The sediments used for sorption experiment were taken from the Sai River in Kanazawa City, Japan. Sediment was air dried and sieved into three different size fractions and the smallest fraction (<75 μm) was used.

Sorption isotherm: A stock solution of HA was prepared by dissolving 74.5 mg HA powder in 0.1M NaOH (5 mL) and diluted with distilled water to 20mL (2000mg-C/L). Approximately 100 mg of sediment was added into a 50mL screw-capped glass centrifuge tube. A volume of 40 mL of 30 mg-C/L HA water was added into the each tube followed by the addition of 20 μL of PAH/methanol stock solutions with concentration ranging from 10 to 80 mg/L at five levels. Finally, NaN_3 was added to minimize biological activity. Then, the tubes were sealed tightly with

screw cap with Teflon liners. All tubes were hand-shaken for a few minutes to make them uniformly mixed. The tubes were horizontally placed in a shaker oscillating at 150 rpm for up to 7 days at 20 °C. After shaking, the mixtures in each tube were filtered through 0.5 µm pore glass fiber filter. The filtrates were extracted twice with 15 mL of hexane. The extracts were combined together and concentrated by rotary evaporation to 1mL in preparation for the analysis by HPLC with fluorescence detection. The mobile phase was a mixture of HPLC-grade acetonitrile and distilled water of 75 % acetonitrile 25 % water for Phe, 85 % acetonitrile, 15 % water for Pyr and 100 % acetonitrile for BaP. The flow rate of mobile phase was kept at 1.0 mL/min. The fluorescence condition for detecting Phe, Pyr and BaP was 280nm/340nm, 331nm/392nm and 264nm/407nm (excitation/emission) respectively.

The amount sorbed to sediment of Phe, Pyr and BaP were determined by the difference of total initial mass and the determined mass in water.

Dissolved humic acid concentration was quantified by absorbance measurement at 280nm by the spectro-photometer (BioSpec 1600 Shimazu).

3. RESULTS AND DISCUSSION

3.1. Partition of PAHs between water and sediment with, without the presence of HA

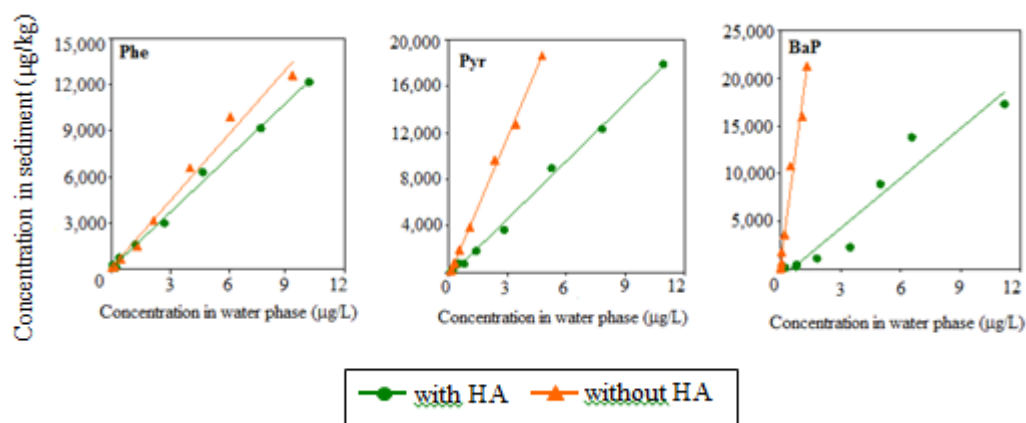


Figure. 1. Partition isotherm of PAHs in water-sediment system with and without the presence of HA.

The partition of Phe, Pyr and BaP between water and sediment with and without the presence of HA at the level of 30mg-C/L are presented in Fig.1. The presence of HA in the water-sediment system shifted the sediment water partition of all three PAHs to the water phase.

This is consistent with the findings of Chiou *et al.* [6] that HA enhanced the elution of Pyr from activated carbon into aqueous solution. For all of the three investigated PAHs, the isotherm is essentially linear in both cases of with and without HA in water-sediment system. Partition coefficient values K_d were estimated from the linear correlation between concentration of PAHs in sediment and concentration of PAHs in water. In the following, K_d^* is used for the apparent partition coefficient in the presence of HA.

Table 1 summarizes the sediment water partition coefficients K_d and K_d^* and the ratio of K_d/K_d^* . K_d/K_d^* ratios increased from Phe to BaP, as the hydrophobicity of PAHs increases. In other words, the more hydrophobic the PAHs, the larger the difference between K_d^* and K_d . These results indicate that the effect of dissolved HA on the partition between sediment

and water of PAHs depends on the hydrophobicity of PAHs. HA has amphiphilic characteristic and their molecular contain hydrophobic moieties. Therefore, PAHs with higher hydrophobicity would have higher affinity to HA resulting in more diffusing to water.

Table 1. Sediment water partition coefficients of PAHs.

PAHs	$\log K_{ow}$	$\log K_d$		K_d/K_d^*
	[7]	With HA	Without HA	ratio
Phe	4.57	3.13±0.29	3.20±0.21	1.02
Pyr	5.22	3.58±0.13	3.94±0.08	1.10
BaP	6.50	2.54±0.13	4.22±0.45	1.66

3.2. Effect of HA concentration on the partition of PAH between water and sediment

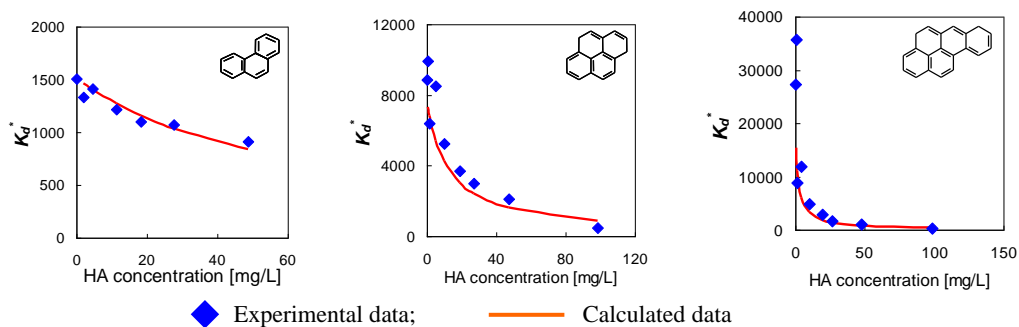


Figure 2. Relationship between HA concentration and K_d^* .

The effect of HA concentration on the partition of PAHs in water-sediment system was investigated by altering the concentration of HA in water-sediment system. The amount of PAHs adding to the system was kept constant at the initial concentration of 10 mg/L in water phase, the concentrations of HA in water phase were changed from 0 to 100 mg-C/L.

As the concentration of dissolved HA increases, the apparent partition coefficient K_d^* decreases as shown in Fig. 2. Among the three investigated PAHs, Phe exhibited the smallest decrease of K_d^* and BaA exhibited the largest decrease of K_d^* . Also, it is noted that for Pyr and BaP, a very steep decrease of K_d^* was observed near the HA concentration of 0. This indicates that even at very low concentration of HA, its effect on the partition of PAHs between water and sediment can be significant and are not negligible, for PAHs having 4 or more rings. For three investigated PAHs, the more ring of PAHs has, the stronger the effect of HA on partition characteristic of PAHs on sediment was.

3.3. Adsorption of HA on sediment

As an organic matter group, HA is expected to be adsorbed on sediment. This can affect the partition of the DOM-water-suspended solids/sediment system, but has not been paid so much attention. We measured the HA in the water and calculated the amount of adsorption of HA to the sediment based on mass balance. The adsorption of HA in the sediment is fitted with the linear isotherm, and the relationship between concentration of HA in water and sediment was described as Eq. 1.

$$C_{HA}^{Sed} = K_{ads} C_{HA}^{Wat} \quad (1)$$

where K_{ads} represents the experimental adsorption coefficient of HA, C_{HA}^{Wat} is the concentration of HA dissolved in water phase [kg/L], C_{HA}^{Sed} is the concentration of HA adsorb to the sediment [kg/kg].

3.4. Three phase model

3.4.1. The model

Most of the current models used in risk assessment describe the behavior of substances in the aquatic environment with two-phase partition between sediment/suspended solids and water. Few studies have focused on the effect of DOM on the partition of organic chemicals in a three phase-system DOM-water-suspended solids/sediment. Mitra *et al.* [7] applied the three-phase to consider the partition of PAHs between particles, colloids, DOC, and freely dissolved phase. The three-phase partitioning was described by the following equation:

$$K_d^* = \frac{K_d}{1 + K_{DOM}[DOM]} \quad (2)$$

where K_d^* is the apparent water sediment sediment water coefficient of partition for PAH in

three-phase system, K_d is sediment water partition without the presence of HA, K_{DOM} is the DOM binding coefficient and [DOM] is the concentration of dissolved organic matter.

In the system of free water, dissolved organic matter and free water, dissolved organic matter has potential to adsorb to particulate matter. In equation 2, Mitra *et al.* [6] did not consider the adsorption of DOM to particulate matter. However, as we have seen in part 3.3, HA certainly adsorbs to sediment. Here we construct a three-phase model taking into account the effects of the sorption of HA to the sediment.

Incorporating the adsorption of DOM to sediment, K_d^* of PAHs in water-sediment system containing HA were calculated as follows ,

$$K_d^* = \frac{C_{solid}}{C_{liquid}} = \frac{C_{PAH}^{Sed} + C_{PAH}^{HA-Sed}}{C_{PAH}^{free} + C_{PAH}^{HA-Wat}} \quad (3)$$

where, K_d^* is apparent sediment water partition in the presence of HA in the system, K_d is sediment water partition without the presence of HA, C_{PAH}^{Sed} is the concentration of PAH in sediment [$\mu\text{g}/\text{kg}$], C_{PAH}^{HA-Sed} is the concentration of PAH associated with HA in sediment [$\mu\text{g}/\text{kg}$], C_{PAH}^{free} is the concentration of free PAH in water [$\mu\text{g}/\text{L}$], C_{PAH}^{HA-Wat} is the concentration of PAHs associated with HA in the water phase [$\mu\text{g}/\text{L}$] and was calculated as

$$C_{PAH}^{HA-Wat} = PAH_{[HA]} C_{HA}^{Wat} \quad (4)$$

where C_{HA}^{Wat} is the concentration of HA dissolved in water phase [kg/L], $PAH_{[HA]}$ is the amount of PAH bound in HA [$\mu\text{g}/\text{kg-HA}$]. The adsorption of HA-PAH on sediment is supposed to be similar to that of an HA molecule [8]. Thus,

$$C_{PAH}^{HA-Sed} = PAH_{[HA]} C_{HA}^{Sed} \quad (5)$$

where C_{HA}^{Sed} is the amount of HA adsorb to the sediment [kg/kg].

Replacing the term C_{PAH}^{HA-Wat} from Eq. 4 and the term C_{PAH}^{HA-Sed} from Eq. 5 to Eq. 3 and rearranging Eq. 1 we get,

$$K_d^* = \frac{\frac{C_{PAH}^{Sed}}{C_{PAH}^{free}} + \frac{PAH_{[HA]} C_{HA}^{Sed}}{C_{PAH}^{free}}}{1 + \frac{PAH_{[HA]} C_{HA}^{Wat}}{C_{PAH}^{free}}} = \frac{K_d + K_{DOM} C_{HA}^{Sed}}{1 + K_{DOM} C_{HA}^{Wat}} \quad (6)$$

$$K_d^* = \frac{K_d + K_{DOM} K_{ads} C_{HA}^{Wat}}{1 + K_{DOM} C_{HA}^{Wat}}; \quad \text{or} \quad K_d^* = \frac{K_d + K_{DOM} K_{ads} [DOM]}{1 + K_{DOM} [DOM]}$$

Equation 6 shows the relationship between apparent sediment water partition in the

presence of dissolved organic matter in system K_d^* and concentration of dissolved organic matter C_{HA}^{Wat} or [DOM].

3.4.2. Partition coefficient K_{DOM}

As can be seen from Eq. 6, the binding coefficient of PAH to DOM, K_{DOM} , plays a major role in determining the apparent partition coefficient K_d^* . K_{DOM} was estimated by re-arranging Eq. 6, and K_{DOM} at different levels of HA can be determined by using the following equation.

Table 2. Estimated K_{DOM} .

$$K_{DOM} = \frac{K_d - 1}{C_{HA}^{Wat} (K_d^* - K_{ads})} \quad (7)$$

Table 2 shows the values of K_{DOM} calculated in this work and estimated K_{DOM} from other studies. We can see that the observed K_{DOM} values were different in case by

	log K_{DOM}		
	Phe	Pyr	BaP
This study	4.34±0.28	4.90±0.13	5.71±0.27
Durjava <i>et al.</i> [9]	4.78	5.55	
Poerschmann <i>et al.</i> [10]	4.01, 3.98	4.47, 4.52	4.90; 5.19
Fukushima <i>et al.</i> [8]		4.90	

case because different organic matter was used in estimating K_{DOM} values, however, most of the reported K_{DOM} is within the range of one order of magnitude.

4. CONCLUSIONS

Partition of Phenanthrene (Phe), Pyrene (Pyr), and Benzo[a]pyrene (BaP) in the sediment water system with the presence of humic acid (HA) was investigated and the effect of HA on the partition was investigated. The presence of dissolved humic acid shifted the equilibrium partition to the water phase, and decreased the apparent sediment water partition coefficient K_d^* . The more hydrophobic the PAHs is, the stronger the effect of HA on the partition was. Also, for Pyr and BaP, the decrease of K_d^* with an increase of HA was steepest near the HA concentration of 0. This suggests even in low concentration, effect of HA is not negligible for PAHs of four or more rings. Three phase model consisting of the water, DOM and the sediment, incorporating the adsorption of DOM to the sediment was constructed. Estimated binding coefficient of PAHs to the humic acid, K_{DOM} , can be regarded as constant for the HA concentration of less than 100 mg/L, and found to be fitted well with the linear free energy relationship. With the estimated K_{DOM} , and the HA adsorption coefficient K_{ads} , the model successfully describes the experimental

relationship between HA concentration and the apparent partition coefficient K_d^*

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