

A Study of PAHs Binding to Humic Acids in Seawater by Solid-Phase Microextraction Technique

Qingling Li, Frank S.C. Lee, Lei Li, Xiaoqin Xu, Xiaoru Wang

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants of major health concern because of their suspected carcinogenic activities. Upon entering the marine environment via atmospheric deposition or land sources, PAHs are distributed among various phases including water, suspended particles, colloidal matter, and sediment. The subject has been extensively studied by environmental scientists in order to gain better understanding on the environmental transport and bioavailability of PAHs. [4]. However, despite the past efforts, our understanding of the phase distributions of PAHs in marine environment remains limited because of the difficulties involved in differentiating and quantifying the concentrations of PAHs which exist in a state of dynamic equilibrium among these different phases. Previous studies have shown that PAHs can bind strongly with dissolved organic carbon (DOC) in aquatic environment. Such binding enhances their apparent solubility, but making them unavailable to partition in water and sediment phases [2]. The content of humic acid in common surface water ranges from 1~5mg/L, and as high as 10mg/L in some waters. Thus, for hydrophobic pollutants such as PAHs, a significant portion of the PAHs could be partitioned into the humic substance phase. In earlier reports using SPE technique, the binding of PAHs [3], pesticides and PCBs [6~8] to natural humic substance were studied. As a followup to these earlier studies, the dual purpose of this study are to: (1) develop and optimize SPME technique for the analysis of PAHs in seawater, and (2) quantify the binding of PAHs to DOM, followed by an examination of the relationship between the two partition coefficients of PAHs: K_{DOM} and K_{ow} (octanol-water partition coefficient).

2. Experimental

Chemicals All PAH standards and perdeuterated PAHs of Acenaphthene- d_{10} , Perylene- d_{12} , and Naphthalene- d_{10} used as internal were purchased commercially from Alfa or Aldrich. Stock solutions of 16 PAHs were prepared in acetone in the concentration range of 84-200mg/L. A stock solution of 16 selected PAHs was prepared. The humic acid standard was purchased from Alfa and dissolved in ultra-pure water at the concentration of 10mg/ml as stock solution.

GC/MS Instrument An Agilent 5890N GC-MS system equipped with a 7683series auto sampler was used for analysis. Chromatographic separation of the 16 PAHs and the three internal standards was accomplished with a HP-5MS capillary column (30m x 0.32 mm I.D., 0.25 mm film thickness). Helium was the carrier gas at a flow-rate of 1.0 ml/min; Sample injection was in the splitless mode with an injection volume of 1 μ l. The GC oven temperature programme was as follows: initial temperature 70°C and then ramped at 5°C/min to 120°C. followed by another ramp of 10°C/min to 300°C, held for 7min. The temperatures of the injection port and the interface with the MS system were set at 250°C and 300°C respectively. For selected ion monitoring (SIM), and for each compound, one ion was chosen for quantification while another ion was for identification. The retention times and quantitative ions for the analytes and I.S. are listed in Table 1.

SPME analysis The SPME device and polydimethylsiloxane fibers (100 μ m film thickness) were purchased from Supelco. Fibres were conditioned in the injection port of a gas chromatography (GC) for 10min at a temperature of 300°C according to the manufacturer's instructions before use.

The operating parameters including fibre-water contact time, size of the sample containers, stirring speed and exposure time has been optimized. Samples of PAH solutions were prepared by ultrapure water (10 ml) spiked with PAH standard (16 compounds) and three internal standards to a concentration of 320 ng/L for each PAH species, which represents the concentration levels to be expected in real water samples. The SPME fiber was entirely immersed in solutions with gentle mixing for an hour. In PAH-humic substance binding experiments, The humic acid solution was added into the PAH solutions to different final DOM concentrations ranged between 0~100 mg/L. The solutions were placed in the dark at 25 °C for 5 days before extraction by SPME as stated above. The analytical

performance of the SPME methods is illustrated in Table 1.

3. Results and Discussion

The difference between the amounts of individual PAHs extractable by SPME before and after the addition of humic acids represents the very portion of PAH species which are bound to the humic substance. Figures 1a through 1d show graphically the dependence of SPME extractable PAHs as a function of humic acids concentration. The data can be used to calculate the partition coefficients of individual PAHs as shown by the equations given in Eq. (1) below.

Eq. (1):

$$K_{DOM,i} = \frac{C_{bound,i}}{C_{free,i}} \times \frac{1}{C_{DOM}} = \frac{C_{total,i} - C_{free,i}}{C_{free,i}} \times \frac{1}{C_{DOM}}$$

$$= \frac{C_{blank,i} - C_{free,i}}{C_{free,i}} \times \frac{1}{C_{DOM}}$$

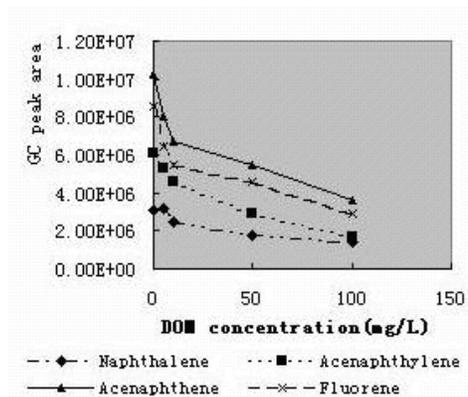
In the above Eq., $C_{free,i}$, $C_{bound,i}$ and $C_{total,i}$ are the concentrations of the analyte i in the truly dissolved state, PAH bound on the DOM phase and the total amount of PAHs ($C_{total,i} = C_{blank,i}$) in the water samples. $K_{DOM,i}$ is the partition coefficient for the analyte i between DOM and water and C_{DOM} is the concentration of DOM in the water sample. As shown in Table 3, the partition coefficients measured in this study for some of the PAHs are in good agreement with the ones reported in the literature. A correlation plot between the two sets of results is shown in Figure 2

There is a obvious trend in increasing DOM sorption capability with increasing hydrophobicity of the PAHs, which can be expressed by their octanol-water partition coefficient (K_{ow}). For several of the 16 PAHs studied, the measured K_{DOM} are in good agreement with those reported in previous investigations [1] as shown in Table 2. The correlation of $\log K_{DOM}$ versus $\log K_{ow}$ ($r^2=0.62$) indicates the dominance of hydrophobic interaction in the sorption of PAHs to DOM.

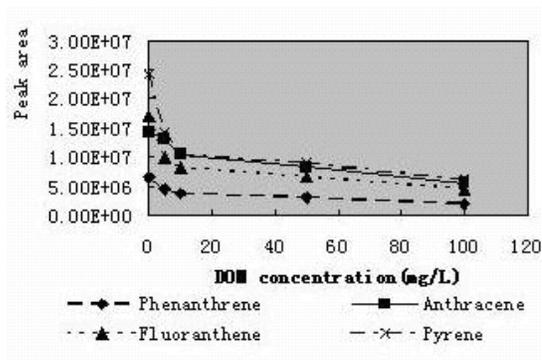
Table 1 Limit of Detection and Linear Dynamic Range of SPME Methods for the Analysis of PAHs

Compounds	R^2	RSD (%)	Recovery (%)	LOD (ng/L)
Naphthalene	0.998	18.8	87.5	0.25
Acenaphthylene	0.998	17.3	88.3	0.66
Acenaphthene	0.999	20	85.4	0.33
Fluorene	0.998	25.3	75.6	0.25
Phenanthrene	0.990	44.5	52.5	0.16
Anthracene	0.999	26.3	89	0.39
Fluoranthene	0.997	33.3	79.5	0.15
Pyrene	0.998	33.3	78.7	0.15
Benzo [a] Anthracene	0.995	25.7	89.2	0.10
Chrysene	0.980	36.2	76.8	0.28
Benzo [b] fluoranthene	0.989	24.1	81.3	0.80
Benzo [k] fluoranthene	0.996	27.6	85.7	1.73
Benzo [a] Pyrene	0.992	22.8	98.3	1.12
Indeno [1,2,3-cd] pyrene	0.988	21.2	97.1	1.00
Dibenzo[a,h]anthracene	0.900	30	138.5	3.47
Benzo [g, h, i] perylene	0.958	32.5	107.4	1.37

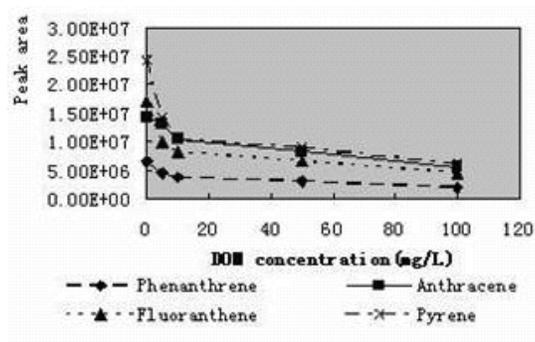
Figure 1 the effect of sample DOC concentration on the extraction of PAHs by SPME. Aqueous solutions containing 0~100mg/L and 5ug/L 16PAHs were extracted by SPME for an contact time of 1 hour



(a)



(b)



(c) (d)

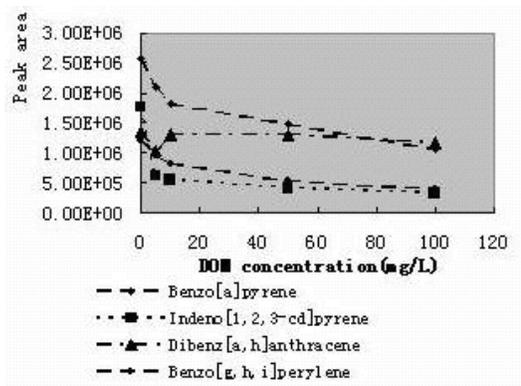


Figure2 LogK_{DOM} vs. log K_{ow} for PAHs (water solutions with DOM concentration of 50ppm)

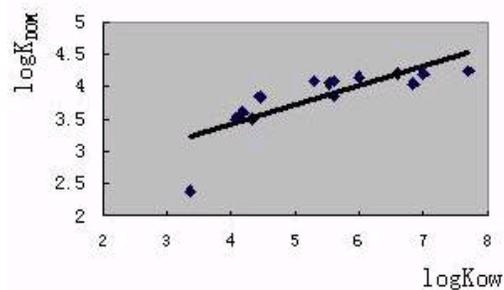


Table2 Experimentally Determined Kow's and Kdom's of different PAHs

sorbate	C _{total} (ug/L)	C _{free} (ug/L)	LogK _{ow}	logK _{DOM}	
				Calculated according to Eq.(1)	From literature [1]
Naphthalene	5.63	5.57	3.36	2.38	2.79
Acenaphthylene	5.96	5.01	4.08	3.5	
Acenaphthene	6.12	5.16	4.32	3.5	
fluorene	6.28	5.04	4.18	3.6	3.58
phenanthrene	11.4	7.62	4.46	3.82	3.98

Anthracene	8.75	5.71	4.45	3.84	4.11
fluoranthene	6.31	2.8	5.53	4.05	4.44
pyrene	11.21	4.46	5.3	4.08	4.53
benza[a]An	5.21	2.09	5.6	4.08	
chrysene	4.61	2.97	5.6	3.85	
Benzo[b] fluoranthene	8.27	1.72	6.6	4.2	
Benzo[k] fluoranthene	5.91	2.68	6.84	4.04	
Benzo[a]Pyrene	6.39	2.02	6	4.14	
Indeno[1,2,3-cd] pyrene	4.05	0.56	7.7	4.24	
1,2:7,8-Dibenzo	7.91	2.55	6	4.13	
Benzo[g,h,i]	3.81	0.83	7	4.19	

4. Conclusion

As a solvent -free technique, SPME is an effective method for the determination of truly dissolved PAHs concentrations in aquatic environment. SPME analyses of PAH solutions with and without the addition of humic acid: can be used to measure the partition coefficient of PAHs in the humic acids vs the water phase. The degree of PAH-binding to humic acid was found to correlate with the hydrophobicity of the PAH species.

Acknowledge

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