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POLYCYCLIC AROMATIC HYDROCARBONs (PAHs) IN RIVER WATER IN KANAZAWA CITY

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Abstract

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are classified as persistent organic pollutants. They exist ubiquitously in various environmental components. In a multi-phases system of water environment, hydrophobic organic contaminants like PAHs exist in several different forms causes PAHs to exhibit a complicated behavior in their distribution and transport. For these reasons, understanding the distribution, behavior and transport of PAHs in water environment is the essential to evaluate the dispersion of the contamination as well as the pollution of PAHs and to manage and to control PAHs level in environment. To understand, evaluate, and control the level of PAHs in water environment as well as propose a prediction for future condition, monitoring is the foundation of creating the data base for clarifying the distribution and analyzing dynamics of PAHs in water environment. We chose the rivers in Kanazawa as a case study to investigate the dynamic of PAHs in water environment. Kanazawa locates in Hokkuriku Area of Japan, and has two main rivers, Asano River and Sai River, flowing into the Sea of Japan. As the Sea of Japan is a relative closed water environment surrounded by the Asian continent, Korea peninsula and Japanese archipelago, it is considered to be vulnerable to the anthropogenic pollution. However, no data are currently available. Monitoring PAHs in these rivers have been carried since Nov. 2004 to create a database of PAHs level in these two rivers. This study focuses on the distribution and partition of PAHs in water, particulate matter and sediment at the estuaries of these two rivers.

Sampling and analysis

Water and surface sediment at the estuaries of the rivers were collected from Asano and Sai Rivers. Sampling period was from Nov. 2004 to Aug. 2006 in monthly frequency except for Mar. and Apr. 2005. SPM was separated from water by filtration through $0.5\mu m$ glass fiber filter. PAHs in water, SPM, sediment were quantified by HPLC/Fluorescence detector. Partition coefficients K_d were calculated as Eq.(1)

$$K_d = \frac{C_s}{C_{aq}}$$
 (1) C_s : PAH concentration in the solid phase (SPM, or sediment) C_{aq} : PAH concentration in the dissolved phase

Result and discussion

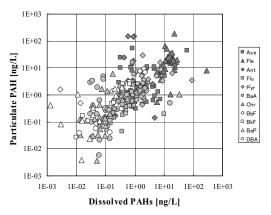
PAHs, like many other hydrophobic organic contaminants, have very low solubility and are rapidly sorbed onto particles. The strong association of PAHs with particle affects their transport and fate in water environment. Particulate-water partition coefficient K_d values are often used to evaluate the distribution of PAHs between dissolved and particulate phase and interpret clearer the predominant existing status of PAHs in river. Table 1 showed the summary of particulate-water partition coefficient K_d in Asano and Sai Rivers. The average of $\log K_d$ of all PAHs was larger than 4 confirming that PAHs strongly associate to particulate matter. The more number of benzene ring in molecular the larger the value of K_d were observed. This finding was consistent with the fact that PAHs in high molecular weight exhibit more hydrophobic characteristics, which results in associating more strongly to particulate mater. All PAHs revealed a wide distribution of partition coefficient, and the low molecular PAHs showed wider variation of K_d than the high molecular PAHs. Three ring PAHs such as fluorence, anthracene have lower hydrophobicity making these PAHs easily exchange between dissolved and particulate phase when there is any change of

environmental condition dissolved organic compound level or suspended solid content. This flexible exchange between dissolved and particle phase of three ring PAHs brings about the wide fluctuation of their partition coefficient values. Even **PAHs** strongly associate particulate matter, like in Asano and Sai River, the amount suspended of solid in the monitoring period was low: SPM concentration of these two rivers varied from 1.2 to 255mg/L with most

Table 1. Water-particulate matter partition coefficient K_d of PAHs in Asano and Sai Rivers

	Log K _{ow}	$-$ Log K_d			
PAHs		Asano River		Sai River	
		A1	A4	S1	S4
Ace	3.70-4.33	4.73	4.68	4.59	4.53
		(2.59-6.50)	(3.13-6.02)	(3.45-5.50)	(3.55-5.94)
Ant	3.45-4.67	4.51	4.63	4.81	4.80
		(1.94-5.91)	(3.52-5.42)	(3.68-5.89)	(3.86-5.44)
Pyr	4.50-6.70	4.34	4.70	4.67	4.83
		(2.26-5.55)	(3.61-5.49)	(3.54-5.67)	(2.70-6.81)
BaA	5.49-7.50	4.74	5.29	4.60	5.39
		(2.79-5.95)	(3.92-6.63)	(2.02-5.93)	(4.53-6.00)
BbF	5.78-6.60	5.23	5.79	5.13	5.59
		(4.74-5.85)	(5.31-6.47)	(3.62-6.06)	(3.59-7.06)
BaP	4.05-8.50	4.95	5.57	5.21	5.81
		(4.12-5.43)	(5.04-6.64)	(3.62-6.06)	(5.01-7.02)
DBA	5.97-7.19	4.66	5.07	5.08	5.44
		(3.51-5.59)	(4.12-5.73)	(4.32-5.84)	(4.78-5.98)

values varied around tens of mg/L, which results in the portion of particulate PAHs in river water as low as the portion of dissolved PAHs as shown in fig.1.



Asano: •Ant, •Pyr; Sai: •Ant, •Pyr

Fig.1. Portion of PAHs in dissolved phase and particulate phase of river water in Asano River

Fig.2. Plots of K_d of anthracene and pyrene vs organic carbon content in sediment collected from Asano and Sai River

In sediment, it is very clearly to see the general tendency in both rivers that K_d values always highest in the small size fraction of sediment (data not shown). In sediment, the role of organic carbon is controlling the ability of association to sediment of hydrophobic contaminant like PAHs. Means *et al.* (1980) [1], Wang *et al.* (2001) [3], and Zhou *et al.* (2003) [2] indicated sediment organic matter as an important phase for the accumulation of PAHs. In our sediments the small size fraction had highest content of organic carbon. To clarify the role of organic carbon in partition of PAHs between water and surface sediment at our site, K_d values for selected PAHs between sediment and water were plotted against sediment organic content TOC as showed in fig.2. The results suggest that correlation existed between K_d and TOC values. The values of K_d were proportional to organic carbon content of sediments, K_d increased with increasing organic carbon content in sediments.

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