Monitoring of Polycyclic Aromatic Hydrocarbons (PAHs) in Water and Sediment of the Rivers in Kanazawa, Japan

Monitoring of Polycyclic Aromatic Hydrocarbons (PAHs) in Water and Sediment of the Rivers in Kanazawa, Japan

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Abstract

Level of 16 US EPA PAHs except for acenaphthylene was monitored monthly in the two main rivers Asano and Sai River of Kanazawa, Japan from November 2004 to October 2005. Concentration of total PAHs during the monitoring time in water, SPM, and surface sediment in Asano River varied from 13.53 to 131.7ng/l, from 0.01 to 33.43μg/kg and from 25.37 to 68.17μg/kg dry weight, and in Sai River was from 10.79 to 122.43ng/l, 0.34 to 52.39 μg/kg, and from 67.68 to 489.11 μg/kg dry weight, respectively. Low molecular weight PAHs were abundant in water, SPM and sediment samples. The amount of high molecular weight PAHs was found higher in sediment than in SPM and water. The seasonal trend of PAHs in water was observed, especially in Asano River: in winter, was observed higher than in summer. PAHs in sediment revealed a complicated distribution between different size fractions. Asano River sediment exhibited a similar affinity to all PAHs: all PAHs tend to bind more in small and medium size fractions. In Sai River sediment higher amount of low molecular weight PAHs bound to small and medium size fraction than to large size fraction while high molecular weight PAHs showed a reverse trend: their concentration in large size fraction was higher than in medium and small size fraction.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are known to be and semi-volatile and persistent organic contaminants, and have been found widely distributed in various environmental components. PAHs are emitted to environment mostly from anthropogenic sources such as the combustions of organic materials, especially fossil fuels [3], road runoff, street dust and petroleum related activities [1]. PAHs are of environmental concern because of their ubiquitousness, persistence in environment [4, 8] and toxic, mutagenic, carcinogenic potentials [5].

Aquatic environment is a multi-phases system in which hydrophobic organic contaminants like PAHs exist in several different forms: dissolved in water, bounded to dissolved organic matter (DOC), adsorbed to suspended particulate matter(SPM), and associated with sediments [9, 11]. This causes PAHs exhibit a very complicated behavior in distribution and transport in aquatic systems.

For the prediction of the changes in PAHs contents in various media in the water environment, constant monitoring of PAHs is very important. Kanazawa is located in Hokkuriku Area of Japan, and it has two main rivers 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, it we lack systematic data of PAHs in rivers flowing into it. The objective of this study is monitoring PAHs in the two main rivers, Asano River and Sai River of Kanazawa City to clarify the distribution and the transport of PAHs in these rivers as well as their contribution to contaminating the Sea of Japan.

2. Materials and method

2.1. Sampling and sample treatment

Water, SPM along the rivers and surface sediment at the down stream of the rivers were collected from the two main rivers of Kanazawa City, Japan. The sampling locations are

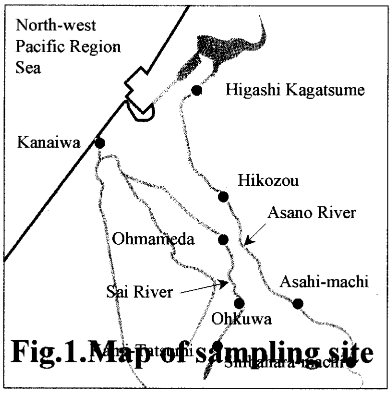

Fig.1.Map of sampling site

indicated in Fig.1. Sampling period was from November 2004 to October 2005 in monthly frequency except for March and April 2005. Water samples (4 litters each) were collected by using glass bottle and kept in the refrigerator at 4°C; surface sediment samples were collected by using grab sampler and stored at –10°C before analysis.

Water samples were filtrated through 0.5μm glass fiber filter (Advantech) to separate SPM. The SPM samples were dried in desiccators and calcium chloride was used as descant [2]. Sediment samples were air-dried and sieved through a series of sieves into three fractions: <75μm, 75-250μm, and >250μm.

2.2. PAHs extraction

Extraction PAHs in water samples: PAHs in water were extracted by using solid phase extraction using C_{18} cartridge (Waters). The flow rate of sample through the cartridge was 10ml/min. PAHs in cartridge were eluted by dichloromethane [6].

Extraction PAH in SPM and sediment samples: PAHs in SPM and sediment samples were extracted by ultrasonic with a mixture of benzene and ethanol 3:1 v/v ratio in 30 min for twice.

2.3. Clean-up

PAHs extracts were clean up by using the silica gel cartridge, and eluted with mixture of hexane: acetone 9:1 (v/v).

2.4. HPLC-Fluorescent Detector

HPLC system consisted of dual pump and degasser (Toso SD 8013), an auto-sampler (Toso AS 8011) (sample volume 20μl), a system controller, a column oven (GL sciences 556), fluorescence detector (Shiseido S1-2). The analytical column and guard column were Inertsil ODS-P (4.6i.d.x250mm, 5μm), GL Sciences and Inertsil ODS-P (4.0i.d.x10mm, 5μm), GL Sciences, respectively, both of which were kept at 20°C. The mobile phase was a mixture of acetonitrile and water set in gradient elution at a flow rate of 1.0ml/min. Sixteen US EPA PAHs except acenaphthylene were detected by fluorescence detector.

3. Results and Discussion

Concentration of PAHs is shown in table 1: grouped by the number of aromatic rings in the molecules. In general, the levels of PAHs in water, SPM, and sediment of the two rivers were low, varied widely. Concentration of PAHs found highest in sediment and lowest in water. It is reasonable because PAHs are the hydrophobic compounds; they have higher ability to bind to particle especially organic fractions than to dissolve in water. In water, SPM as well as sediment, low molecular weight PAHs were found most abundant. Comparing between the two rivers, the level of PAHs in water and SPM in both rivers were similar while the level of PAHs in sediment of Sai River was three or four times higher than that in Asano River. The reason is probably at down stream of Sai River is Kanazawa Port where the environment is contaminated from the activity of the port.

The changing trend of level of PAHs along river during the monitoring period is shown in Fig. 2. While in Asano River had a slightly increase in PAHs concentration was observed when we go down the stream especially from May 2005, the level of PAHs along Sai River seemed quite similar in all sampling stations. The both rivers exhibited a little high concentration of PAHs in winter than summer. Hayakawa et al. reported that the level of PAHs in atmosphere in Kanazawa found higher in winter probably because of the using heater in winter. This perhaps effect on the level of PAHs in water environment. However, this trend wasn't observed well in SPM.

Table 1 Concentration of PAHs in water, SPM and sediment from main rivers of Kanazawa Prefecture

Compound	Asano River		Sai River	
	Range	Mean	Range	Mean
	In Water (ng/l)			
Σ(less than 4 ring PAHs)	11.82-92.18	32.42	8.47-112.84	29.78
Σ(4 ring PAHs)	1.25-59.37	6.48	0.02-45.16	5.05
Σ(more than 4ring PAHs)	n.d.-3.07	0.45	n.d.-12.01	0.80
ΣPAHs	13.53-131.7	39.35	10.79-122.43	35.59
	In SPM (μg/kg)			
Σ(less than 4 ring PAHs)	0.01-32.54	6.03	0.27-40.73	8.73
Σ(4 ring PAHs)	n.d.-3.85	0.56	0.02-8.16	0.89
Σ(more than 4ring PAHs)	n.d.-2.86	0.22	n.d.-10.34	0.51
ΣPAHs	0.01-33.43	7.01	0.34-52.39	10.13
	In Sediment (μg/l)			
Σ(less than 4 ring PAHs)	17.55-47.36	32.29	41.82-414.23	151.78
Σ(4 ring PAHs)	5.58-20.09	9.84	0.04-95.28	34.85
Σ(more than 4ring PAHs)	2.25-36.47	12.90	7.84-80.42	50.92
ΣPAHs	25.37-68.17	55.03	67.68-489.11	237.54

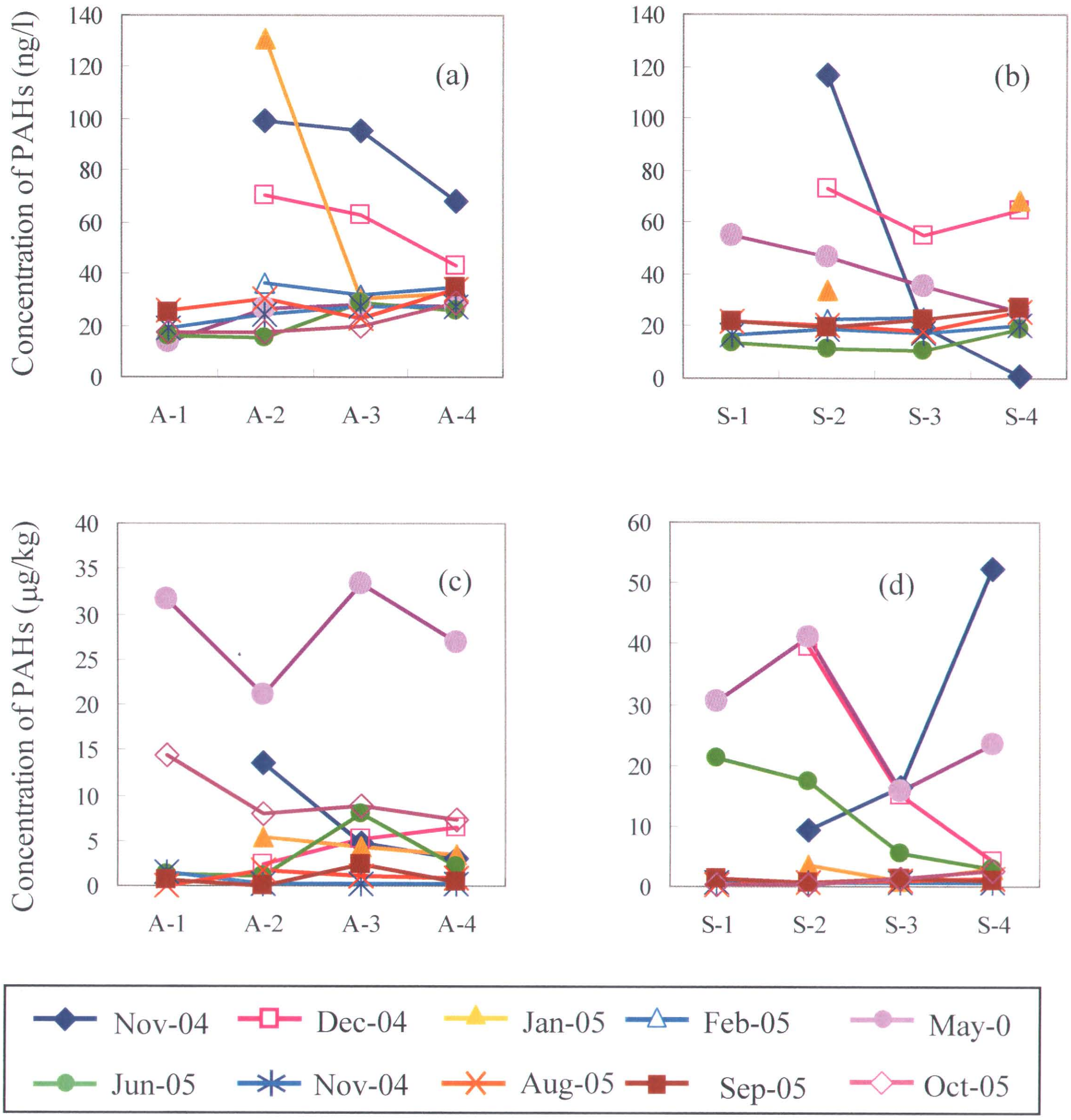

Fig. 2. Variation of total PAHs in water and SPM along the rivers through monitoring time

(a) Water of Asano River ; (b) Water of Sai River;

(c) SPM of Asano River; (d) SPM of Sai River

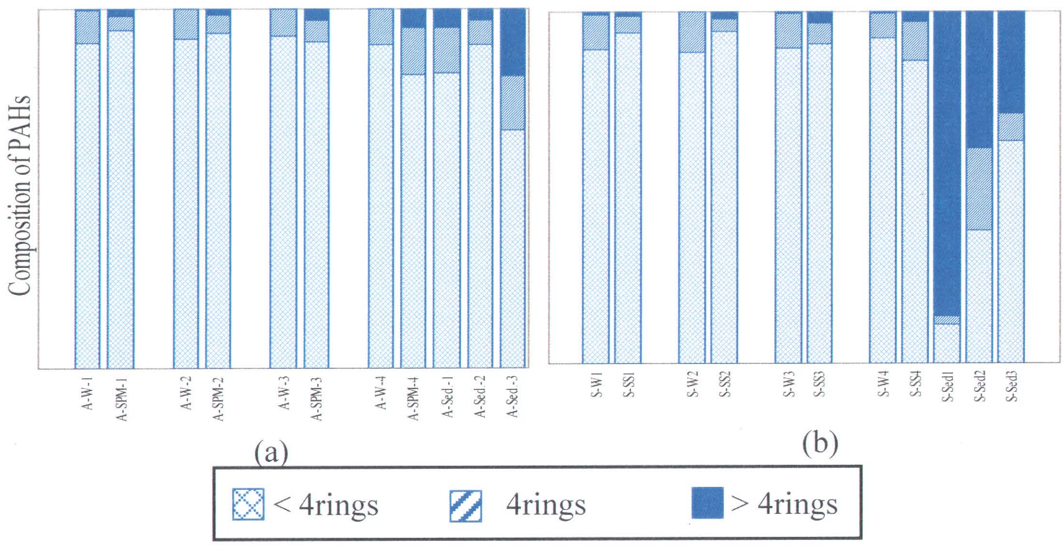

Fig. 3. Pattern of PAHs distribution in water, SPM and sediment of rivers

(a) Asano River (b) Sai River

From Fig.3 we can see the difference of composition of PAHs in water, SPM and sediment. Low molecular weight PAHs tend to bind more to SPM and much more in sediment. This can be seen clearer in Sai River. As a hydrophobic compound PAHs show tendency of binding to organic fraction. Wang *et al.* [10] reported that PAHs found in high concentration in large size fraction (>250μm) and small size fraction (<62μm). The small and large size fractions are enriched organic matter from condensed organic materials and fragmentary plant materials, respectively [7]. For our sediment samples, Sai River sediment is richer in organic matter than Asano River and organic carbon content decrease when increase particle size. The concentration of PAHs in different size fraction was proportional to the content of organic carbon in sediment.

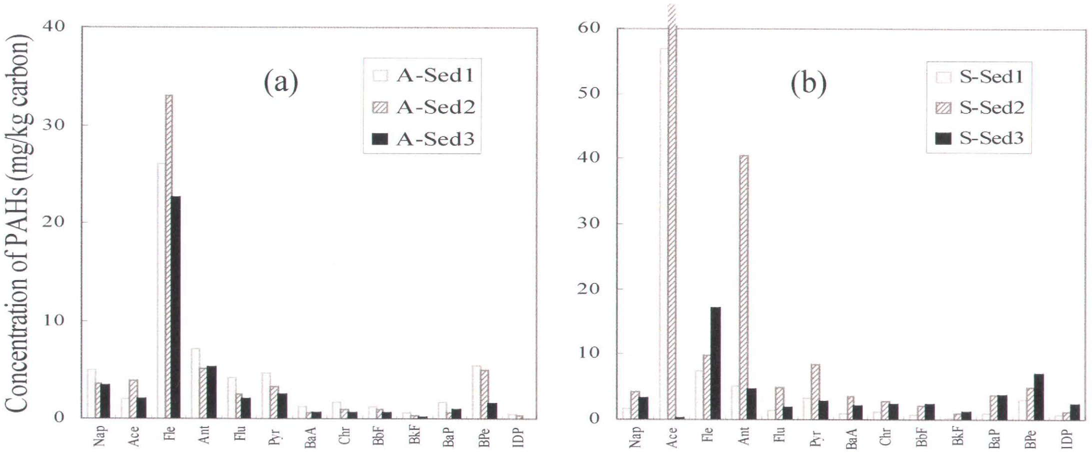

Fig. 4. Amount of PAHs bound to organic matter of different size fraction in sediment

(a) Asano River (b) Sai River

To clarify the effect of organic matter on the concentration of PAHs in sediment the amount of PAHs associated with organic matter in different size fraction were calculated and shown in Fig.4. It can be seen that the organic matter in different size fraction showed different affinity to PAHs, and in the same particle matrix different PAHs express different binding ability. Asano River sediment showed a similar affinity to all PAHs: amount of PAHs associated to in small and medium size fractions was higher than to large size fraction. In case of Sai River sediment higher amount of low molecular weight PAHs bound to small and medium size fraction than to large size fraction while high molecular weight PAHs show a reverse trend: their concentration in large size fraction was higher than in medium and small size fraction.

4. Conclusion

Level of PAHs in the water environment of the two rivers in Kanazawa City was rather low. The seasonal change of level PAHs in water was observed especially in Asano River: in winter concentration of PAHs seemed higher than in summer. PAHs

Level of PAHs in SPM had some relation with the amount of SPM in water and found complicatedly changed along the rivers as well as through monitoring time.

PAHs in sediment showed a different distribution pattern from the upper SPM. It seemed that PAHs in sediment was originated from other sources beside the deposition from upper water. Analysis more about characteristics of sediment is necessary to clarify the complication of distribution of PAHs in different size fractions of sediment.

Refference

[1] I. Bouloubassi, A. Saliot, Source and transport of hydrocarbons in the Rhone delta sediment (Northwestern Mediterranean), *Fres. Jour. Anal. Chem.*, vol. 339, pp.765-771, 1991

[2] M.B. Capangpangan, I.H. Suffet, Optimization of a dry method for filtered suspended solids from natural waters for supercritical fluid extraction analysis of hydrophobic organic compounds, *Jour. Chrom. A*, vol. 738, pp.253-264, 1996

[3] R.E. Countway, R.M. Dickhut, E.A. Canuel, Polycyclic aromatic hydrocarbons (PAH) distributions and associations with organic matter in surface waters of the York River, VA Estuary. *Org. Geochem.* vol. 34, pp.209-224, 2003

[4] R.A. Hittes, R.E. Laflamme, J.W. Farrington, Polycyclic aromatic hydrocarbons in recent sediments, *Science* vol. 198, pp.829-831, 1977

[5] IARC, IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans, *Overall evaluation of carcinogenity: an updating of IAPC monographs* Vol. 1-42, Suppl. 7. International Agency for Research on Cancer, Lyon, France, 1987.

[6] G. Kiss, Z. Varga-Puchony, J. Hlavay, Determination of polycyclic aromatic hydrocarbons in precipitation using solid-phase extraction and column liquid chromatography, *Jour. of Chrom. A* vol. 725, pp.261-272, 1996

[7] B.C. Lee, Y. Chimizu, T. Matsuda, S. Matui, Characterization of Polycyclic Aromatic Hydrocarbons (PAHs) in different Size Fraction in deposited road particles (DRPs) from Lake Biwa

Area, Japan, *Environ. Sci. Technol.* vol. 39, pp. 7402-7409, 2005

[8] J.C. Means, S.G, Wood, J.J. Hassett, W.L Banward, Sorption of polycyclic aromatic hydrocarbons by sediments and soils, *Environ. Sci. Technol.*, vol. 29, pp.1542-1550, 1980

[9] J.W. Readman, R.F.C. Mantoura, M.M. Rhead, A record of polycyclic aromatic hydrocarbons (PAH) pollution obtained from accreting sediments of the Tamar Estuary, UK: evidence for non-equilibrium behaviour of PAH. *The Sci. Total Environ.* vol.66, pp.73-94, 1987

[10] X.C. Wang, Y.X. Zhang, R.F. Chen, Distribution and partitioning of Polycyclic Aromatic Hydrocarbons (PAHs) in different size fractions in Sediments from Boston Habor, United States, *Mar. Poll. Bull.,* vol. 42, pp.1139-1149, 2001

[11] J.L. Zhou, T.W. Fileman, S. Evans, P. Donkin, C. Llewellyn, J.W. Readman, R.F.C. Mantoura, S.J. Rowland, Fluoranthene and pyrene in the suspended particulate matter and surface sediments of the Humber Estuary, UK, *Mar. Poll. Bull.,* vol. 36, pp.587-597, 1998

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