

# Monitoring polycyclic aromatic hydrocarbons in the main rivers of Kanazawa, Japan : spatial distribution, seasonal trends and partition behavior

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## Abstract

Levels of polycyclic aromatic hydrocarbons (PAHs) in surface waters and sediments of the Asano and Sai Rivers in Kanazawa, Japan were monitored to determine distributions, trends, possible sources and partition behavior. Samples were collected monthly from May 2005 to April 2007. PAHs in dissolved water, suspended solid, sediment were determined. During the monitoring time, the total PAH concentration in water of both rivers never exceeded 50ng/L at any of the sampling stations. No significant spatial differences of PAH concentration were observed either along the sampling stations of the two rivers or between the two rivers. PAHs in both rivers were strongly associated with particulate matter. The time average values of  $\log K_{SS-Water}$  roughly correlated with  $\log K_{ow}$ . The sediment-water  $K_{oc}$  and  $K_{ow}$  values of PAHs except for Benzo[k]fluoranthene were fitted to the linear free energy relationship  $\log K_{oc} = a \log K_{ow} + b$ . No apparent relation was found between the  $K_{oc}$  and sediment particle size. The organic carbon content, not the particle size, controls the sediment-water partition coefficient. The presence of dissolved humic acid which played a dissolved organic matter role in water-sediment system altered the sediment water partition behavior of PAHs. HA shifted the equilibrium partition to the water phase, and decreased the sediment water partition coefficients.

### Monitoring Polycyclic Aromatic Hydrocarbons in the main rivers of Kanazawa, Japan - Spatial distribution, Seasonal Trends and Partition behavior -

#### Introduction

Polycyclic aromatic hydrocarbons (PAHs) largely originate from anthropogenic sources<sup>1,2)</sup> such as cooking and oil heating, coal burning, and petroleum-related activities such as vehicular emission. PAHs are of concern because of their ubiquity, persistence and toxic, mutagenic, and carcinogenic potentials<sup>3)</sup>. Numerous PAHs are therefore classified as priority pollutants by the United States Environmental Protection Agency (US-EPA) and by the European Community.

Combustion-derived PAHs in the atmosphere enter the water environment directly by gaseous exchange across the air-water interface, dry deposition of airborne particulate matter, or wet deposition by rainfall, and indirectly by urban runoff. In natural water environment, PAHs can exist freely dissolved or in a bound state associated with dissolved organic matter (DOM), suspended particles and sediment. The sorption and binding of PAH have an impact on their bioavailability, their toxicity, and their general fate in the environment. Understanding the distribution, behavior and transport of PAHs in the water environment is important to evaluate the distribution of the contamination as well as the pollution of PAHs and to manage and to control PAH levels in the environment. In this study, we chose a local region, the Asano and Sai Rivers, Kanazawa City for field of observations. The objectives of this study are

- To periodically monitor the level of PAHs in the Asano and Sai River. To identify their possible sources. To analyze the spatial distribution and seasonal trend based on the long term monitoring result.
- To clarify the partition of PAHs in the water-sediment systems in the downstream regions of the Asano and Sai Rivers. We determine the sediment water partition coefficients of these two rivers and investigated the effects of sedimentary organic carbon content and sediment particle size on the partition coefficients.
- To investigate the role of the dissolved organic matter in the partition of PAHs in water-sediment system.

### 1. Monitoring Polycyclic Aromatic Hydrocarbons in rivers

Surface water samples were collected from 4 stations along rivers and sediment samples were collected at the downstream locations near the estuaries of the Asano and Sai Rivers. The sampling stations were set along the two rivers from upstream at suburb; across the city where had high transport activities; to down stream near the estuaries, to investigate the effect of urban runoff on the PAHs in river water of the rivers (Fig. 1). Samples were taken once a month from May 2005 to April 2007. Water samples were filtered through a 0.5  $\mu\text{m}$  pore glass fiber filter (Advantec GC50) to separate the dissolved phase from the particulate phase (suspended solid - SS). Sediment samples were air-dried and sieved into three fractions: <75  $\mu\text{m}$ , 75-250  $\mu\text{m}$ , and >250  $\mu\text{m}$ . PAH concentration in dissolved water, SS and different size fractions of sediments were quantified by HPLC with fluorescence detector.

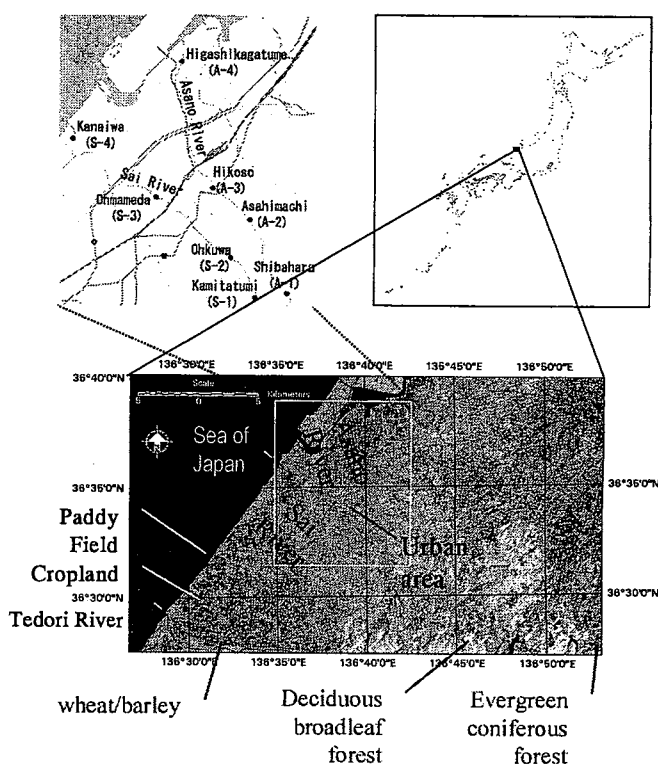


Fig. 1 Map of sampling site (samples were collected at downstream locations of the Asano and Sai Rivers named A4 and S4, respectively)

Throughout the study period, PAHs in the Asano and Sai Rivers never exceeded 50ng/L at any of the sampling stations. The patterns of change of total PAHs were the same at all sampling stations in both rivers. PAH concentrations tended to fluctuate in the beginning of the study period (May-Sep. 2005) then remain stable in Dec. 2005-Mar. 2006 period, decrease to lowest levels around 5ng/L in Apr-Sep.2006, and increase again in Sep.2006-Apr.2007 period. The pattern of variation of two to four-ring PAHs except for BaA were similar to the patterns of variation of total PAHs.

No significant spatial differences in total PAHs were found among the sampling stations in either river in the first three periods from May 2005 to September 2006

In both rivers, the PAH levels varied greatly among the three size fractions of the sediments. The small size fraction (<75 μm) had highest total PAH concentrations >250μm size fractions had the lowest total PAH concentration. In most months, the total PAH concentrations in the Sai River were more than twice of those observed in the Asano River, especially in small size fraction.

Three-ring and four-ring compounds were the most abundant PAHs in all water, SS and sediment samples contributed more than 70% of the total PAHs. However, PAHs in water and PAHs in sediment showed different profiles. In sediment, five-, six- ring PAHs were 23-28% of the total PAHs, accounted for higher proportion of five-, six-ring PAHs in water column.

The [BaA]/([BaA]+[Chr]) ratio and [Flu]/([Flu]+[Pyr]) ratio were used to identify the possible sources of PAHs in investigated site. An analysis of PAH isomer pair ratio showed that PAHs in both rivers originated from several sources but mainly from combustion processes.

## 2. Partition of Polycyclic Aromatic Hydrocarbons between dissolved phase and particulate phase in rivers

The partition coefficient is defined as

$$K_d = \frac{C_s}{C_w} \quad (1)$$

where  $C_s$  [μg/kg dry wt.] and  $C_w$  [μg/L] are the concentrations of the chemical in the sediment and water (i.e., freely dissolved phase), respectively. Organic matter is the predominant particulate component responsible for the sorption of hydrophobic organic compounds in sediment-water systems<sup>4,5</sup>. When sorption is due solely to the presence of organic carbon, an organic carbon normalized partition coefficient  $K_{oc}$  can be used<sup>6</sup>, where

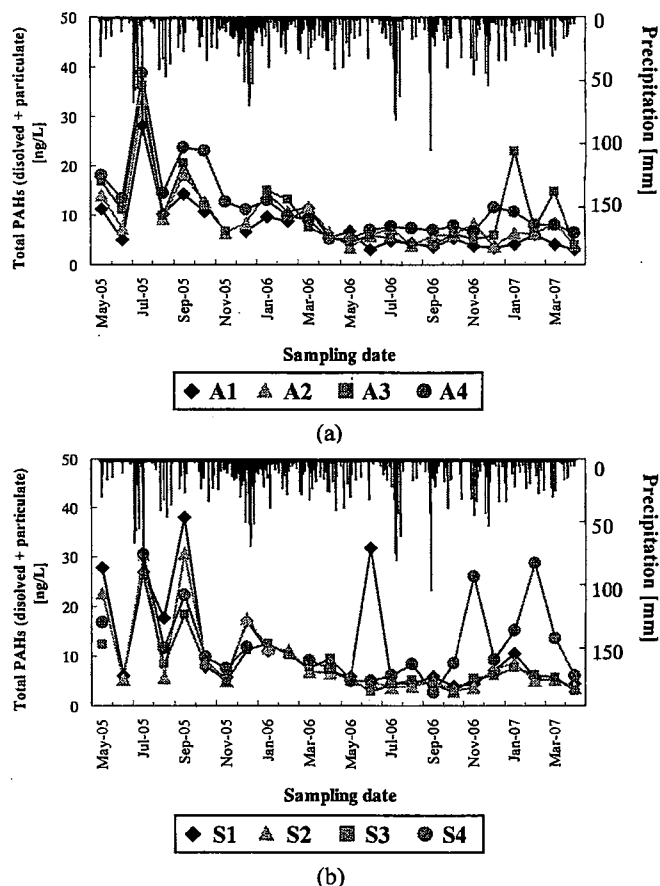


Fig. 2 Variation of total PAH concentration along (a) Asano River and (b) Sai River with time (Precipitation source: Precipitation data were collected for Kanazawa City from the database of Japan Meteorological Agency - [www.jma.go.jp](http://www.jma.go.jp))

$$K_{oc} = \frac{K_d}{f_{oc}} \quad (2)$$

SS water and sediment water partition coefficients  $K_{SS-Wat}$   $K_{Sed-Wat}$ , respectively of each PAH was calculated for all the samples where PAHs were detected in both SS/sediment and water samples.

$K_{SS-Wat}$  values of all PAHs cover a wide range. The results suggest the dynamic nature and heterogeneity of the samples obtained,

In the present study, even though the  $K_{SS-Wat}$  values exhibited a wide variation throughout the monitoring period, the general tendency of a rough correlation between the time average value of  $\log K_{SS-Wat}$  and  $\log K_{ow}$  was observed. This result shows the overall partition behavior of PAHs between water and SS in our study sites. The fact that no significant difference of distribution of  $K_d$  among the sampling stations indicated that PAHs transported along the rivers from upstream to down stream in the stable status

$K_{Sed-Wat}$  was positively related to  $f_{oc}$  in both rivers. These findings are consistent with previous results obtained in the laboratory<sup>5,6</sup> and in the field<sup>7</sup>.

The correlation between PAH concentrations and sedimentary organic carbon content explains why high concentrations of PAH relate to small size fractions having higher organic matter contents

However, the data is somewhat scattered especially for the sediments that had low organic carbon content. The scattering may be due to differences in the organic matter matrices or the presence of sorbent materials other than organic matter.

The relationship between  $\log K_{oc}$  ( $K_{oc}$  were sedimentary organic carbon normalized partition coefficients) and  $\log K_{ow}$  for PAHs in the water-sediment systems of the Asano and Sai River is shown in Fig. 3.  $\log K_{oc}$  was linearly correlated with  $\log K_{ow}$ , which is consistent with the so-called linear free energy relationships<sup>8</sup> except for BkF. BkF revealed a distinctly higher  $K_{oc}$  than that given by the regression lines. As far as we know, there has been no report of this kind of behavior, and the cause has not been identified.

The estimated linear free energy relationships between  $K_{oc}$  and  $K_{ow}$  for all PAHs except BkF are

$$\text{Asano River: } \log K_{oc} = 0.562 \log K_{ow} + 3.55 \quad (r^2 = 0.919)$$

$$\text{Sai River: } \log K_{oc} = 0.814 \log K_{ow} + 2.19 \quad (r^2 = 0.974)$$

### 3. Partition of Polycyclic Aromatic Hydrocarbons in water-sediment system containing humic acid

Natural dissolved organic matter 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. Recent studies have considered the partition of PAHs between water and dissolved organic matter<sup>9,10</sup>, but there is few work focusing on the partition of PAHs in the water-sediment system with the presence of humic substances as the dissolved organic matter. 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 water sediment 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 in batch experiment.

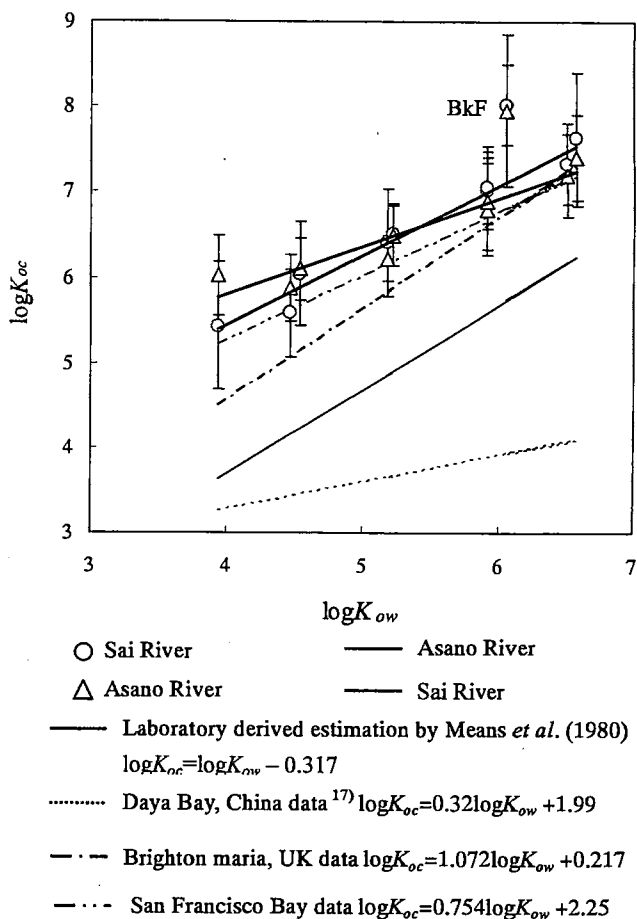


Fig. 3 Relationship between  $\log K_{oc}$  and  $\log K_{ow}$  for PAHs in sediment-water system.

There was a correlation between the concentrations of PAHs in water and in sediment (Fig. 4). The presence of HA in the water sediment system shifted the water sediment partition of PAHs to the water phase. The results were consistent with the finding of the enhancement of HA to the elution of Pyrene from activated carbon into aqueous solution<sup>11</sup>. The sediment water partition coefficients ( $K_d$ ) were decreased by HA. The effect of dissolved HA on the partition between sediment and water of PAHs depends on the hydrophobicity of PAHs.

In the presence of HA, water sediment system was considered as a three phase system consisting of free water, DOM and sediment and we can define DOM water partition coefficients ( $K_{DOM}$ ). Determined  $K_{DOM}$  was decreased when increasing the HA level in water. This finding was different with the obtained by Durjava *et al.* (2007)<sup>12</sup>.

With the presence of dissolved HA in water-sediment system, the partition of PAHs was considered as a three phase system: free water - DOM - sediment. The equation expressed the relationship between apparent partition coefficients between sediment water and HA concentration was established. This equation successfully described the partition behavior of PAHs in water-sediment system with the presence of dissolved HA as dissolved organic matter.

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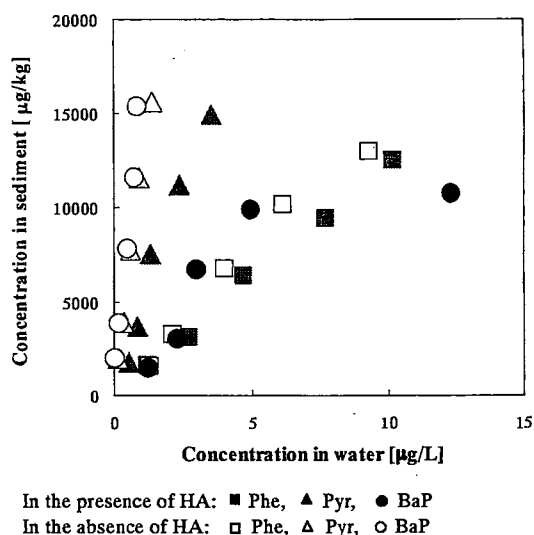


Fig. 4 Partition of PAHs between sediment and water in the presence and absence of HA

## 学位論文審査結果の要旨

〔審査経過〕 各委員による面接と諮問を行い、平成19年7月30日に第1回審査委員会を行った。8月2日に口頭発表（最終試験）を行い、その後同日に開催した最終審査委員会にて、次のように判定した。

〔審査結果〕 本論文は、金沢市の主要河川である犀川と浅野川において、2年間にわたり、河川水、浮遊固形物質、底質中の多環芳香族炭化水素濃度をモニタリングし、測定地点による差異、季節変動、固液間の分配を検討したものである。また、室内実験で、フミン酸などの溶存有機物質が固液間分配に及ぼす影響について検討を行っている。成果としては、両河川における13成分の多環芳香族の濃度が50 ng/Lを越えないこと、市街地上下流での差異はほとんどないことなどを明かし、浮遊物質と水の間での分配係数に関して、平均値、SS濃度と分配係数の関係を明らかにした。河口域の底質では、固液間分配は、底質の有機物に支配されており、その関係は、線形自由エネルギーモデルで表されることを明らかにした。また、室内実験で、フミン酸が Phenanthrene, Pyrene, Benzo[a]pyrene と底質との分配に及ぼす影響について検討し、環数の大きいものほどフミン酸の影響が大きいこと、分配の正確な記述のためには、フミン酸の底質への吸着を考慮する必要があることを明らかにした。以上のように本論文は環境科学に関して有用な知見を与えるものであり、博士（学術）に値すると判定した。