

Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in the Brackish Water and Sediments of Citarum Irrigation System, Pakis Jaya, Karawang, Indonesia

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Abstract. Fifteen priority polycyclic aromatic hydrocarbons (PAHs) were determined in the sediments and brackish water of Citarum Irrigation System (CIS), Pakis Jaya, Karawang Regency. The samples were analyzed with liquid-liquid extraction for brackish water and Soxhlet Extraction for sediments. The final concentration of PAHs was determined with Gas Chromatography-Mass Spectrometry (GC-MS) and the origins of PAHs were identified through diagnostic ratios method. The total PAH concentrations ranged from 1782 to 2386.88 ng/L in water and from 113 to 405 ng/g dry weight (dw) in sediments. The concentration of total PAHs in sediment was lower than the SQG effects range-low (3442 ng/g). High molecular weight of PAHs dominated both in sediments and water. The origins of PAHs in the sediment and water-based on diagnostic ratios were from petrogenic and pyrogenic sources including petroleum, petroleum combustion, and combustion of organic materials. Overall, environmental conditions in the Citarum irrigation system and its river mouth was moderate level of PAHs contamination.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic pollutants that consist of two or more benzene rings which are persistent and widely distributed in the environment [1, 2]. In general, PAH compounds are easy to accumulate in sediment and biota because of their hydrophobic characteristics [3]. Thus, the sediments are acting as the most important PAH reservoir in the environment and potentially affected benthic organisms [4]. The sources of anthropogenic PAHs in the environment have been classified into two sources based on their molecular dynamic and benzene's ring biomarker: petrogenic and pyrolytic sources. The petrogenic inputs are related to petroleum products and represented with a low molecular weight of individual PAHs (e.g. phenanthrene, fluoranthene, pyrene), while pyrolytic sources include biomass combustion and are characterized by a high molecular weight of individual PAHs (e.g. acenaphthene and fluorene) [5, 6].

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Citarum irrigation system (CIS) in Pakis Jaya, Karawang Regency, West Java Province, Indonesia are important infrastructure for aquaculture and agriculture in the Karawang Regency [7]. The water sources of CIS is derived from Citarum River which flows about 297 km through 12 rapid urbanization districts in West Java and numerous industrial zones along Citarum River Basin which all potentially release PAH contained waste [8]. Indicated as one of the most polluted river in the world, the waters in Citarum River was unsuitable as the source for drinking due to potentially contains hazardous substances that leached from the main city and industrial areas along the river catchment [8]. With these conditions, ecological risk assessment is needed to conduct not only in the main river but also in the irrigation system that potentially affected by massive pollution in the main river. Besides that, through this assessment, the quality of the environment in the aquaculture system, irrigation system and estuary ecosystem will be guaranteed.

Therefore, This study was set out to assess the current condition of brackish water and sediments from CIS in Pakis Jaya, particularly as baseline information of sources, concentrations, and potential ecological risk of PAHs.

2. Materials and method

2.1. Study area and sampling

The study area was the Citarum irrigation system (CIS) and their estuary around Pakis Jaya, Karawang Regency, West Java Province, Indonesia. The area mainly was used for aquaculture and agriculture in the Karawang Regency [8]. Besides that, the area also was a habitat for Javanese medaka fish, a bioindicator species from *Oryzias* genus.

Sediments and brackish water were collected from six sampling sites in March 2014 (**Fig. 1**). Station 1 located in the estuary area, while Station 2, 3, 4, 5, and 6 located in waterways of fishing ponds that connected to CIS. Surface water samples obtained with a stainless water sampler and immediately filtered through 0.45 μm GFC glass fiber filters (47 mm \times 0.7 μm ; Whatman), and stored in icebox at 4°C during transport to the laboratory for analysis [5], while sediment samples were collected using grab sampler and then surface sediment (depth 5cm) were put into a glass bottle, covered with aluminum foil, and finally stored in icebox at 4°C for further analysis [9].

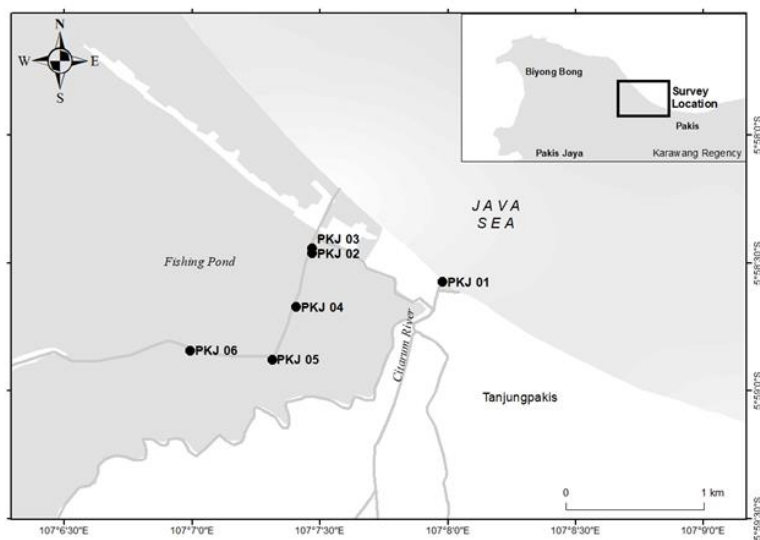


Figure 1. Sampling site in the Citarum irrigation system (CIS)

2.2. Chemical analysis

In the laboratory, seawater and sediment were extracted following the previous study from Falahudin et al (2012) with some modification [10]. Briefly, 2 liters of filtrate water were extracted subsequently with 60, 30 and 30 ml n-hexane using a separatory funnel. The hexane extracted were dried from water by passing through Na₂SO₄ and evaporated with a rotary evaporator until 1 ml. As for sediment samples, 10 g of wet sediment was dried in the oven at 50°C overnight, added Na₂SO₄ powder, and grounded in a mortar until smooth and homogeneous. After that, the fine sediments were extracted with 120 ml dichloromethane (DCM) using a Soxhlet system for 8 hours and the extracts were evaporated until 1 ml.

Furthermore, evaporated extracts were cleaned up and fractionated through alumina and silica column chromatography, respectively. Alumina column was prepared as follows: glass wool and 4 g Al₂O₃ WB 5 basic (SIGMA) were added separately to chromatography column and directly conditioned with 10 ml DCM and 10 ml hexane. Then, the extract was added to the column and eluted with 4% diethyl ether in hexane, and evaporated again until 1 ml. The cleaned extracts were separated and fractionated through a silica gel chromatographic column which consists of glass wool in the bottom and 4 gram of neutral silica (Merck 7754). The conditioning step was similar to the alumina column. The PAHs fraction was eluted with 10% diethyl ether in Hexane and concentrated to 1 mL. The polar fraction (F2) was analyzed using Thermo Scientific Gas Chromatography-Mass Spectrometry (GC-MS). The concentration unit was expressed in ng/l for water and ng/g dry weight (dw) for sediment.

The GC-MS separation using the TG5-SilMS column was performed with conditions as follows: length: 30 m; ID: 0.25 mm; Films: 0.25 μm; oven: 50°C (0.5 minutes), Gas rate: 160°C (15 minutes), to be increased up to 290°C and held at 290°C for 13 minutes then to be increased again up to 300°C and held at 300°C for 4 minutes. Gas System: 1.2 ml of Helium/min (constant flow); Split flow: 10 ml/min, Splitless time: 0.5 minutes.

External standard calibration was conducted using QTM PAHs standard mixture (QTM PAH mix 479330-U) [11]. A calibration curve with 5 concentrations of PAHs (3, 6, 12, 24, and 48 ppb) were determined and R² values of each PAH compound were naphthalene (Nap: 0.929), acenaphthylene (Acy: 0.956), bromo-naphthalene (BrNap: 0.966), acenaphthene (Ace: 0.972), fluorene (Fl: 0.964), anthracene (Ant: 0.963), phenanthrene (Phe: 0.963), fluoranthene (Flu: 0.955), pyrene (Pyr: 0.945), benzo(a)anthracene (BaA: 0.949, chrysene (Chr: 0.945), benzo(k)fluoranthene (BkF: 0.944), benzo(a)pyrene (BaP: 0.952), indeno (1,2,3-cd)pyrene (InP: 0.927), dibenzo(ah)anthracene (DbA: 0.953), and benzo(ghi) perylene (BghiP: 0.832). RSD of each PAH compound is below 10%.

2.3. Risk assessment

To determine the possible hazard effect, the concentration of PAHs in sediment were compared with the sediment toxicity screening guidelines from the US National Oceanic and Atmospheric Administration. In those guidelines, two target values were set: effects range low (ERL) and effect range medium (ERM) [12, 13].

2.4. Sources apportionment

Diagnostic ratio methods were used to distinguish natural and anthropogenic sources of PAHs [2, 5, 14]. These methods were based on differences in thermodynamic stability among PAHs species including phenanthrene/anthracene (Phe/Ant) (D-1), fluoranthene/pyrene (Flu/Pyr) (D-2), indeno(123-cd)pyrene/(indeno(123-cd)pyrene+benzo(ghi)perylene) (InP/(InP+BghiP)) (D-3), fluoranthene/(fluoranthene+Pyrene) (Flu/(Flu+Pyr)) (D-4), benzo(a)pyrene/(benzo(a)pyrene+chrysene) (BaP/(BaP+Chr)) (D-5), anthracene/(anthracene

+Phenanthrene) (Ant/Ant+Phe) (D-6), anthracene/178 (Ant/178) (D-7), benzo (a) anthracene/228 (BaA/228) (D-8), and low molecular weight/high molecular weight (LMW/HMW).

Table 1. Diagnostic ratio of individual PAHs

Sources	Ratio Values								
	D1	D2	D3	D4	D5	D6	D7	D8	D9
Oil	>10	<1	<0.2	<0.4	0.6 - 0.9	<0.1	<0.1	<0.2	>1
Oil combustion	-	-	0.2 - 0.5	0.4 - 0.5	-	>0.1	-	-	-
Organic material combustion	<10	>1	>0.5	>0.5	<0.2	0.1	>0.1	>0.35	<1
Mixture of Oil and organic material combustion	-	-	-	-	0.4 - 0.6	0.1	-	0.2 - 0.4	-

3. Results and discussion

3.1. Distribution and composition of PAHs

PAHs were detected in all samples including water and sediment in the area of study. The concentrations of total PAHs in surface water and sediments of CIS and its estuary ranged from 1782 to 3268 ng/l, with a mean value of 2413.33±478.15 ng/l and from 113 to 405 ng/g dry weight (dw), with a mean value of 254.45±106.62 ng/g dw (Table 2 and 3). The highest concentration of PAHs in water and sediments was detected at St 5 which located in the upstream of CIS and followed by St 4, St 3, St 2, St 6 and St 1 (**Fig. 2** and **3**). The compositional pattern of PAH in surface water and sediments were dominated by high molecular weight of PAHs with number of benzene more than 3 rings such as Fluoranthene, Pyrene, Chrysene, Benzo (ghi) Perylene, Benzo (b) Fluoranthene, Benzo (a) Pyrene, Benzo (a) Anthracene, and Indeno (123-cd) Pyrene. These results are coherence with previous studies [2, 3, 15].

There were several factors that derived variation of PAHs concentration and composition between stations. Firstly, the direction and speed of the current in surface water caused heterogeneous distribution of PAHs [16]. In this study, the reservoir from Citarum River to the irrigation system in Pakis Jaya might trigger the variation on concentration and distribution along with the system [17]. As St 5 closed to the main river, higher concentration occurred because of the low turbulence [9] than other stations where mixing processes with seawater such as at St 1. In addition, the concentration of PAHs also influenced by degradation processes by microorganisms, UV light and temperature [18-20]. It is known that the temperature has a role in the evaporation and reaction of PAHs in the environment [21]. Furthermore, the evaporation process can also eliminate low molecular weight PAHs in the water surface [22-24].

Total PAHs concentration in water of CIS and its estuary are lower than the results of other studies. For example, total concentrations of PAHs in the waters from the Baron, Opka, and Serang rivers (Yogyakarta) were between 8100 ng/l and 28900 ng/ [25] and from Indian Brahmaputra river ranged from 3351 to 72893 ng/l [26]. However, total PAHs concentrations in this study also were higher than the concentration of PAHs found in Shonghua River, China (conc. 163 to 2746 ng/L) and Kor river, Iran (45 to 375 ng/L) [27-28].

Table 2. Individuals and concentrations of PAH in surface water (ng/l)

No	PAH	St 1	St 2	St 3	St 4	St 5	St 6
1	Nap	nd	nd	nd	nd	nd	Nd
2	Acy	nd	nd	nd	nd	nd	Nd
3	BrNaph	305	202	246	270	229	208
4	Ace	44	31	37	41	36	33
5	Fl	nd	nd	nd	nd	188	Nd
6	Phe	156	159	155	155	168	157
7	Ant	nd	nd	nd	nd	nd	Nd
Total Concentration (LMW)*		505	392	438	466	621	398
8	Flu	nd	273	271	271	272	272
9	Pyr	nd	383	381	381	384	381
10	BaA	nd	nd	nd	Nd	694	Nd
11	Chr	nd	nd	nd	nd	nd	Nd
12	BbF	477	486	476	470	484	479
13	BaP	800	810	803	796	813	803
14	InP	nd	nd	nd	nd	nd	Nd
15	DbA	nd	nd	nd	nd	nd	Nd
16	BghiP	nd	nd	nd	nd	nd	Nd
Total Concentration (HMW)#		1277	1952	1931	1918	2647	1935
Σ LMW+HMW		1782	2344	2369	2384	3268	2333
LMW/HMW		0.4	0.2	0.2	0.2	0.2	0.2

Note : nd: not detection ; LMW : Low molecular weight ; HMW : High molecular weight

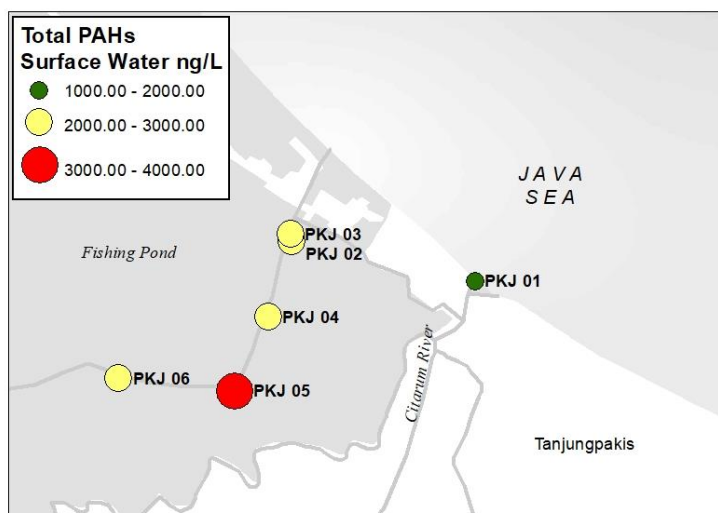


Figure 2. Spatial distribution of PAH in the surface water

Table 3. Total PAH (ng/g) concentrations in sediments

No	PAH	St 1	St 2	St 3	St 4	St 5	St 6
1	Nap	nd	nd	nd	nd	nd	Nd
2	Acy	nd	nd	nd	nd	nd	Nd
3	BrNaph	17	17	17	18	nd	Nd
4	Ace	3	nd	2	2	nd	Nd
5	Fl	17	nd	nd	16	12	Nd
6	Phe	15	14	nd	13	13	30
7	Ant	32	nd	nd	nd	nd	Nd
Total Concentration (LMW)*		84	31	19	49	25	30
8	Flu	27	26	22	24	20	52
9	Pyr	38	36	32	34	28	74
10	BaA	nd	nd	nd	nd	0.7	Nd
11	Chr	47	46	40	nd	nd	Nd
12	BbF	46	45	nd	42	33	93
13	BaP	93	81	nd	91	62	156
14	InP	nd	nd	nd	nd	nd	Nd
15	DbA	nd	nd	nd	nd	nd	Nd
16	BghiP	nd	nd	nd	nd	nd	Nd
Total Concentration (HMW)#		251	234	94	191	144	375
LMW+HMW		335	265	113	240	169	405
LMW/HMW		0.3	0.1	0.2	0.3	0.0	0.1

Note : nd: no detection ; LMW : Low molecular weight; HMW : High molecular weight

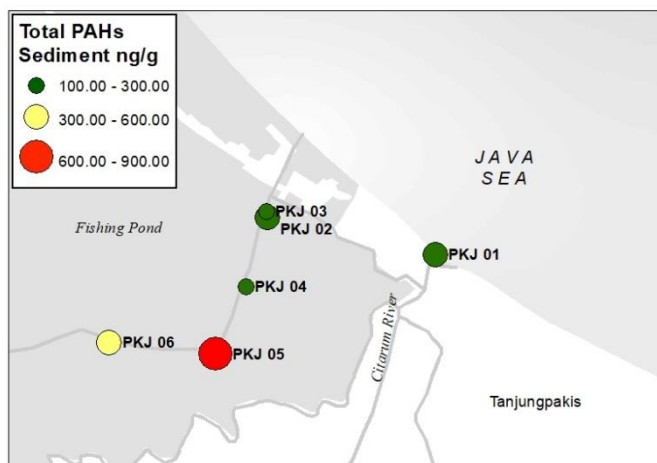


Figure 3. Spatial distribution of PAH in sediment

To assess the level of PAHs contamination in the sediments, Baumard et al. (1998) classified the contamination level of PAHs into four categories: (1) low : 0-100 ng/g; (2) moderate : 100-1000 ng/g; (3) high : 1000-5000 ng/g; and (4) very high : >5000 ng/g [29].

Therefore, based on these classifications, the contamination level of PAHs in sediments from CIS and its estuary were categorized as moderate levels of contamination. In addition, compared with other areas, the total concentration of PAHs in sediment from this study was higher than Evrotas and Mahakam rivers, but was still lower than other rivers present in Table 4.

Table 4. Concentrations of PAH in river sediments from different locations in the world

Study area	Concentration range (ng/g dw)	Number of PAHs measured	Ref.
Klang River, Malaysia	3803.2–7442.7	16	[30]
Donggang River, Taiwan	23–2534	16	[31]
Evrotas River, Greece	0.3–195.4	8	[32]
Warri River, Nigeria	42–2298.7	11	[33]
Negro River, Brazil	5.6–1187	11	[34]
Haihe River, China	774.81–255371.91	16	[35]
Arc River, France	153–1311	17	[36]
Gomti River, India	5.24–3722.87	16	[37]
Nzhelele River, South Africa	206–13710	10	[38]
Mvudi River, South Africa	440–21600	10	[39]
Mahakam River, Indonesia	0.395-0.817	6	[40]
Citarum irrigation system	113-405	10	The present study

3.2. The sources of PAHs

In this study, due to the limited data to conduct diagnostic ratio, only two ratios of individual PAHs that available to use for sources identification (fluoranthene/pyrene) (Flu/Pyr); and fluoranthene/(fluoranthene+pyrene) (Flu/(Flu+Pyr)) [5, 17], plus ration between low molecular weight (LMW) with high molecular weight (HMW) of PAHs (LMW/HMW). Results showed that ratios of Flu/Pyr, Flu/(Flu+Pyr), and LMW/HMW in sediment and water from all stations were <1, between 0.4-0.5, except St 1 that were not available for PAHs in water, and <1, respectively. Those results suggested that mixed sources were derived from petroleum, petroleum combustion, and pyrogenic sources [41]. These results were also supported by a cross plot diagram between BaA/228 vs Flu/(Flu+Pyr), Ant/178 vs Flu/(Flu+Pyr), Ant/(Ant+Phe) vs Flu/(Flu+Pyr), Phe/Ant vs Flu/Py, and BaP/(BaP+Chr) vs Ant/(Ant+Phe) (**Fig.4**). These results suggested that possible PAH input to the Citarum irrigation system and its estuary mainly from oil leakage and its emission from the industrial area that passed through by the main river.

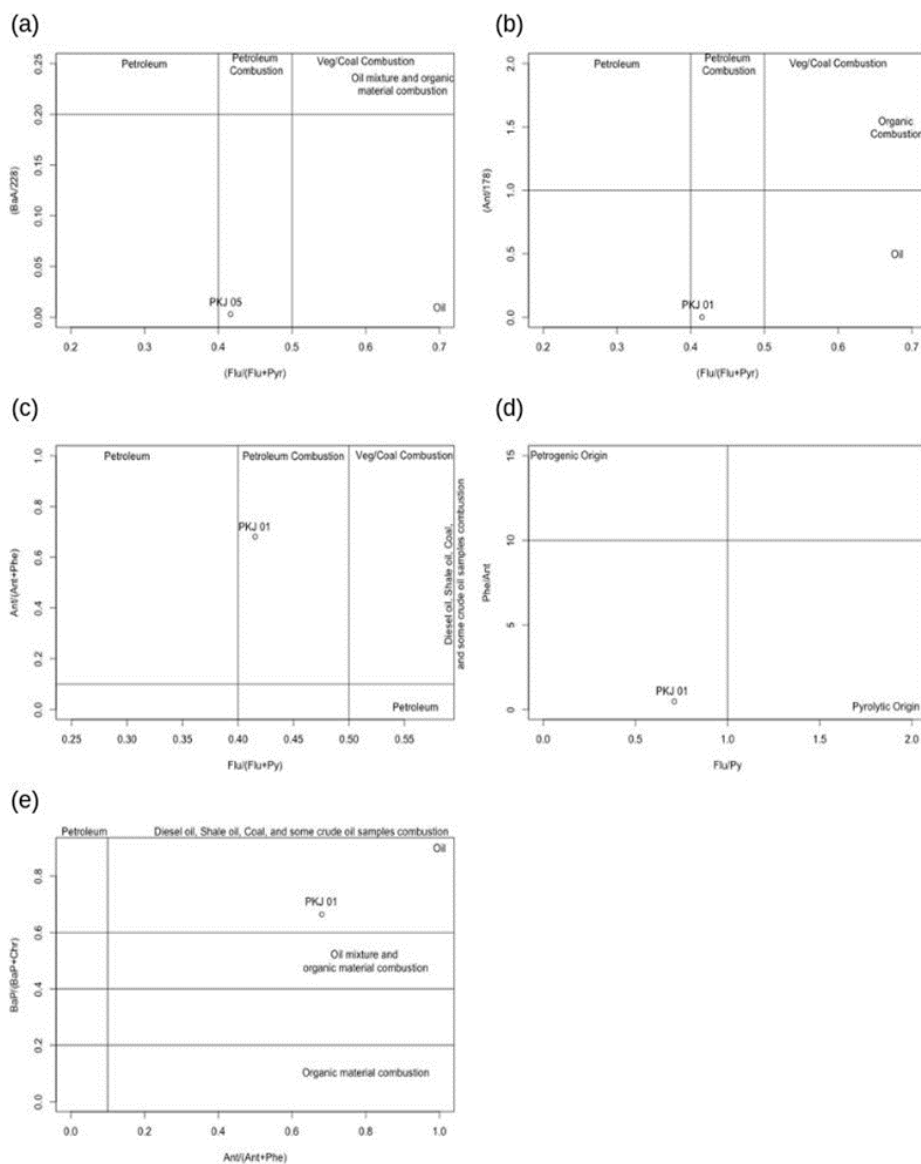


Figure 4. Diagnostic ratio plot for PAHs concentration in sediments

3.3. Ecological risk assessment

The concentrations of total PAHs and individual PAHs from all the studied stations were lower than the SQGs for the ERL and the ERM (Table 1). These findings suggest that the sediments from CIS and its estuary would be unlikely to cause adverse effects to the organisms within these areas. Moreover, the adverse effects of pollutants on the organism or ecosystem can be used as an early warning indicator of environmental health and potential impact on human health [6]. However, further investigation is needed to observe the accumulation of the high molecular weight PAHs in the sediment and their impact on benthic organisms.

4. Conclusion

The study concluded that environmental conditions in the Citarum irrigation system and its estuary was at a moderate level of PAHs contamination. Where compared to sediment quality guidelines from the US National Oceanic and Atmospheric Administration (NOAA), the quality of sediment from the study area is not toxic to the organism. However, further care is needed particularly on dominated by high molecular weight PAHs in sediments and water. Besides that, as the source of PAHs was indicated from petroleum and its emission, our suggestions are to manage potential leakage of petroleum to the river and decreasing petroleum product emission to the environment.

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