Concentrations of PAHs (Polycyclicaromatic Hydrocarbons) Pollutant in Sediment of The Banten Bay

Konsentrasi Polutan (PAH) Polisiklikaromatik Hidrokarbon dalam Sedimen di Teluk Banten

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ABSTRACT: Banten Bay is end of stream for a few rivers from Banten mainland where many manufactures and petrochemical industries are built. This may give environmental pressure of water quality of the bay due to pollutant input, such as Polycyclic Aromatic Hydrocarbons (PAHs). This study is to identify those pollutants and determine their total concentration and distribution in sediments. Surface sediment samples were collected in four zones: inner coastline within the bay, middle bay, coastline off the bay and outer of the Bay in April 2016. PAH components were extracted and measured using a gas chromatography-mass spectrometry. Levels of total PAHs in sediments in inner coastline within the bay ranged between 0.381-2.654 ppm with an average of 1.288 ppm, middle of the bay ranged between 0.747-1.762 ppm with an average of 1.198 ppm, outer of the bay ranged between 0.192-1.394 ppm with an average of 0.921 ppm, and east coast of the bay ranged between 0.191-1.394 ppm and an average of 0.778 ppm. The levels of total PAH contamination is apparently lower than those of PAH threshold in sediments (i.e. 4.5 ppm).

Keywords: PAHs (Polycyclic Aromatic Hydrocarbons), Banten Bay

ABSTRAK: *Teluk Banten merupakan muara dari beberapa sungai di daratan utama Banten yang sebagian besar berupa kawasan industri dan kegiatan lain sekitar laut. Kondisi ini berpotensi memberikan tekanan terhadap kualitas perairan Teluk Banten karena masukan bahan pencemar diantaranya senyawa Polisiklik Aromatik Hidrokarbon (PAH). Penelitian ini bertujuan mengidentifikasi PAH dan menentukan konsentrasi total dan distribusinya di sedimen. Pengambilan sampel sedimen permukaan pada April 2016 diempat zona: zona pantai bagian dalam teluk, bagian tengah teluk, pantai bagian luar teluk, dan bagian luar teluk. Konsentrasi PAH diukur menggunakan alat kromatografi gas spektrometer massa (GCMS). Konsentrasi total PAH dalam sedimen pantai bagian dalam berkisar antara 0,381-2,654 ppm dengan rata-rata sebesar 1,288 ppm. Bagian tengah teluk berkisar antara 0,747-1,762 ppm dengan rata-rata sebesar 1,198 ppm, bagian luar teluk antara 0,192-1,394 ppm dengan rata-rata sebesar 0,921 ppm dan pantai bagian timur teluk antara 0,191-1,394 ppm dengan rata-rata sebesar 0,778 ppm. Level pencemaran total PAH di perairan Teluk Banten dalam sedimen mengindikasikan masih lebih rendah dari standar bakumutu PAH dalam sedimen yaitu 4,5 ppm.*

Kata kunci: PAH (Polisiklik Aromatik Hidrokarbon), Teluk Banten

INTRODUCTION

Banten Bay, the north coast of West Java as a part of the Java Sea, has potential fisheries economic resources. Various industries such as petrochemical, polymer, manufacture, food and beverages, oil and gas refinery and also increasing settlement have been developed in those surrounding area (Badan Pusat Statistik Provinsi Banten 2016). This development has tended to elevate recently and could influence the quality of marine environment. Most of these activities could discharge the waste containing various pollutants through oil spills, vehicle emission, ballast water from maritime transportation, and land runoff from mainland into the channels or stream and end up to the marine environment.

Many studies showed that the quality of marine environment has been degraded by heavy metals such as Pb, Cd, Cr and Hg. Previous studies showed that heavy metals has contaminated the bay (Jalius et al. 2008; Putri 2012). Although the metals may derived from natural sources, anthropogenic activities surrounding the bay could possibly contribute their existence. In addition, polycyclic aromatic hydrocarbons (PAHs), another important family of environmental pollutants because of their persistent, toxic and carcinogenic (Mastral et al, 1996; Arzayus et al, 2001), may co-

release through waste water discharge. This fused ring structure compounds are ubiquitous and have been found in water, air, sediments, fossil fuels such as coal and oil, and even in pristine areas such as the Poles (Laflamme and Hites, 1978). Many activities surrounding the bay such as maritime transportation, oil and petrochemical industry, sea port activity, and land runoff from mainland possibly emit and discharge these low water solubility, low volatility and high hydrophobicity to the Banten Bay. This study was to identify the possible source of PAHs, possible mechanisms of their distribution within the bay.

METHODS

Sampling was located at 25 stations of the Banten Bay waters, Banten Province (Figure 1). Analysis of PAHs concentration was accomplished in the sediment samples collected using a grab McIntyre, in April 2016. The location was spatially grouped into four zones representing possible various depositions. Four stations represented inner coast of the bay (i.e. TB1, TB2, TB3 and TB4). Eight stations were grouped as middle of the bay (i.e. TB5, TB6, TB7 ,TB8, TB9, TB10, TB11 and TB12). Four stations represented a zone of outer of the bay (i.e TB13, TB14, TB15, and TB16). Nine stations were located in east-coast of the bay (i.e. TB17, TB18, TB19, TB20, TB21,TB22, TB23, TB24 and TB25).

Surface sediment samples (5-10 cm depth) were collected and put into pre-cleaned glass bottles (Dsikowitzky et al. 2011, 2014). The samples were kept in an ice box at temperature 4^{o}C during transportation to the laboratory. Each homogenized sample (10 grams) was dried in oven 40^{o}C overnight, and subsequently extracted with 3 x 40ml *dichloromethane* Emsure Merck and *n-Hexane* Emsure Merck. The extract was cleaned up and fractionated using a column chromatography filled with both alumina powder at the top and silica gel type 60 below (70-230 mesh ASTM), and then eluted by 120 ml (1:1) of dichloromethane/n-pentane. Analysis of PAH used GCMS ISQ LT 1310, column TG5SilMS, length: 30m; ID: 0.25mm; Film: 0.25um; Oven: 50^{o}C (0.5 min), The chromatography were programmed at the initial temperature 160^{o} C for 15 minutes, increased to 290^{o}C at rate 10^{o} C/13 minutes, and increased to 300^{o} C and finally attained that temperature for 4 minutes. Gas system: Helium 1.2

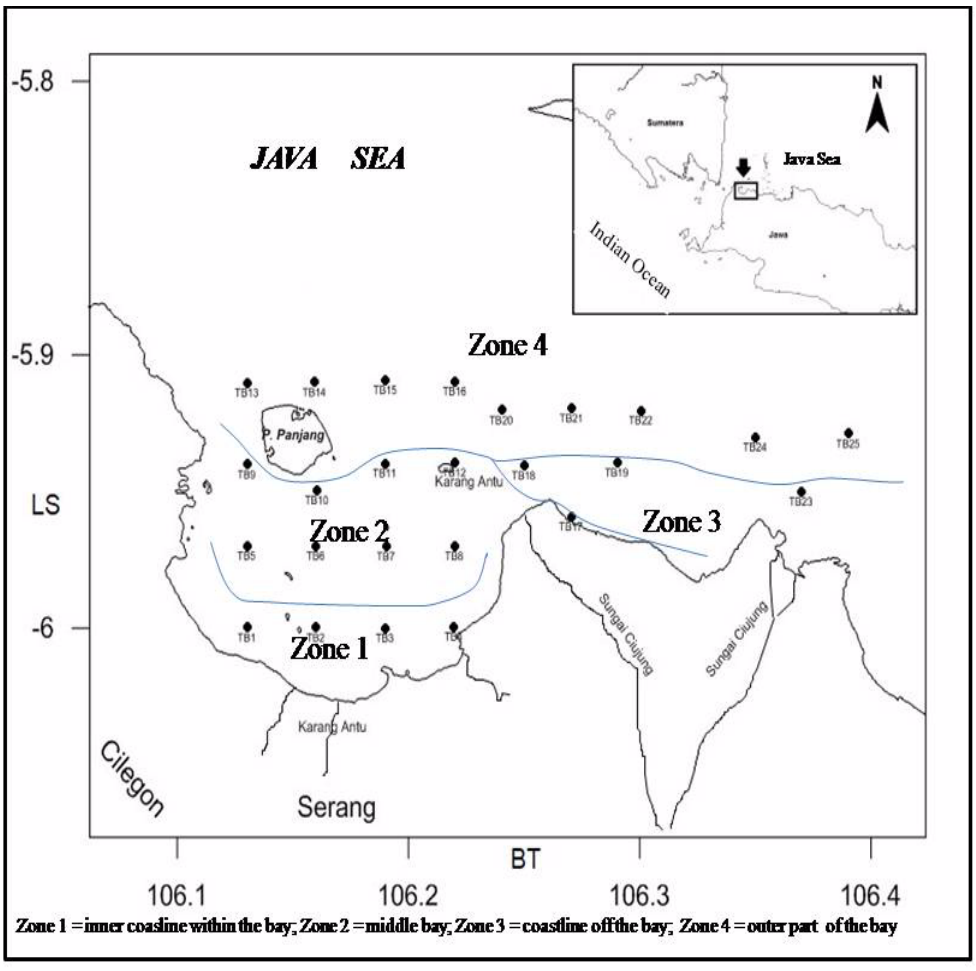

Figure 1. 25 Sampling locations of sediments in the Banten Bay

ml/min (constant flow); Split flow: 10 ml/min; Splitless time: 0.5 min. MS condition were potential ionization/ electronenergy 70eV, ion source temperature 230^{o} C and interface temperature 250^{o} C. Full mass data were recorded between 45–600 Dalton per second. PAHs were identified based on using mass spectra and retention time with full scan method.

RESULT

The PAHs in sediments samples detected were 10 types of the 16 priority pollutant compounds; naphthalene (N), acenaphthene (Ace), fluorene (F), phenanthrene (P), anthracene (AN), fluoranthene (FL), pyrene (PY), chrysene (C), benzo (b) fluoranthene (BbF), andbenzo (a) pyrene (BaP) (Table 1-4). Those consistently undetected were acenaphthylene (Acl), benzo (a) anthracene (BaA), benzo (k) fluoranthene (BkF), indeno (1, 2, 3-c, d) pyrene ((ID), dibenzo (a,h) anthracene (DA) and benzo (g,h,i) perylene (BgP). The most consistence PAH found in the sediment samples was naphthalene, while the others varied. In the zone 1 (inner coast of the bay), total concentrations of PAH varied from 0.381-2.358 ppm (Table 1). The lowest was naphthalene (0.177 ppm), whereas the highest concentration was benzo (b) fluoranthene (0.657 ppm).

In the middle of the bay (zone 2), total concentrations of PAH varied from 0.670-1.768 ppm (Table 2). The lowest was acenaphthene (0.087 ppm). whereas the highest concentration was chrysene (0.271 ppm).

In off bay zone, total of PAH content ranged from 0.192-1.394 ppm (Table 3). The lowest concentration was Acenaphthene (0.088 ppm), whereas the highest was Chrysene (0.271 ppm).

In east-coast of the bay (zone 4), total of PAH content ranged from 0.192-1.394 ppm (Tabel 4). The lowest concentration was Acenaphthene (0.088 ppm), whereas the highest was Chrysene (0.271 ppm).

Table 1. The concentration of PAH compounds in sediment (ppm), in the inner coast of the bay (zone 1)

PAH Compound	Concentration (ppm)			
	TB 1	TB 2	TB 3	TB 4
Naphthalene (N)	0.192	0.192	0.177	0.192
Anthracene (AN)	0.189	ud	0.191	0.189
Fluoranthene (FL)	0.248	ud	0,298	ud
Pyrene (PY)	0.233	ud	0.266	ud
Chrysene (C)	0.272	ud	0.518	ud
Benzo_(b)_fluoranthene (BbF)	0.204	0.185	0.549	ud
Benzo_(a)_pyrene (BaP)	0.214	0.188	0.657	ud
Total PAH	1.551	0.565	2.358	0.381

Note: ud = undetected

Table 2. Concentrations of PAH compounds (ppm) in sediment (ppm), in the middle of the bay (zone 2)

PAH compound	Concentration (ppm)							
	TB 5	TB 6	TB 7	TB 8	TB 9	TB 10	TB 11	TB 12
Naphthalene	0.189	0.191	0.191	0.191	0.192	0.189	0.188	0.189
Acenaphthene	0.088	0.087	0.088	0.087	ud	0.088	0.088	0.088
Fluorene	0.178	ud	ud	0.178	ud	ud	0.178	0.178
Phenanthrene	0.195	0.195	0.195	0.195	ud	ud	ud	ud
Anthracene	ud	ud	ud	ud	ud	ud	0,190	0,190
Fluoranthene	0.247	0.247	0.247	0.247	0.247	0.247	0.247	0.247
Pyrene	0.231	0.231	0.231	0.231	0.231	0.231	0.231	0.232
Chrysene	0.271	0.271	ud	ud	ud	0.271	0.271	0.271
Benzo (b) fluoranthene	0.183	ud	ud	ud	ud	ud	ud	ud
Benzo (a) pyrene	0.186	ud	ud	ud	ud	ud	ud	ud
Total PAH	1.768	1.223	0.952	1.129	0.670	1.216	1.393	1.394

Note: ud = undetected

Table 3. Concentration of PAH compounds (ppm) in sediment, outer of the bay (zone 3)

PAH compound	Concentration (ppm)			
	TB 13	TB 14	TB 15	TB 16
Naphthalene	0.191	0.190	0.190	0.190
Acenaphthene	ud	0.088	0.088	0.088
Fluorene	ud	0.178	ud	ud
Anthracene	ud	0.189	0.189	0.189
Fluoranthene	ud	0.247	0.247	0.247
Pyrene	ud	0.232	0.231	0.231
Chrysene	ud	0.271	ud	ud
Total PAH	0.191	1.394	0.945	0.945

Note: ud = undetected

Table 4. The concentration of PAH compounds (ppm) in sediment, east-coast of the bay (zone 4)

PAH compound	Concentration (ppm)								
	TB 17	TB 18	TB 19	TB 20	TB 21	TB 22	TB 23	TB24	TB25
Naphthalene	0.191	0.183	0.186	0.19	0.192	0.192	0.192	0.192	0.192
Acenaphthene	0.088	0.088	0.088	0.088	ud	ud	ud	ud	ud
Fluorene	ud	ud	0.178	0.178	ud	ud	ud	ud	ud
Anthracene	ud	0,190	0,190	0.189	0.189	ud	ud	ud	ud
Fluoranthene	ud	ud	0.247	0.247	ud	ud	ud	ud	ud
Pyrene	ud	0.231	0.232	0.231	ud	ud	ud	0.231	ud
Chrysene	ud	ud	0.271	0.271	ud	ud	ud	ud	ud
Total PAH	0.279	0.502	1.202	1.394	0.381	0.192	0.192	0.423	0.192

Note: ud = undetected

DISCUSSION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous contaminants in several environmental compartments. In coastal sediments, direct input of PAHs by atmospheric deposition or discharge of petroleum products is derived from riverine contribution of urban and industrial effluents as well as urban runoff containing PAHs from asphalt and car exhaust particles (Baek et al. 1991; Atal and Levendis 1995; Mu et al. 2014). In Banten Bay waters PAHs come from pyrogenic process, it might be come from discharge of industry process in the Banten mainland whenever organic substances are exposed to high temperatures under low oxygen or no oxygen conditions, such as destructive distillation of coal into coke and coal tar. Pyrogenics PAHs are generally could be found in greater concentrations in urban areas and in locations close to major sources of PAHs (Abdel-Shafy and Mansour, 2016). In other words, Banten Bay waters may be pyrogenic sources.

Naphthalene is a common compound found in each stations of the bay. According (USEPA 1984; Magi et al. 2002), naphthalene included of the 16 PAHs priority grouped into 2–3 rings low-molecular weight PAHs (LMW) (Deng et al., 2013; Li et al., 2015). Some

Table 5. Ratio of Low Molecular Weight (LMW)/High Molecular Weight (HMW)

Station	Ratio	Station	Ratio
TB1	0.325	TB13	0.191
TB2	0.515	TB14	0.463
TB3	0.167	TB15	0.494
TB4	0.381	TB16	0.494
TB5	0.581	TB17	0.279
TB6	0.633	TB18	5.424
TB7	0.497	TB19	0.856
TB8	1.362	TB20	0.861
TB9	0.402	TB21	0.381
TB10	0.370	TB22	0.192
TB11	0.890	TB23	0.831
TB12	0.860	TB24	0.831
		TB25	0.192

Note: <1 = Pyrogenic Perocess, >1 = Petrogenic Process

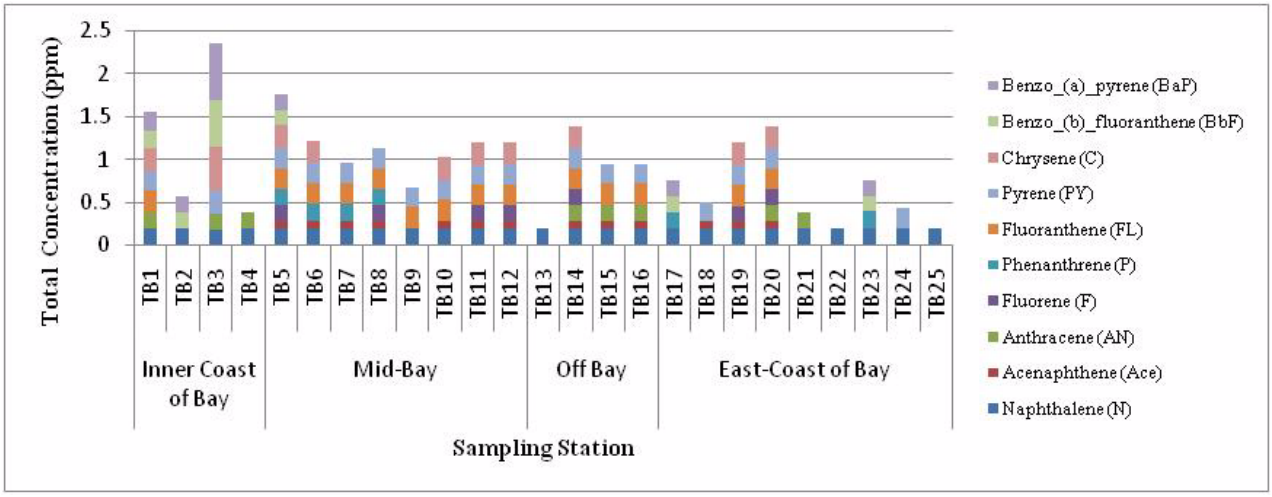

Figure 2. Distribution of ten compounds and total concentration of PAHs (ppm) found in Banten Bay

of others compounds of PAH, such as acenaphthene, anthracene, fluoranthene, fluorene, phenanthrene and pyrene, may be come from manufacture of pigment, dyes, plastics, pharmaceutical, resin, and other polymers. A few of industries in Banten could suggest to contribute PAH compounds.

Station 3 has the highest concentration of PAH in Banten Bay due to close to river mouth of Karang Antu and Banten industry zone (see Figure 2). This pollutant could be an accumulation site from land runoff, anthropogenic activities, domestic and industrial waste. Meanwhile in other location, total concentrations of PAHs are relatively simliar among in the middle, outer and east coast of the bay.

CONCLUSION

As many as 10 of the 16 priority pollutant PAH have been identified in the Banten Bay. The most common PAHs was naphthalene, while several important PAHs were Acenaphthene, Anthracene, Fluorene, Pyrene, Chrysene, benzo (b) fluoranthene and benzo (a) pyrene. The high value of total PAHs concentration was found in the inner coast of the Bay (zone 1), while the other zones such as the middle, outer and east coast of the bay have relatively similar concentrations. These PAHs are mostly pyrogenic of origin.

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