Polycyclic Aromatic Hydrocarbon (PAHs) compound in seawater of Cimandiri river estuary, Pelabuhan Ratu

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Abstract. Polycyclic Aromatic Hydrocarbon (PAHs) is a polycyclic aromatic organic compound that is toxic to humans and aquatic organisms. This research aims to determine the level of pollution of PAH compounds in seawater at the estuary of Cimandiri River, Pelabuhan Ratu. This research was conducted in April 2017 by survey method. Seawater samples were taken using a water sampler at 15 research stations. The levels and types of PAHs compounds were determined using Gas Chromatography-Mass Spectrometer (GC-MS), and PAHs sources with individual ratios diagnose. The results showed that seawater in the Cimandiri River Estuary still relatively low from contamination of PAH compounds. The type of PAH in seawater at the estuary of the Cimandiri River is dominated by low molecular weight naphthalene compound. PAH contained in seawater at the estuary of the Cimandiri River possibly comes from various sources, likely oil spills, burning petroleum, and combustion of organic compounds. PAH content in seawater of Cimandiri River estuary relatively small and still within the criteria for marine organism life state by The State Ministry Office for Life Environment.

1. Introduction
Pelabuhan Ratu, sub-district of Sukabumi regency, West Java is a tourist area in which the relatively large Cimandiri river, in the eastern partflows. This river possibly carries waste of human activities from land to marine environment and it includes toxic materials such as Polycyclic Aromatic Hydrocarbons (PAH). Polycyclic aromatic hydrocarbon (PAH) contamination is a major hazard for aquatic life in marine sediments, especially those close to anthropogenic sources [1][2]. These hydrophobic, persistent and ubiquitous environmental pollutants consist of several cyclic aromatic chains, and more than 100 different chemical structure formed during incomplete combustion of coal, oil and gas, waste, and other organic substances [3]. The PAH, naturally, derive from two sources; i.e. natural and anthropogenic sources. Natural sources include forest and grassland fires, oil seepage, volcanoes, chlorophyll plants, fungi, and bacteria, while those of anthropogenic sources are petroleum, power generation, incineration, home heating, coal, black carbon, asphalt, and combustion engines [4].

PAH levels derived from natural processes are generally lower than anthropogenic sources [5]. Many researches showed that PAH contaminations in the sea such as the coastal, estuary, and continental bed sediments are relatively high compared to anthropogenic inputs [6]. Research in the East China Sea found high levels of PAH at stations near the coast [7][8]. Once in marine environment, PAH will be
transferred and accumulated in marine organisms due to undigested in the body. PAH compounds that settle to the bottom of the waters are very toxic to aquatic organisms. The accumulation of PAH in green shellfish of Jakarta Bay has been reported although they were insignificant levels with regard to this safety for consumption [10] [11]. Many research results indicate that PAH can cause cancer and mutagenic effects in organisms [9].

This study is to determine the levels, types, and the sources of PAH, in the estuary of Cimandiri River, Pelabuhan Ratu concerning marine life. The will provide information for management of coastal and marine environment of Pelabuhan Ratu with regard to the quality status of marine resources.

2. Method

2.1. Time and Research Place
This research was conducted at the estuary of the Cimandiri River Pelabuhan Ratu, West Java in April 2017 (Figure 1). As many as 15 research sites determined by the Geographic Position System (GPS) are located in the estuary area of the Cimandiri River (in front of the power plant).

![Figure 1. Research sites at the estuary of Cimandiri River](image)

2.2. Sample Analysis
The materials used for analysis are seawater samples, chemicals: DCM (dichloromethane), sodium sulphate, diethyl ether, n-hexane, alumina powder type WB 5 basic SIGMA, silica powder type Merck 7754, ammonium paramolybdate, concentrated sulfuric acid, ascorbic acid, potassium antimonial tartrate, ammonium chloride, sulphanilamide, chloride acid, N-(1-Naphthyl) -ethylenediamine dihydrochloride, copper sulphate, metol, oxalic acid, and distilled water. All chemicals used are pro analysis (pa). The equipment used in this study were GC-MS, column chromatography, Soxhlet, rotary vapor, analytical scales (sartorius), vacuum pump, Shimadzu UV Vis spectrophotometer, Horiba U7 Water Checker, and glass tools. Sample was analysed using the Standard Operation Procedure (SOP) of the Organic Chemistry Laboratory P2O-LIPI (2013). Seawater samples were collected using an aluminium scoop, then put in a brown bottle and stored in an icebox. In the laboratory, 1 litter of 2.5 litters vacuum pump filtered seawater was extracted with 40 ml n-hexane in a Separatory funnel, for about 3 minutes shaking. The extract was passed to 0.45micron GFC filter paper and Na2SO4 powder filled funnel for collection. Re extraction with 40 ml and 60 ml of n-hexane, respectively, was carried out to collect 100
ml extract sample). Furthermore, these extracts were concentrated by evaporating with a rotary vapor tool until 1 ml.

The sample was cleaned up using a glass wool and Merck 7754 silica powder filled chromatography column and eluted by 5 ml of DCM (dichloromethane) for fraction 1 (F1), then eluted by 15 ml of the (40:60) DCM: Pentane mixture solution for fraction 2 (F2). The F2 was reevaporated in the water bath to reach 2 ml and put in the vial.

PAH levels in seawater was measured using Thermo Scientific Trace 1310 mass spectrometer gas chromatography, Model: trace 1310 ISQ LT. Detector: single quadrupole mass spectrometer (320 °C). Inlet: 260°C (split less) temp. Column: Thermo TR-5, Length: 30 m; ID: 0.25 mm; Film: 0.25 µm. Oven: 50°C (0.5 min), 160°C (14 min), 290°C (13 min), 300°C (4 min). Gas system: Helium 1.2 ml / min (constant flow); Split flow 10 ml / min; Split less time 0.5 min. The results are expressed in µg / L (ppb) for seawater. The PAH standard used is QTM PAH MIX, this standard covers all types of PAHs (16 types) produced by SUPELCO-USA.

2.3. Equipment Validation
Prior to the analysis with GCMS, the instrument validation was firstly performed by making a standard curve in series with 5 concentrations, respectively 3, 6, 12, 24, and 48 ppb. Each standard solution consists of 16 types of PAH compounds. The R2 values of each PAH compound from the standard solution were: Naphthalene (0.929), Acenaphthylene (0.956), Br-Naphthalene (0.966), Acenaphthene (0.972), Fluorene (0.964), Anthracene (0.963), Phenanthrene (0.963), Fluoranthene (0.955), Pyrene (0.945), B (a) Anthracene (0.949), Chrysene (0.945), B (k) Fluoranthene (0.944), B (a) P (0.952), Ind (1,2,3-Cd) P (0.927), Db (ah) Anthracene (0.953), and B (ghi) Perylene (0.832). The RSD of each PAH compound was 0.0%. The R2 and RSD values indicated that the measurement procedure was valid.

2.4. Data Analysis
Data were analyzed to provide information for management of coastal and marine environment of Pelabuhan Ratu regarding the quality status of marine resources. The source of PAH was traced using the ratio diagnosis method [14]. The ratio method was used because of differences in the thermodynamic stability of each PAH compound [15].

Table 1. Diagnostic method of individual PAH ratio [14]

| Pollutant Sources | D1 | D2 | D3 | D4 | D5 | D6 | D7 | D8 |
|-------------------|----|----|----|----|----|----|----|----|
| Oil              | >10| <1 | <0.2| <0.4| 0.6-0.9| <0.1| <0.1| <0.2|
| Burning oil      | -  | -  | 0.2-0.5| 0.4-0.5| >0.1| -  | -  |
| Organic Burning  | <10| >1 | >0.5| >0.5| <0.2| 0.1| >0.1| >0.35|
| Oil mix and burning of organic matter | 0.4-0.6| 0.1| - | 0.2-0.35|

There are several ratios of PAH compounds used, namely: Phenanthrene/Anthracene (D-1), Fluoranthene / Pyrene (D-2), Indeno[123-cd] Pyrene/ (Indeno[123-cd] Pyrene + Benzo (ghi) Perylene ratio) (D-3), Fluoranthene / (Fluoranthene + Pyrene) (D-4), Benzo (a) Pyrene / (Benzo (a) Pyrene + Chrysene) (D-5), Anthracene / (Anthracene + Phenanthrene) (D-6), Anthracene / 178 (D-7) and Benzo (a) Anthracene / 228 (D-8). The data were analysed in a descriptive analytical manner by comparing with the results of other studies and sea water quality standards for marine biota.
3. Result and Discussion

3.1. Result

3.1.1. Polycyclic Aromatic Carbon. The levels and types of Polycyclic Aromatic Hydrocarbons (PAH) in seawater in the waters of the estuary of the Cimandiri River are presented in Tables 2 and 3. Total levels of low molecular weight (BMR) PAH range from 0.0001-0.0103 ppb. The highest total PAH content was found at the Station 4, the lowest at the Station 2. This low molecular weight PAH compound was dominated by Naphthalene and was found at all stations, Acenaphthylene undetected at all stations, Acenaphthene was found at the Stations 4, 10, 11, 12, 13 and 14, Fluorene is found at the Station 8 and Station 13, Phenanthrene is found at the Stations 8, 10, 12, and 14, Anthracene is found at the Stations 1, 3, 4, 7, 8, 9, 10, 12, 13, 14 and 15.

| No | PAH                  | St.1     | St.2     | St.3     | St.4     | St.5     | St.6     | St.7     | St.8     |
|----|----------------------|----------|----------|----------|----------|----------|----------|----------|----------|
|    | Low Molecular Weight (LMW) |          |          |          |          |          |          |          |          |
| 1  | Naphthalene          | 0.0003   | 0.0001   | 0.0011   | 0.009    | 0.0004   | 0.0003   | 0.0005   | 0.0077   |
| 2  | Acenaphthylene       | NF       | NF       | NF       | NF       | NF       | NF       | NF       | NF       |
| 3  | Acenaphthene         | NF       | NF       | NF       | 0.001    | NF       | NF       | NF       | NF       |
| 4  | Fluorene             | NF       | NF       | NF       | NF       | NF       | NF       | NF       | 0.0004   |
| 5  | Phenanthrene         | NF       | NF       | NF       | NF       | NF       | NF       | NF       | 0.0013   |
| 6  | Anthracene           | 0.0001   | NF       | 0.0003   | 0.0003   | NF       | NF       | NF       | 0.0002   |

Table 2. Types and levels of total PAH in seawater at the estuary of the Cimandiri River

| No | PAH                  | St.9     | St.10    | St.11    | St.12    | St.13    | St.14    | St.15    |
|----|----------------------|----------|----------|----------|----------|----------|----------|----------|
|    | Low Molecular Weight (LMW) |          |          |          |          |          |          |          |
| 1  | Naphthalene          | 0.0005   | 0.0013   | 0.0013   | 0.0013   | 0.0019   | 0.0010   | 0.0013   |
| 2  | Acenaphthylene       | NF       | NF       | NF       | NF       | NF       | NF       | NF       |
| 3  | Acenaphthene         | NF       | 0.0001   | 0.0004   | 0.0003   | 0.0004   | 0.0002   | NF       |
| 4  | Fluorene             | NF       | NF       | NF       | NF       | NF       | NF       | NF       |
| 5  | Phenanthrene         | NF       | 0.0001   | NF       | 0.0002   | NF       | 0.0002   | NF       |
| 6  | Anthracene           | 0.0001   | 0.0001   | NF       | 0.0002   | 0.0014   | 0.0002   | 0.0002   |

| Total Levels | 0.0006 | 0.0015 | 0.0017 | 0.0020 | 0.0040 | 0.0016 | 0.0015 |

| Number of types | 2 | 4 | 2 | 4 | 4 | 4 | 2 |

3.2. Discussion

The levels and types of Polycyclic Aromatic Hydrocarbons (PAH) in seawater in the waters of the estuary of the Cimandiri River are presented in Tables 2 and 3. Total levels of low molecular weight (BMR) PAH range from 0.0001-0.0103 ppb. The highest total PAH content was found at the Station 4, the lowest at the Station 2. This low molecular weight PAH compound was dominated by Naphthalene and was found at all stations, Acenaphthylene undetected at all stations, Acenaphthene was found at the Stations 4, 10, 11, 12, 13 and 14, Fluorene is found at the Station 8 and Station 13, Phenanthrene is found at the Stations 8, 10, 12, and 14, Anthracene is found at the Stations 1, 3, 4, 7, 8, 9, 10, 12, 13, 14 and 15.
PAH with high molecular weight, Fluoranthene is only found at the Station 3, 4, 7, 8, 10, and 13. Pyrene was found at the Stations 3, 4, 7, 13. B(a) Anthracene and Chrysene are not found at all stations, B (b) Fluoranthene is only found at the Station 10. B(a) Pyrene is found at the Stations 1, 13, 14, and 15, Indeno (123-cd) Pyrene, Dibenzo (ah) Anthracene, and Benzo(ghi)Perylene is not found at all station.

3.2. Discussion

3.2.1. Polycyclic Aromatic Hydrocarbon. The level of total PAH (LMW + HMW) in seawater ranges from undetected to 0.0103 ppm, showing lower than that mentioned in Threshold Value (NAV) for [12] for marine biota (3 ppb), and hence, possibly not harmful for the marine life. Total PAH levels in March 2011 at 17 research stations in Jakarta Bay ranging from 106.61 to 474.68 ppb [16]. Total PAH levels in Jakarta Bay in July-August 2015 ranging from NF-0.081 ppm [17], and in Klabat Bay, total PAH levels in March 2006 ranged from 0.375 to 44.486 ppb, 1.392-27.826 ppb in the month July [18]. Furthermore, The total PAH content in the Timor Sea ranged from 54.46-213.70 ppb[19].

From the table above, it can be seen that the ratio between low molecular weight PAH levels and high molecular weight. The LMW/HMW ratio at stations 3, 4, 7, 8> 1 indicating petrogenic sources, while the other stations the PAH comes from pyrogenic sources (LMW/HMW ratio < 1).

The source of origin of PAH contamination compounds in waters can come from various activities, both natural activities (oil seepage, forest fire smoke, volcanic eruptions) or anthropogenic sources (industrial activities, transportation, and household activities) [9]. PAH molecules with large molecular weights (PAH> 3 benzene rings) usually come from incomplete combustion (pyrogenic) whereas PAHs with small molecular weights (PAHs with 2-3 benzene rings) are very dominant in petroleum products (petrogenic) [20]. The ratio diagnostic method was carried out because of differences in the thermodynamic stability of each PAH compound [15].

Table 3 shows that the D1 value was only found in two stations, Station 8 and Station 14, whose values were 6.5 and 1.0, respectively. This value is <10, which means that PAH comes from the combustion of organic compounds. D2 values are found at four stations, namely Stations 3, 4, 7, 13, whose values are 2, 1, 0.5, and 1 respectively. The value of D2 at Stations 3, 4, and 13> 1, this value indicates the PAH contained at Station 3, 4, and 13 it comes from petroleum, while at Station 7 the value of D2 <1, which means that PAH comes from the combustion of organic compounds. The values of D4 at Stations 3, 4, 7, 8 and 13 are 0.6, 0.5, 0.3, 1 and 1. The values of D4 at Stations 3, 8, and 13 are> than 0.5 which means PAH comes from the combustion of organic compounds, while at Station 4 the value of D4 is in the range 0.4-0.5, which means that PAH comes from burning oil, and at station 7 the value of D4 is <0.4 which means that PAH comes from petroleum. The value of D5 at Stations 1, 13, 14, and 15 is 1.0 respectively, this value is close to 0.9. The value of D5 with a value range of 0.6-0.9 indicates
that PAH comes from petroleum, considering that the value of 1.0 is closer to 0.9, it is predicted that PAH will come from an oil spill. The values of D6 at Stations 8, 9, 10, 12, 13, 14 and 15 are 0.133, 1.0, 0.5, 0.5, 1.0, 0.5 and 1.0, respectively. These values are > 0.1 which means the PAH comes from burning petroleum. Overall, the results showed that the type of PAH in seawater at the estuary of the Cimandiri River was dominated by Naphthalene (PAH with low molecular weight), while other types were almost undetectable.

Table 3. Diagnosis of Ratio of Individual PAH Levels in Seawater at the estuary of the Cimandiri River

| St | D1 | D2 | D3 | D4 | D5 | D6 | D7 | D8 |
|----|----|----|----|----|----|----|----|----|
| Phe/Ant | Flu/Pyr | In(123-cd)P/In(123-cd)P +B(ghi)P | Flu/(Flu+Pyr) | B(a)P/(B(a)P+Chr) | Ant/(Ant+Phe) | Ant/178 | B(a)A/228 |
| 1  | 0  | 0  | 0  | 0  | 1  | 0  | 0  | 0  |
| 2  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  |
| 3  | 0  | 2  | 0  | 0.6| 0  | 0  | 0  | 0  |
| 4  | 0  | 1  | 0  | 0.5| 0  | 0  | 0  | 0  |
| 5  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  |
| 6  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  |
| 7  | 0  | 0.5| 0  | 0.3| 0  | 0  | 0  | 0  |
| 8  | 6.5| 0  | 0  | 0  | 0  | 0.133| 0  | 0  |
| 9  | 0  | 0  | 0  | 0  | 0  | 1  | 0  | 0  |
| 10 | 1  | 0  | 0  | 0  | 0  | 0  | 0  | 0  |
| 11 | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  |
| 12 | 1  | 0  | 0  | 0  | 0  | 0.5| 0  | 0  |
| 13 | 0  | 1  | 0  | 1  | 1  | 1  | 0  | 0  |
| 14 | 1  | 0  | 0  | 0  | 1  | 0.5| 0  | 0  |
| 15 | 0  | 0  | 0  | 0  | 1  | 1  | 0  | 0  |

The results of the PAH individual concentration ratio analysis above show that the PAH contained in seawater comes from various sources, namely petroleum, burning petroleum, and combustion of organic matter. PAHs can come from the air or soil which will affect water quality.

4. Conclusion
That the PAH seawater in the Cimandiri River Estuary was still relatively low and most of the undetected. The type of PAH in seawater at the estuary of the Cimandiri River is dominated by low molecular weight naphthalene compound. PAH contained in seawater at the estuary of the Cimandiri River possibly comes from various sources, likely oil spills, burning petroleum, and combustion of organic compounds.

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Acknowledgement
Thank you to Mrs. Ricky Rositasari as a research coordinator, Mr. Herman Rahayaan, and Tolak Yogaswara who have helped in sampling and analysis at the organic chemistry laboratory P2O-LIPI Jakarta.