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# The Characteristics of Naphthalene and Phenanthrene as Polycyclic Aromatic Hydrocarbons (PAH) Compounds in The Marine Sediment of Tanjung Bayang Beach in Makassar

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**Abstract.** This research is an exploratory study that aims to determine the levels of naphthalene and phenanthrene PAH compounds and the level of pollution contained in the marine sediments of The Tanjung Bayang Makassar Beach. The steps of this study include sample preparation, extraction using the socletation method with n-hexane: dichloromethane solvent, fractionation using Chromatography Column Flash (CCF) methods and determination of naphthalene and phenanthrene levels using the HPLC instrument. The results of the PAH fraction in the form of yellow powder were identified using HPLC by comparing the retention time of the standard chromatogram of naphthalene and phenanthrene with of the chromatogram sample. In this study, the concentration of naphthalene and phenanthrene PAH compounds was observed in three stations coded as TB1, TB2 and TB3. TB1 Station has the highest PAH level where the naphthalene content reaches 165.5450 ppm and phenanthrene content is 934.3698 ppm with a total content of 1099.9148 ppm. TB2 Station has the lowest PAH with 85.4858 ppm naphthalene level and phenanthrene at 509.0401 ppm with a total of 594.5259 ppm. TB3 station is at 120.8489 ppm naphthalene level and phenanthrene levels of 693.9341 ppm with the total levels of 814.7832 ppm. The marine sediments PAH content in Tanjung Bayang Makassar Beach is at moderate-high pollution levels.

**Keywords:** *Characteristics, Marine Sediment, PAH, naphthalene, phenanthren*

## 1. Introduction

Indonesia is an island nation consisting around 17.504 either small or large islands. The coastal and marine areas of Indonesia have an enormous natural wealth providing various environmental services such as fisheries, coral reef and mangrove ecosystems, as well as tourism. Tanjung Bayang, as one of tourist attractions in Makassar, is a coastal area managed by the locals and the governments. It is located in Tanjung Merdeka sub-district, Tamalate district, Makassar, South Sulawesi, with about 456.1 metre-length and 202.828 m<sup>2</sup>-width beach [1].

Locals' activities such as the number of hotels, resorts and housings which allegedly dispose the wastewater to the beach have become the source of contaminants. Moreover, Tanjung Bayang beach is also located near the sewerage system and the incineration spot of Tanjung Merdeka district. The pollutant source channeling into the sea will eventually precipitate to the bottom of the sea and mix in



with the marine sediments. One of the dangerous pollutants is polycyclic aromatic hydrocarbons (PAHs) compounds [2].

The existence of PAHs in nature is originated either from natural or anthropogenic sources. Natural sources of PAHs are plants chlorophyll, fungus, and bacteria while anthropogenic sources can be derived from the combustion of organic compounds at high temperatures such as of motor vehicles [3].

PAHs are widespread contaminants, stable in the environment, and one of the toxic, mutagenic, carcinogenic and hydrophobic pollutants. The PAHs precipitating into the bottom of the sea are highly toxic to aquatic organisms. Recent research show that PAHs resulted from human activities can cause cancer and mutagenic effects on organisms [4]

Many of research about PAHs in the aquatic environment have been conducted, but for the distribution of the PAH compounds in Indonesia, especially in South Sulawesi, is still limited. A research regarding the PAH compounds in Indonesia was conducted by Ahmad, examining the content of the PAHs in Teluk Jakarta. He found that the PAHs level either on the seawater or the sediments is relatively high ranged from 1.92 to 64.241 ppm and the total of 107.931 ppm [5]. Moreover, Edward examines the content and the source of PAHs containing in the sediment water of Pakis Jaya, Karawang District and the result shows that the substances are ranged from decontaminated to contaminated at a moderate level (PAHs at 0.113 – 0.862 ppb) and dominated by high molecular weight PAHs [6,7].

Naphthalene and phenanthrene, as parts of PAHs, which are difficult to be degraded, will be accumulated in the environment, then get into the food chain causing problems for both animals and humans ecosystem. Therefore, the source and the spread of naphthalene and phenanthrene PAHs in the environment must be monitored frequently. One of the areas that is prone to pollution by naphthalene and phenanthrene is the coastal area of Tanjung Bayang Makassar, due to the fact that there are many activities conducted in such location. Therefore, the authors aim to analyze the naphthalene and phenanthrene PAH compounds contained in the sediment around Tanjung Bayang Beach.

## 2 Methodology

### 2.1 Sample Preparation

Sediment samples from Tanjung Bayang beach were collected on the same day in three different spots by using the Van Veen grab. The samples were taken from a depth of 120 cm. The collected sediments were put in a plastic container then wrapped with aluminum foil to prevent contamination. The dry-air drying was done at room temperature then the dried samples were crushed and sieved at 60 Mesh [8].

### 2.2 Post-sampling Procedure

The light intensity was measured at the laboratory using a refractometer. The acidity of sea water was tested using a pH meter. The moisture content of the samples was also measured.

### 2.3 The Extraction of Sediment Samples

The samples were extracted by applying the extraction method used by [8]. Each 25 gr dried, sieved sediment was wrapped with filter paper and then put into the Soxhlet with 75ml DCM and 75 ml n-hexane solvent for 8 hours. The extracted organic matter was further filtered and collected in a bottle and then vaporized by the evaporator until the each sample dries. The weight of the organic matter was measured.

### 2.4 Sample Fractionation

The extracted organic matter was then fractioned by applying Press Column Chromatography (PCC) method. The adsorbent used was a 70-230 Mesh silica gel, alumina and anhydrous sodium sulfate. Each adsorbent was inserted into the column, with 7 cm height of alumina, 7cm silica gel, and 1cm anhydrous sodium sulfate. The column was then washed with n-hexane repeatedly until the stationary phase of the column is saturated and free from air bubbles. The organic matter was applied with 20mL

n-hexane and 20 mL DCM solvents. The aliphatic fraction decomposes in the n-hexane solvent and the PAHs fraction decomposes in the DCM solvent. Following that, each fraction of DCM was dried and measured to determine the mass of compounds.

### 2.5 PAHs Analysis

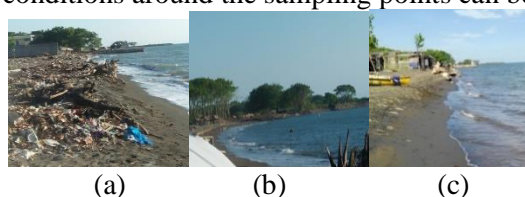
Analysis of PAHs level in the sediment was done by utilizing HPLC. The aromatic fraction (PAHs) obtained from each sample was dissolved with 1000  $\mu$ L of acetonitrile solvent and analyzed using HPLC instrument.

The concentration of the sample was calculated using the equation of standard calibration curve which has been provided beforehand. To ensure the PAH compounds in the sample, the retention time of the standard chromatogram was compared to the retention time of the sample chromatogram. The obtained data of standard chromatogram in the form of the width of the area determine the value of a, b and r by comparing the concentration of the sample (ppm) to the width of the area by using the equation of linear regression  $y = a + bx$ . The results of the chromatogram of the sample in the form of the width of area (y) are included in the regression equation linear [9].

## 3 Results and Discussion

### 3.1 Sampling Condition

The sediment samples were collected from 3 locations on The Tanjung Bayang Beach using Van Veen Grab. Each determined spot was expected to represent its area. The first spot, coded as TB<sub>1</sub>, is located near the sewerage system and the incineration spot of Tanjung Merdeka district. The second spot, TB<sub>2</sub>, is an area that has not been functioned. The third spot, TB<sub>3</sub> station, is around the residential areas and tourism sites. The conditions around the sampling points can be seen in figure 1.



**Figure 1.** the condition of each station (a) TB<sub>1</sub> (b) TB<sub>2</sub> (c) TB<sub>3</sub>

The condition of the seawater around Tanjung Bayang and its pollution level can be affected by several factors such as temperature, acidity, and refractive index. The seawater conditions on Tanjung Bayang Beach are shown on Table 1.

**Table 1.** Seawater condition at sampling collection

Location	Temperature (°C)	pH	The refractive index (% Brix)	Moisture content in average (%)
Spot I (TB <sub>1</sub> )	31.5	8.1	4.367	4.4670
Spot II (TB <sub>2</sub> )	31	8.1	4.337	3.2787
Spot III (TB <sub>3</sub> )	31	8.1	4.310	4.9652

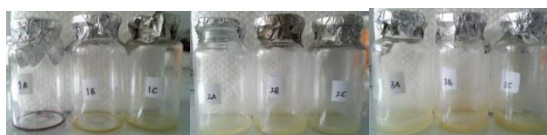
The seawater temperature when collecting samples is average 31 °C. The degradation of PAH in the environment caused by sunlight is influenced by the temperature of its environment. High temperature will result in the evaporation of PAHs while low temperature will result in the distribution of PAHs in the sediment [10]. The temperature of Tanjung Bayang Beach is at the low level indicating that the PAHs pollutant is distributed into the sediment.

Beside the temperature, the degree of acidity (pH) also affects the presence of PAH compound in an environment. Based on the results of the acidity measurement in Tanjung Bayang beach, each spot is at 8.1 pH. The presence of microorganisms which decompose the PAHs in the environment is strongly influenced by the level of acidity. It is also stated by [11] that organisms responsible for the degradation of PAHs exist in the environment which is extremely acidic (pH 2.0). Therefore it can be concluded that the process of PAHs degradation in Tanjung Bayang beach environments by microorganisms cannot be performed because of the acidity status. Hence, the natural PAHs exist there.

The third condition which is observed is the index of refraction of Tanjung Bayang seawater. The refractive index is directly related to the level of turbidity, i.e. the higher the refractive index, the higher the turbidity level is in a sample. The turbidity level indicates the level of pollution in the environment. The level of the refractive index in Tanjung Bayang beach is measured using a refractometer. A study conducted by [12] showed a correlation between the level of turbidity and the concentration of PAHs in seawater, where the higher the turbidity level, the higher the concentration of PAHs in the water. The refractive index measured at station TB<sub>1</sub>, TB<sub>2</sub> and TB<sub>3</sub> can be seen in Table 1. TB<sub>1</sub> has the highest refractive index, followed by TB<sub>2</sub> and TB<sub>3</sub>. Thus, it can be station TB<sub>1</sub> is the most polluted area followed by TB<sub>2</sub> and TB<sub>3</sub>.

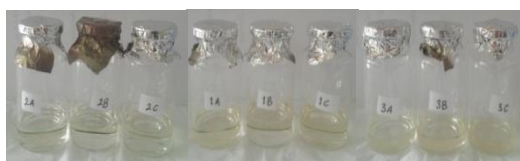
### 3.2 Extraction and Fractionation of Sediment Samples

The extraction of marine sediments was done with soxhletation method using n-hexane and DCM solvent. The process of extraction of was carried out for 8 hours with a heating temperature of about 70°C with 2 times circulation at average per hour. The results of the extraction were sieved and the filtrates were evaporated with a temperature of 45 °C and a speed of 50 rpm until the volume reached about 2 mL. The soxhletation method produces yellowish and greasy extract. According to Edward (2018), such extracts contain aliphatic and aromatic compounds. The obtained extracts are shown in Figure 2.



**Figure 2.** Extract of the dried marine sediment of Tanjung Bayang beach

The dried extract was fractionated to separate the aromatic and aliphatic compounds using flash Chromatography Column Flash (CCF) with silica gel, alumina powder and sodium sulfate at the stationary phase. The aliphatic and aromatic fractions were separated based on the polarity. The non-polar aliphatic fraction is attached to the solvent n-hexane while the semi-polar aromatic fraction is attached to the DCM solvent. The PAHs fraction is pale yellow. According to [10], the color PAHs ranging from colorless, to white or pale yellow. The aromatic fraction resulting from CCF extraction is shown in Figure 3.



**Figure 3.** The aromatic fraction samples Tanjung Bayang beach sediment

### 3.3 Measuring PAHs Level in the Marine Sediment

The determination of the PAHs naphthalene and phenanthrene level utilizes HPLC SHIMADZU in the wavelength range of 280 nm – 389 nm, a temperature of 40-85°C, Isocratic pump method, and fluorescence detector with a flow speed of 0.5 mL per minute. The composition at the mobile phase consisting of acetonitrile; distilled water (aquades) with a ratio of 4:6 (v/v) [13]. On such composition, the retention time of naphthalene is 0.413 minutes while of phenanthrene is 3.038 minutes.

Based on the comparison of naphthalene and phenanthrene standard concentration to the with of the area, the PAHs standard curve. The determination of the PAHs naphthalene and phenanthrene level was setting a standard/calibration curve of naphthalene with various concentration that produces the correlation value (r) of 0.9992 with the equation of calibration curve  $y = 263449x - 1 \times 10^7$ . Standard phenanthrene shows the correlation value (r) of 0.9958 with the equation of calibration curve  $y = 467712x - 2 \times 10^8$ . The value of linearity is close to 1 indicating that there is a positive correlation between the levels of naphthalene and phenanthrene with the area of the chromatogram so that the linear regression equation can be used for quantitative analysis to calculate the naphthalene and phenanthrene level in the extracted sediments of Tanjung Bayang beach. Calculations of PAHs compound concentration from HPLC follows the calculation method by Aryani [14] in calculating the level of genistein from soybean seed extract using HPLC method and [8] in the calculating of the levels of PAHs in marine sediments. Having been measured and calculated, the levels of naphthalene and phenanthrene in the sediment Tanjung Bayang beach are shown on Table 2.

**Table 2.** The levels of naphthalene and phenanthrene on sea sediment samples

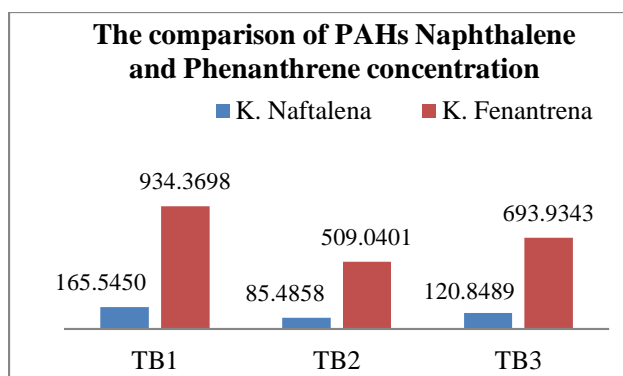
Sample Codes	Concentration	Concentration	Total (ppm)
	Naphthalene (ppm)	Phenanthrene (ppm)	
TB <sub>1</sub>	165.5450	934.3698	1099.9148
TB <sub>2</sub>	85.4858	509.0401	594.5259
TB <sub>3</sub>	120.8489	693.9343	814.7832

Table 2 shows the average levels naphthalene at station TB<sub>1</sub>, TB<sub>2</sub> and TB<sub>3</sub>, where the highest concentration of the PAHS naphthalene and phenanthrene is at the station TB<sub>1</sub>, followed by station TB<sub>3</sub>, and the lowest concentration is at station TB<sub>2</sub>.

Station TB<sub>1</sub> is an area with the highly contaminated PAHs with 1099.9148 ppm, and it is assumed that the PAHs are originated from the incineration system and the locals' activities which utilize motorized vehicles that can contribute to the amount of PAH in the sediment due to the incomplete combustion. Fuel oil used by and the result of the incomplete combustion is one of the sources of PAHs contamination [9]. Based on the total content of PAHS naphthalene and phenanthrene, station TB<sub>1</sub> is an area with high level of pollution.

Station TB<sub>2</sub> is an area which is slightly contaminated as the PAHs are in low level with a total content of PAH is at 594.5259 ppm, because there are not many activities around the area. The land around the sampling spot is still a vacant land that has not been used by the locals so the contamination of PAH in these areas is also low. It is suspected that PAHs contained in this area are originated from the motor vehicles around the area. Based on the total PAHs naphthalene and phenanthrene, the pollution at station TB<sub>2</sub> is at moderate level.

Station TB<sub>3</sub> is an area with moderate contamination, with 814.7832 ppm. The PAHs source in this area is supposedly derived from the locals' and tourists' activities around the beach as the main source of PAHs pollution. The types of PAHs in a neighborhood are originated from human activities. Based on the total content of PAHs naphthalene and phenanthrene, station TB<sub>3</sub> is at moderate level. Comparison diagram of naphthalene and phenanthrene in the sediment samples from Tanjung Bayang Beach is shown in Figure 4.



**Figure 4.** The comparison diagram of PAHs naphthalene and phenanthrene concentration contained in marine sediment in Tanjung Bayang Beach

The diagram above shows that at each station, the concentration of PAHs phenanthrene tend to be much higher compared to the naphthalene. This happens since phenanthrene with 3 benzene rings has a higher molecular weight than naphthalene with 2 benzene rings resulting that phenanthrene is more resistant to environmental degradation [14]. Moreover, the  $K_{OC}$  of phenanthrene is higher than  $K_{OC}$  of naphthalene (Table 1 thing. 11) which indicates the large amount of potential phenanthrene compared to naphthalene to be bound to organic carbon in soil and sediment by chemical.

PAH compounds with low molecular weight such as naphthalene and phenanthrene are originated from human activities such as housings, shipping and aquafarming [7]. Based on the criteria of the PAHs pollution level in the sediment according to [15], the level of pollution in Tanjung Bayang beach is categorized as medium to high level of pollution with total PAHs of 0-100 ppm.

Based on the results of this study, overall showed that the levels of PAHs in marine sediments in the coastal area of Tanjung Bayang have exceeded the quality standard set by the ministry of Environment on marine biota, i.e. at 0.003 ppm, and the levels of PAHs in the sediment which cause negative effects on the marine biota is 45 ppm [16]. Sediment sampling with limited number of stations i.e. 3 locations needs further research because it is only considered as introductory research and does not represent the levels of PAHs thoroughly.

#### 4. Conclusion

Based on the research conducted, it can be concluded that the levels of PAHs naphthalene and phenanthrene on TB<sub>1</sub> is at 1099.9148 ppm in total, TB<sub>2</sub> at 594.5259 ppm in total, and TB<sub>3</sub> at 814.7832 ppm. Station TB<sub>1</sub> is the most contaminated area while TB<sub>2</sub> is an area with low PAHs contamination. Moreover, based on the PAHs naphthalene and phenanthrene concentration, Tanjung Bayang beach is categorized in medium-high level of PAHs pollution.

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