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The Identification and Distribution Components of Polycyclic Aromatic Hydrocarbon Contaminants at the Port of Paotere, Makassar, South Sulawesi

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Abstract: The ASTM standard recommends that the 16 most common types of PAHs are found in petroleum processing activities, the chemical industry and marine loading ports. This research aims to identify and determine the distribution of PAHs contaminants at three sampling points of seawater around Paotere Port, Makassar, South Sulawesi, using the GC-MS instrument. Sampling point A is the center of Paotere Port activity, Point B with a radius of 3 km and point C with a radius of 6 km from the center of port activity. Sampling at each point was carry out at a depth of 100 cm above sea level. There are 10 PAHs identified at sampling point A and B, while at point C there are 8 components with relatively the same type of PAHs. The dominant PAHs components at each sampling point are relatively the same, namely at point A: Pyrene, Chrysene, Benz[a]pyrene and Dibenz(a,h)anthracene, point B: Pyrene, Chrysene and Benz(a)anthracene, while at point C only Pyrene. The total concentration of PAHs at point A: 4,217±.106 ppm, medium polluted category, at point B: 2,124±.087 ppm, medium polluted category and at point C: 1,264±.112 ppm, light polluted category.

1. Introduction

The port is one of the fulcrum for the transportation of ships and the center of loading and unloading activities that take place throughout the day. This condition places the port and its surrounding waters very vulnerable to being contaminated by various kinds of waste, especially the polycyclic aromatic hydrocarbons and heavy metals. Both types of waste are very toxic, carcinogenic and some even mutagenic [1,2]. Ocean currents that are influenced by salinity, wind speed, season cause the distribution of these dangerous components to be distributed over a wider water area, potentially having a negative impact on the life of the surrounding marine biota, even by the life cycle, PAH contaminants and heavy metals can target and affect human health even though they are not there is a direct relationship with the port and the surrounding waters [3,4,5].



The type, distribution pattern and level of exposure to PAH in the port area and surrounding waters need to be known and mapped for the purpose of minimizing the adverse impacts that may occur both on the marine biota in it and on human activities, especially fishermen in the exploration and exploitation of marine biodiversity, especially business, cultivation and fishing. Determination of contaminant status by identification, distribution and level of PAH contamination in the port area and its surroundings is important as an early effort to prevent the negative effects that this hazardous substance can cause, it can also be used as a reference for zoning by the local government in formulating policies and by fishermen in carrying out fishing and cultivation activities [6,7].

The Paotere port of Makassar City began to exist since the Dutch era about 4 centuries ago until now it is still a port for people's boats, Pinisi and Lambo types and a berth for various types of cargo ships. Long before the independence era, Paotere Port was used as one of the main ports for loading and unloading various types of agricultural, fishery, machinery and industrial goods such as cement from various regions of Eastern Indonesia for the destinations of other islands in Indonesia and even abroad [8,9]. Around the Port of Paotere there is the largest fish auction center in Makassar and South Sulawesi, so the role of Paotere Port is very strategic which is visited by many people from all over the archipelago. The strategic role of the Port of Paotere is a strong reason for conducting research aimed at identifying the types of contaminants, distribution patterns and levels of PAH exposure at a certain radius [10,11]. The research was conducted as an effort to produce data and information about the types and levels of contamination of toxic and carcinogenic substances, especially in areas that have a lot of contact with humans.

2. Materials and methods

2.1 Materials and equipment

The research materials consisted of samples of sea water, Na₂SO₄, dichloromethan (brand), methanol, alcohol, KOH pa, HCl pa, while the equipment used included polyethylene plastic bottles, pH meters, Turbidimeters, Conductometers, test kits, ice boxes, hot plates, magnetic stirrer, GPS, reflux set, condenser, thermometer, ultrasonic, electric vacuum pump, separating funnel, 2 µm filter paper, glassware set, GC-MS (Agilent 7890). The operating conditions for GC-MS: maximum temperature of 330°C, the increase in temperature of 10°C every 3 minutes, a Helium gas carrier, a speed of 130 mL / min, pressure 18.401 psi, capillary column [Agilent 19019S-436HP- 3 ms], dimensions of 60 mx 230 µm x 0.23 µm, separation 26,117 cm / sec and retention times of maximum 30 minutes.

2.2 Sampling

Seawater samples were obtained by means of a 600 mL volume polyethylene plastic bottle which had been labeled immersed in the body of water until the bottle sank to 100 cm above sea level, the bottle was opened and let the sea water enter until the entire bottle was full. The bottle is closed until it is tight, then the bottle is lifted from the water body and immediately put in an ice box. Seawater samples were taken in duplicate at three predetermined stations, in order to obtain 6 sample bottles which were all entered into the analysis laboratory. At the station, observation and recording of pH, salinity, sampling depth, sea water temperature and coordinate points were carried out. There are three station locations, namely station A at the activity center of Paotere Port, station B as far as ± 3 km from station A towards the outer sea and station C as far as ± 6 km from station A towards the outer sea. Detailed information about the station is presented in Figure 1

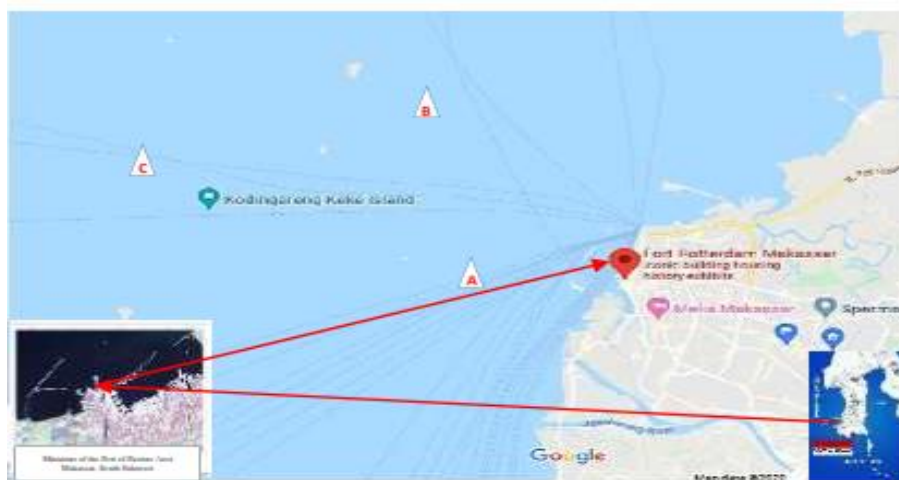


Figure 1. Seawater sampling locations at three stations around Paotere Port, Makassar, South Sulawesi

2.3 Sample preparation and measurement

Sample preparation was carried out by the procedure: sample A was obtained from station A, filtered using filter paper size of 2 μm on top of a vacuum pump. Sample as much as 100 mL at reflux for 1 hour and cooled. A total of 13 mL was extracted by inserting it into a separating funnel. In the separating funnel, 13 mL of dichloromethan were added and shaken for ± 13 minutes [12]. The process of drawing the PAHs component from the sample was carried out four times for each sample. The dichloromethane extract was put in a wattle and ready for analysis of PAHs components using GC-MS. The same process is carried out for sample B and sample C, respectively obtained from stations B and C. The concentration of each type of PAHs component in the sample is calculated using the equation:

$$\text{Conc. Comp. n} = \frac{\text{peak area component } n}{\text{standar peak area}} \times \text{Conc. standart} \times \text{multi factorial}, \dots\dots\dots [1]$$

3. Results and discussion

The physic-chemical characteristics of seawater sampling locations need to be known for the purpose of analyzing the level of contaminants of polycyclic aromatic hydrocarbons (PAHs) and other hydrocarbon components that have the potential to influence biogeochemical processes including the potential for remediation by biological, physical and chemical reactions that may occur. , including other marine biota activities. The pH, temperature, salinity, and depth of sample collection are variables that are seen as contributing to the various dynamics that occur in the sea, so measuring these variables is important to do to assist the analysis process.

Table 1. The Physic-chemical characteristics of the sampling sites

Sampling	Coordinate		Into sea level sampling (cm)	Temperature (°C)	pH	Salinity (‰)
	LS	BT				
station A	3°06'34.6"	119°23'09.3"	100	31	6,2	28,2
station B	3°06'23.4"	119°23'21.4"	100	29	7,1	31,4
station C	3°06'38.0"	119°23'19.9"	100	28	7,3	32,3

The water temperature at the three stations, namely station: A reached 31⁰ C, station B: 29⁰C and at station C at over 28⁰C. This situation illustrates that the activity that occurs in the area around point A is very dynamic, so it affects the surrounding sea water temperature. This condition is reinforced by the pH and salinity data of the waters at station A as the center of Paotere port activity. This situation indicates that the quality of the aquatic environment in Paotere Port is worse than in waters that are 3 -

6 km to the outside or the deep sea. This situation reflects that the low quality of waters in Paotere Port is influenced by ship traffic activities, loading and unloading activities, as well as the influence of household waste from the community living around the port. Traffic of various types of vessels and loading and unloading activities at the port is very vulnerable and contributes greatly to the contamination of hazardous and toxic substances [13].

According to the recommendations of the world environmental agency and ASTM America, it states that about 16 types of components of the PAHs class are very dangerous to living things in the exposed area. Figure 2, shows the measurement results of seawater samples obtained at station A, showing a chromatogram of 12 peaks of the component suspected of being PAHs. The results of the analysis found that there were 10 types of components in the PAH group and 2 peaks of which were polycyclic molecules of not aromatic hydrocarbon components.

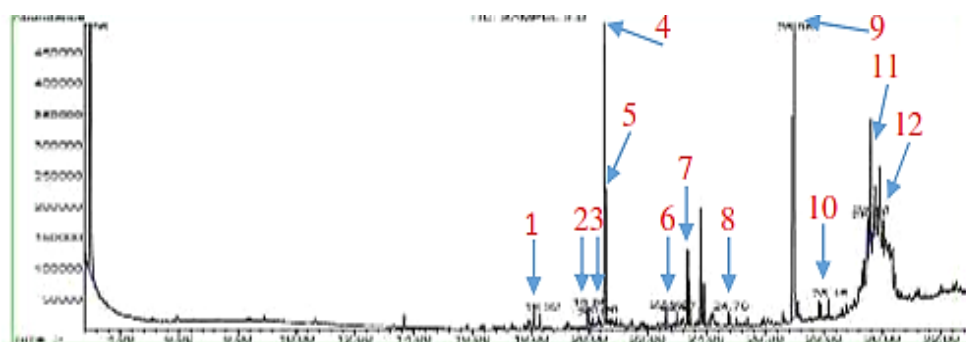


Figure 2. Chromatogram identification results of the PAHs component of sample A obtained from seawater at station A

Figure 3 is a chromatogram from GC-MS measurements of station B marine water samples. Among the visible peaks, only 11 peaks were successfully analyzed, 10 of which were components of the PAH group of hydrocarbons and 1 peak was a polycyclic non-aromatic hydrocarbon molecule. Comparing the peak height between the chromatograms of Figure 2 and Figure 3, shows that the concentration of the PAH component of sample A has a higher concentration, this can be seen in the abundance or peak of sample A is higher than the peak of sample B. The PAH component in sample A (Figure 2) is indicated by the successive peak numbers: 1-3; 5-10 and 12, while the peaks number 4 and 11 are polycyclic non-aromatic hydrocarbon molecules and the other peaks without numbers are non-cyclic hydrocarbon components and are also not aromatic groups, these results are not much different from the results in previous studies. [12,13].

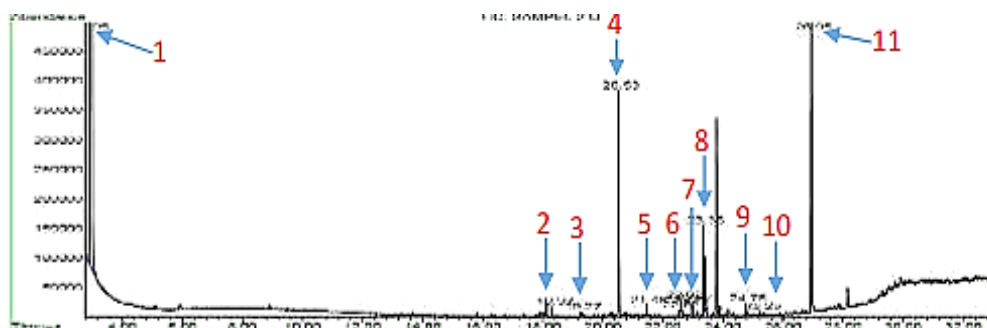


Figure 3. Chromatogram identification results of the PAHs component sample B obtained from seawater at station B

The chromatogram shown in Figure 3 with a total of 10 peaks, is indicated by the number of peaks respectively: 1-3 and 5-11 are PAH components, whereas peak number 4 is a polycyclic hydrocarbon

molecule of not aromatic type and there are 3 peaks without a number which are components of other hydrocarbons of non-polycyclic types and not aromatic types [6,14].

The chromatogram measurement results of GC-MS sample C, showed the number of relatively fewer peaks and the abundance or lower peak height, indicating that the PAH component in the sample was less with a lower concentration. There are 8 PAH components identified in sample C and 1 component is thought to be a non-aromatic polycyclic component, but these components have a high level of toxicity, so that if the two types of hydrocarbon components are combined with the same relative toxicity level and are dangerous, they are categorized as PAHs contaminants. Based on the retention time, it is indicated that the PAHs component in sample C is simpler than in samples A and B.

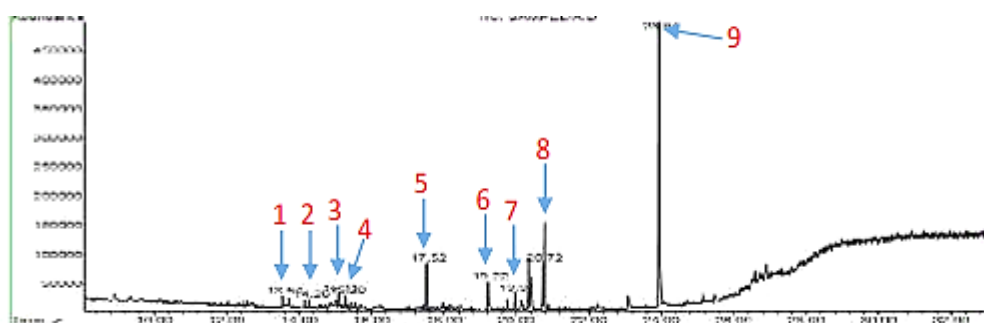


Figure 4. Chromatogram identification results of the PAHs component of sample C obtained from seawater at station C

Chromatogram analysis in Figure 4, shows that there are 8 peaks which are PAH components with peak numbers respectively: 1-3 and 5-9. Peak number 4 is a non-aromatic polycyclic molecule and \pm 7 peaks without number is a non-cyclic and not aromatic hydrocarbon component. Comparing the number of PAHs components and the abundance of each molecule between samples A, B and C, shows that the PAHs contaminants identified in sample A are more than samples B and C, as well as the abundance or concentration of each type of component, showing that the concentration of the PAHs components of the sample much higher than samples B and C, including the types of PAHs in sample A are more complex and very strong types of PAHs with more number of ring members. These results are understood that the influence of ship traffic and human activities in loading and unloading goods at the Port of Paotere has a strong contribution to the presence and high concentration of PAHs. Samples B and C are water obtained at a radius of 3 km and 6 km from the center of Paotere port activity (point A). The distribution of the PAHs components of samples A, B and C is relatively different. In general, it can be said that the marine environment around Paotere Port up to a radius of 6 km to the outer sea is relatively poor for fishing activities by fishermen, because it is suspected that the biota that lives in these waters is exposed to components of PAHs which are dangerous and not good for health [11,15].

The results of the analysis of each peak at the three stations, based on the data obtained, then the concentration of each type of PAH in the waters of the Port of Paotere can be calculated using the standard internal ratio and plotted in equation one. The data in table 2 shows that there are 10 types of PAH components contained in sample A with a high quality range (93–99)%, there are 4 peaks (nd) visible, not polycyclic hydrocarbon components and not PAH types and 2 peaks (nPc).) is a polycyclic hydrocarbon component but not an aromatic type. The number of PAH components identified in sample B was also 10 components with high quality in the range (97-99)%, there is 1 peak (nPc) which is a non-aromatic polycyclic hydrocarbon molecule and 3 peaks (nd) of non-polycyclic and non-aromatic hydrocarbons, whereas in sample C, 8 PAH components were identified with high quality in the range (96-99) %, 1 peak (nPc) was a polycyclic hydrocarbon component not a PAH type and 7 peaks (nd) a not polycyclic hydrocarbon component and also not a PAH type. The concentration of each PAH component in seawater at three stations is shown in Table 2.

Table 2. Identification and distribution of PAHs component contaminants from seawater samples around Paotere Port, Makassar, South Sulawesi

Type of PAHs	Retention time	Sampling location and Quality Component (%)		
		Station A	Station B	Station C
Naphthalene	9.925 ± .012	√ 95	√ 99	nd -
Acenaphthalene	14.612 ± .011	√ 99	√ 99	√ 99
Acenaphthene	15.174 ± .008	√ 98	√ 98	√ 96
Fluorene	16.820 ± .014	nPc	nPc	nPc
Anthracene	19.818 ± .011	√ 99	√ 99	√ 98
Phenanthrene	19.980 ± .008	√ 98	√ 98	√ 99
Fluoranthene	23.414 ± .015	nd	nd	nd
Pyrene	24.070 ± .009	√ 99	√ 97	√ 97
Benz(a)anthracene	27.580 ± .011	√ 98	√ 98	√ 96
Chrysene	27.692 ± .008	√ 99	√ 99	√ 98
Benzo(b)fluoranthene	30.494 ± .013	nPc	nd	nd
Benzo(k)fluoranthene	30.578 ± .012	nd	nd	nd
Benz[a]pyrene	31.300 ± .008	√ 98	nd	nd
Dibenz(a,h)anthracene	33.888 ± .015	√ 99	√ 97	√ 97
Indeno(1,2,3-cd)pyrene	33.878 ± .013	nd	nd	nd
Benzo(g,h,i)perylene	34.438 ± .009	nd	√ 98	nd -

Noted: sign √ = there is PAH; nd = non PAH detected; nPc = detected non-PAH polycyclic components

According to Table 2, it shows that the types of PAH found in sample the A are relatively the same as the aromatic components in samples B and C. The difference is only in the Benz[a]pyrene component which is not present in samples B and C, as well as the Naphthalene component which is not identified in sample C. The striking difference in PAHs contained in each sample is the concentration of each component, where it appears that the PAH concentration of each component in sample A tends to be higher than in sample B, which is 3 km from station A, and much higher than the concentration. the same PAH component in sample C obtained at a distance of 6 km from station previous studies have concluded that the distance to the PAH contaminant source affects the type and concentration [1,16]. The types and amounts of PAH concentrations found in each sample are presented in Table 3.

Table 3. Components of PAHs and Magnitude of Concentrations of Each Component of Seawater Samples around the Port Paotere, Makassar, South Sulawesi

Type of PAHs	Components and Concentration (ppm)		
	Sample A	Sample B	Sample C
Naphthalene	235 ± .008	116 ± .012	nd
Acenaphthalene	268 ± .011	136 ± .009	98 ± .018
Acenaphthene	245 ± .017	168 ± .010	83 ± .011
Anthracene	298 ± .014	154 ± .014	57 ± .014
Phenanthrene	194 ± .005	98 ± .011	47 ± .012
Pyrene	813 ± .012	534 ± .007	368 ± .015
Benz(a,h)anthracene	213 ± .010	298 ± .004	251 ± .019
Chrysene	567 ± .012	422 ± .005	236 ± .014
Benz[a]pyrene	742 ± .015	nd	nd
Dibenz(a,h)anthracene	642 ± .009	73 ± .009	124 ± .009
Benzo(g,h,i)perylene	nd	100 ± .006	nd
Total PAHs	4,217 ± .106	2,124 ± .087	1,264 ± .112

Data Table 3, shows that there are 11 types of PAH components identified in three samples (A, B and C) with details of the 10 types of PAH found in sample A are also found in sample B. Benz[a]pyrene component is found in sample A but were not identified in samples B and C, on the other hand, component the Benzo(g,h,i)perylene was found in sample B but was not found in samples A and C. The results of identification of PAH components in sample C identified 8 components corresponding to the components in sample A. The type of PAH component with the highest concentration in each sample was pyrene, while the lowest concentration was Naphthalene in sample A, type of Dibenz(a,h)anthracene for sample B and type of the Phenanthrene for sample C. The level of contamination of each type of PAH component to the station is in the low category or not in a dangerous stage. The accumulative total PAHs is $4,217 \pm .106$ ppm for station A or medium level exposed category. The total PAHs for samples B and C were $2,124 \pm .087$ ppm and $1,264 \pm .112$ ppm, respectively, both of which were in low contamination levels, however concrete regulations are still needed to restrain the rate of increasing concentrations of PAHs exposure, especially in the water area around the sampling station because the properties of aromatic hydrocarbons are difficult to decompose and increase cumulatively with increasing time, sea transportation activities and loading and unloading of goods [4,17]. Fishing and cultivation activities as well as exploration of marine living materials in the waters around the center of the port of Paotere should be minimized to a radius of 6 km to the deep sea.

4. Conclusion

Some of the conclusions of this study include 10 types of PAH components in samples A and B, while in sample C only 8 components. The concentration of each type of PAH component in samples A, B and C is relatively low. The total PAHs in sample A are at moderate levels while those in samples B and C are at low levels. The PAHs concentration value in the waters tends to decrease along with the increasing distance from the point of the source of the pollution, namely the activity center of Paotere Port. The level of exposure to PAHs in waters around station A is in the alert level while at station B it is at a controlled level and in the area of station C it is at a safe level.

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