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Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Sediments of Losari Beach and adjacent areas, South Sulawesi, Indonesia

Nursiah La Nafie, Asmawati, Musa Ramang, and Adiba Arief

Chemistry Department, Faculty of Mathematics and Natural Sciences,
Hasanuddin University, Jl. Perintis Kemerdekaan KM 10,
Tamalanrea, Makassar, Indonesia 90245

Abstract

Distribution of polycyclic aromatic hydrocarbons (PAHs) was studied in sediment of Losari Beach and adjacent areas, South Sulawesi, Indonesia. PAHs in sediments were extracted with dichloromethane using ultrasonic extraction and finally analyzed by gas chromatography-mass spectrometry. The results showed that in sediment samples, the highest concentration was related to 9447 ng g^{-1} found in Paotere fish market, whereas the lowest concentration was 3555 ng g^{-1} from Metro station. Diagnostic ratio was used for the source identification of PAHs in sediment samples. The concentration ratio of low molecular weight PAHs to high molecular weight PAHs (LPAHs/HPAHs) was higher than one which suggested PAHs compounds came from a petrogenic source. The contrary results indicated by the Ant/Ant + Phe and Flu/Flu + Pyr ratio performed that PAHs in Losari Beach and adjacent area may originate from both of pyrolytic and petrogenic sources. This indicated that the major sources of sediment PAHs came from the polluted urban area. PAHs sources for samples of sediment were mixed anthropogenic sources, due to combustion emissions from industrial activity, ships and atmospheric deposition.

Keywords: Polycyclic Aromatic Hydrocarbons (PAHs), Losari Beach and adjacent, GC-MS, Pyrolytic, Petrogenic

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) represent a wide spread class of environmental chemical pollutants and are ubiquitous contaminants with two or more fused aromatic rings in marine environments. PAHs' solubility in water decreases, while correspondingly their boiling and melting point increases, with increasing molecular weight (Nikolaou *et al*, 2009). PAHs are lipophilic compounds with very low water solubility and therefore, their concentration in water is very low [Nasr et al, 2010; Qiu et al, 2009). As a consequence of their hydrophobic nature, PAHs in aquatic environments rapidly tend to become associated to the particulate matter ending in sedimentation. Therefore, sediments represent the most important reservoir of PAHs in the marine environment. For that reason, PAHs accumulation in coastal sediments is both due to anthropogenic and natural emissions. Among anthropogenic factors, petrogenic and pyrolytic sources are the most important. Whereas pyrolytic sources include combustion processes (e.g., fossil fuel combustion, forest fires, shrub and grass fires), the petrogenic input is closely related to petroleum products (e.g., oil spills, road construction materials) (Qiu et al, 2009; Perra et al, 2009).

The PAH composition within the sediments reflects the source(s) from which the PAHs were derived (Simpson et al, 1998; Yan et al, 2009). Larger concentrations of lower molecular weight PAHs (e.g. acenaphthene and fluorene) most often occur in sample matrices contaminated with naturally occurring (petrogenic) PAHs. PAHs originating from combustion (pyrolytic) sources often contain elevated concentrations of higher molecular weight and higher membered-ring PAHs (e.g. phenanthrene, fluoranthene, pyrene) and fewer low molecular weight PAHs (Heldrich and Amstrong, 1986).

These hydrocarbons can become dangerous especially if they come into the alimentary chain, since some of the higher PAHs and their metabolites, can form DNA adducts which can induce mutations. Because of their carcinogenic and mutagenic properties the USEPA classified 16 of them as priority pollutants. Some authors suggested that PAHs can be synthesized by unicellular algae, higher plants or bacteria but at the same time others concluded that organisms accumulate PAHs rather than synthesize them (Magi, 2002).

Losari Beach is the most important beach in South Sulawesi province, Indonesia. It has a lot of potential that can be exploited, namely as a marine tourism, water sports, the trade and so forth. The rapid development community activities in Losari effect on water pollution in Losari and adjacent areas. This ecosystem during the years, due to its closeness to the town and to the richness of human activities have accumulated in sediments both high PAHs and organic matter levels, so the goal of this work is to study the distribution of PAHs in sediments from Losari Beach and adjacent areas and determination of their source(s) on the basis of their concentrations.

MATERIALS AND METHODS

Sediment samples were collected in October 2016 from 12 stations from Losari Beach and adjacent areas were shown in table 1.

Table 1. Sampling stations in Losari Beach and adjacent areas.

No.	Station	Location
1.	Kayu Bangkoa	S : 05^0 08,248’; E : 119^0 24,270’
2.	Kayu Bangkoa-Soekarno Hatta port	S : 05^0 07,861’; E : 119^0 24,117’
3.	Eastern Pearl Flour Mills	S : 05^0 06,713’; E : 119^0 24,717’
4.	Paotere Fish Market	S : 05^0 06,574’; E : 119^0 25,149’
5.	Paotere Port	S : 05^0 06,673’; E : 119^0 25,334’
6.	Metro	S : 05^0 08,979’; E : 119^0 23,788’
7.	Masjid Terapung	S : 05^0 08,782’; E : 119^0 24,480’
8.	Stella Maris Hospital	S : 05^0 08,674’; E : 119^0 24,481’
9.	Losari Beach	S : 05^0 08,626’; E : 119^0 24,404’
10.	Makassar Golden Hotel (MGH)	S : 05^0 08,315’; E : 119^0 24,294’
11.	Waste of MGH	S : 05^0 08,274’; E : 119^0 24,274’
12.	In front of Kayu Bangkoa	S : 05^0 08,264’; E : 119^0 24,248’

Each sampling was carried out in three replicates. Sediment samples were taken at a depth 5 cm of sediment surface and then transferred to the laboratory. Samples were dried in 50^0 for 48 hours before analysis.

PAHs in sediments were extracted using ultrasonic extraction. A 5 g homogenized sample was extracted with 10 mL of dichloromethane for 15 minutes. This proceed was repeated for three times and all the filtrate was collected and concentrated to 2 mL using vacuum rotary evaporator.

Cleanup sediment was achieved through chromatography with a silica column. Saturated aliphatic hydrocarbons were eluted with 20 mL n-hexane and then aromatic hydrocarbons were eluted with 30 mL of a mixture of hexane and dichloromethane (90:10) (v/v). The volume of the eluted fraction was reduced to 1 mL and then the aromatic fraction was injected into a gas chromatography equipped with a mass spectrometer detector (GC/MS).

RESULTS AND DISCUSSION

1. Distribution and Composition of PAHs in sediments

The distribution of 16 PAHs in sediments of Losari Beach and adjacent areas was shown in table 2. The total amount of PAHs (ΣPAHs) varied from 3555 ng g^{-1} dry weight in Metro station to 9947 ng g^{-1} dry weight in Paotere fish market. The PAHs components were distributed in various stations with different pattern. This difference in PAHs composition might be related to the extent and the nature of input in each station. In addition, the sediment characteristics such as organic carbon content, structure and diameter of sediment particle have also been recognized as important factors influencing the abundance and distribution of PAHs in the sediment.

The concentration of ΣPAHs was higher in Paotere fish market followed by Paotere port. The station of Paotere fish market is exposed to high volume of urban sewage and seem to received great load of organic materials all over the year. Since organic materials could serve as PAHs transmitter from water to sediment, the prevalence of organic matter in Paotere fish market station could be considered as a reason for the presence of high PAHs concentration in sediment. Like Paotere fish market station, Paotere port is also located in urban area. It seems that harbor activities, marine transportation as well as urban discharges negatively affect this station.

The lowest concentration of PAHs was detected in Metro station. Being far from harbors and urbanized areas and the absence of direct discharges might be the main reasons keeping this station cleaner than others.

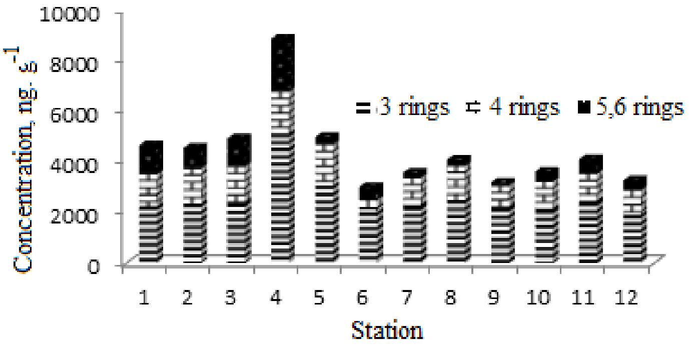
Based on the number of benzene ring in molecular structures of PAHs components, the relative abundance of PAHs compounds in each station is presented in figure 2. The overall order of PAHs abundance in the sediment was: 3 rings> 4 rings> 5+6 rings. The pattern of relative abundance of 3, 4, and 5+6 rings compounds were not similar in all station. Such variation might be related to the input sources of PAHs in each location.

Table 2. PAHs concentration (ng g^{-1} dry weight) in sediment of Losari Beach and adjacent areas

Concentration (ng g^{-1})												
	1	2	3	4	5	6	7	8	9	10	11	12
Napthalene	586	560	577	564	449	533	594	524	533	530	526	620
Acenapthylene	418	449	433	442	556	468	421	477	469	473	475	404
Acenapthene	460	489	495	389	453	249	423	457	518	445	454	366
Fluorene	468	479	491	550	586	442	445	477	460	433	495	376
Phenantrene	464	471	483	1641	800	433	478	567	448	226	474	367
Anthracene	433	468	467	2105	672	422	471	514	283	515	501	402
Fluoranthene	459	499	528	616	620	420	547	644	377	494	490	342
Pyrene	440	451	456	609	582	27	414	473	314	439	408	275
Chrysene	109	116	120	0	0	83	0	0	0	0	0	96
Benzo(a) anthracene	337	391	397	488	473	26	232	300	254	265	303	308
Benzo(k) fluoranthene	0	0	0	0	151	0	0	0	0	0	0	0
Benzo(b) fluoranthene	0	0	0	0	0	0	0	0	0	0	0	0
Benzo(a) pyrene	100	107	85	275	100	79	154	190	78	136	86	103
Indeno(1,2,3-c,d)pyrene	0	379	313	1037	0	0	0	0	0	0	0	0
Dibenzo(a,h) anthracene	719	0	0	731	0	373	0	0	0	195	310	296
Benzo(g,h,i) perylene	262	265	665	0	0	0	0	0	0	0	115	0
Total HAP	5255	5124	5510	9447	5442	3555	4179	4623	3734	4151	4637	3955

Station:

1. Kayu Bangkoa
2. Kayu bangkoa-Pelabuhan Soekarno Hatta
3. Eastern Pearl Flour Mills
4. Paotere fish market
5. Paotere Port
6. Metro
7. Mesjid Terapu
8. Stella Maris Hospital
9. Losari Beach
10. Makassar Golden Hotel (MGH)
11. Waste of MGH
12. In front of Kayu Bangkoa



1 = Kayu Bangkoa
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3 = Eastern Pearl Flour Mills
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Figure 2. The relative abundance of PAHs compounds in the sediment of Losari Beach and adjacent (Based on the number rings)

2. Sources of PAHs in sediment

Diagnostic ratio is useful tool for the source identification of PAHs in sediment samples. Table 3 showed the range of diagnostic ratio for PAHs sources (pyrolytic and petrogenic origins of PAHs). Characteristic values of selected molecular ratios are given in table 3. The concentration ratio of low molecular weight PAHs to high molecular weight PAHs (LPAHs/HPAHs) is a ratio of sum Naphalene, Acenapthylene, Acenapthene, Flourene, Phenanthrene and Anthracence concentrations against sum of Flouranthene, Pyrene, Benzo(a)anthracene, Chrysene, Benzo(b)flouranthene, Benzo(k)flouranthene, Benzo(a)pyrene, Dibenzo(a,h)anthracene, Indeno(1,2,3-c,d), and Benzo(ghi)perylene concentration.

Table 3. The Range of Diagnostic Ratios for PAHs Sources.

	LPAHs/HPAHs	Flu/(Flu+Pyr)	Ant/(Phen+Ant)
Pyrolytic origin	<1	>0,4	>0,1
Petrogenic origin	>1	<0,4	<0,1

The concentration ratio of low molecular weight PAHs to high molecular weight PAHs (LPAHs/HPAHs) was >1, so that based on table 3 suggest PAHs compounds came from a petrogenic source. Pyrogenic sources, such as combustion-derived particles present in urban atmospheric dust, were poor in low molecular weight 2-3 rings PAHs (Low Molecular Weight PAHs: LPAHs) and enriched in high molecular weight 4-6 rings PAHs (High Molecular Weight PAHs: HPAHs), which led to LPAHs/HPAHs <1. Petrogenic sources, such as fuel oil or light refined petroleum products, were dominated by LPAHs and had LPAHs/HPAHs >1. Some researchers thought that those PAHs in sediments with the ratio of anthracene to anthracene plus phenantrene; Ant/(Ant+Phe) <1 were mainly from petroleum contamination (petrogenic source), while those with Ant/(Ant+Phe) >1 were mainly from combustion sources (pyrogenic source).

Some researchers believed that PAHs in sediments with the ratio of flouranthene to flouranthene plus pyrene; Fla/(Fla + Pyr) <4 means petroleum contamination, while Fla/(Fla + Pyr) >0.5 means PAHs are mainly from combustion of grass, wood and coal and 0.4 < Fla/(Fla + Pyr) < 0.5 from combustion of petroleum.

The result showed that Ant/Ant+Phe >0,4; Flu/Flu+Pyr>0,5 suggest a pyrogenic source, and combustion source of biomass (grass, wood, or coal combustion), respectively. If the Flu/Flu+Pyr ratio is between 0.4 and 0.5, combustion of petroleum origin is suggested. Besides, the ratio of LPAHs/HPAHs was >1 showed that the PAHs source was petrogenic source. The contrary results indicated by the Ant/Ant + Phe and Flu/Flu + Pyr ratio suggested that PAHs in Losari Beach and adjacent area may originate from both of pyrolytic and petrogenic source.

CONCLUSIONS

Analysis for 16 PAHs was carried out in sediment samples in Losari Beach and adjacent area. The distribution and possible sources also evaluated. The total concentrations of 16 PAHs varied from 3555 in station Metro to 9947 ng g^{-1} in Paotere fish market. The PAH concentration is relatively high in the Paotere fish market, and gradually diminishes toward the harbor region. This indicated that the major sources of sediment PAHs came from the polluted urban rivers. PAHs sources for samples of sediment were mixed anthropogenic sources, due to combustion emissions from industrial activity, ships and atmospheric deposition.

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