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# Identification polycyclic aromatic hydrocarbons (PAHs) in the Banyuasin river estuary, South Sumatera

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**Abstract.** The Banyuasin river estuary is an aquatic area located on the east coast of south Sumatera and receives waste input from activities along with the river flow. One of organic pollutants that toxicate marine life is polycyclic aromatic hydrocarbons (PAHs). This study was aimed to identify and determine the concentration of PAHs in seawater and sediment samples from Banyuasin river estuary. A sampling of seawater and sediment was carried out in July 2018. Seawater samples were taken using water sampler and sediment samples were taken using grab at 5 research stations. The concentration of PAHs was analyzed by Gas Chromatography-Flame Ionization Detector. The results showed that the PAH content in the seawater ranged from 92.34 to 320.09 ppb while the content of PAHs in the sediment ranges from 3.16-23.28 ppb. Overall, the PAHs content in the seawater Banyuasin river estuary had exceeded the threshold limit value stated by the Indonesian Ministry of Environment, which was 3 ppb or 0.003 ppm

**Keywords:** Banyuasin river estuary, polycyclic aromatic hydrocarbons (PAHs), waters, sediments

## 1. Introduction

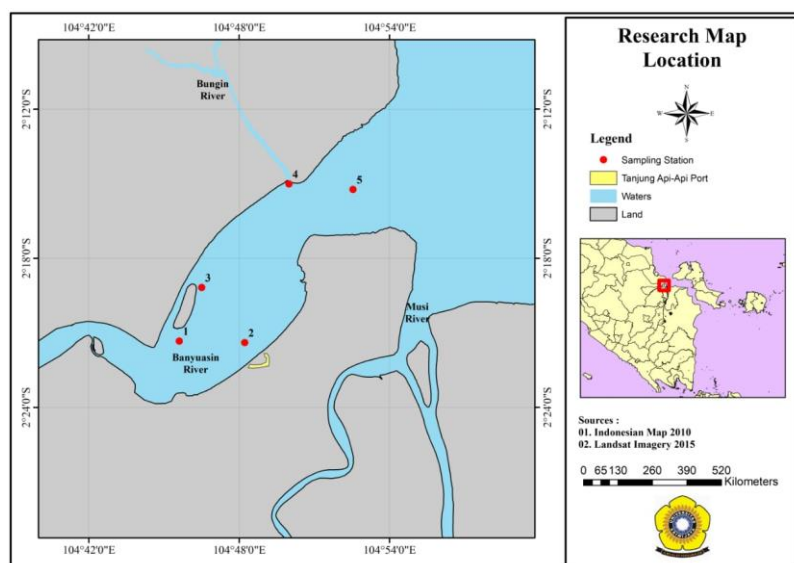
The Banyuasin river estuary is one of the estuary ecosystems with a high diversity of organisms so there are many fishing activities found in this region. Some of the dominant catches are shrimp, small pelagic fishes and demersal fishes that live on the sediment surface. The Banyuasin river estuary is tip of the three rivers estuarine (the Lalan river, the Bungin river, and the Banyuasin river). Utilization along the riverine can cause pollution in the estuary. Some results of research around the Banyuasin river estuary, South Sumatra have been published. Purwiyanto and Lestari (2012) stated that the concentrations of Pb and Cu in the water columns and sediment of the Banyuasin river estuary had exceeded the quality standard. This research also showed the presence of Pb and Cu contents in crab *Scylla serrata* muscle that consumed by humans. Furthermore Cu and Pb are also accumulated in some consumption fish that live on the coast of South Sumatra. Putri *et al* (2016) reported that Cu and Pb accumulated in the three organs (liver, gills, and muscle) of *Mugil chepalus* and *Rasbora* sp. Furthermore, Putri *et al* (2019) founded that concentrations of nitrate and phosphate in Banyuasin river estuary were found exceeded the threshold limit value, while for nitrite, ammonia and BOD parameters were still good for aquatic organism.



The Banyuasin river estuary has an important function in water transportation, especially since the development of the Tanjung Api-Api port area. In addition, industrial activities, settlements, agriculture, and plantations are also found throughout the river. Information about persistent organic pollutants in this area is still limited, one of which is polycyclic aromatic hydrocarbons (PAHs). PAHs are dangerous organic pollutants for all the aquatic environment. It is because PAHs can make carcinogenic effects on organisms. Polycyclic aromatic hydrocarbons (PAHs), having two or more fused benzene rings, are a group of organic pollutants that occur widely in the environment. They are recognized as mutagenic and carcinogenic compounds; benzo[a]pyrene and benzo[a]anthracene are typical carcinogens. Additionally, some PAHs such as benzo[a]pyrene are listed as endocrine disruptors in the environmental hormone category (Neff 1979, Clemons *et al* 1998). They are considered priority organic pollutants in view of their carcinogenic potential and ability to act as mutagenic promoters in biologic systems (WHO 1983, EPA 1987). Based on the number of aromatic rings, PAHs can be divided into two types, low molecular weight (LMW) PAHs with aromatic rings  $\leq 4$  and high molecular weight (HMW) PAHs with aromatic rings of more than 4. In general, the degradation rate is directly proportional to the number of aromatic rings. For example LMW PAHs such as naphthalene, anthracene, and phenanthrene will be more easily degraded. There are 16 types of compounds identified based on molecular weight and retention time or 16 Priority Compounds of PAHs by United States Environmental Protection Agency-USEPA (Rubailo and Oberenkob 2008). Therefore, information and research about PAHs are needed to complete the information about water quality in the Banyuasin river estuary.

## 2. Materials and methods

Sampling was carried out in July 2018 around the Banyuasin river estuary, Banyuasin Regency, South Sumatera Province. Sampling was carried out at five research stations (figure 1). Water and sediment samples for PAHs analysis of 250 mL and 250 mg were taken using water sampler and Eckman grab. Water and sediment samples were put into a glass bottle (APHA-AWWA-WEF 2005). Samples are stored in cool boxes with temperatures of approximately 4°C during transportation to the laboratory.



**Figure 1.** Location of the Research Station.

Analysis procedure of PAHs in sediments refers to the methods carried out by Yamaguchi and Lee (2010). Ten grams of sample (dry weight) was homogenized in mortar and sodium sulfate was added, then put into an Erlenmeyer glass and extracted by ultrasonic devices respectively using 30 mL DCM,

n-hexane and DCM mixtures: n-hexane (v/v:1/1). The extraction evaporated by rotary evaporator to 1 mL. The extraction results cleaned up and fractionated with a chromatographic column consisting of glass wool, Silica gel powder 60 (particle size: 0.063-0.200 mm), alumina powder and activated copper. Then, n-pentane solvent was used for elution of fraction 1 and the mixture of n-pentane: DCM (60:40 v/v) for fraction 2. Furthermore, the results of fraction 2 were evaporated to 1 mL and immediately injected into the gas chromatography mass spectrometer (GCMS). GCMS using the TG5-SilMS column with length of 30 m; ID: 0.25 mm; Film: 0.25  $\mu$ m; Oven: 50°C (0.5 minutes), gas rate: 160°C (15 minutes)  $\rightarrow$  290°C (13 minutes)  $\rightarrow$  300°C (4 minutes). For gas systems, 1.2 mL/min (constant flow) Helium; Split flow: 10 mL/min; Splitless time: 0.5 minutes. The concentration of PAH is expressed in ng. g<sup>-1</sup> dry weight.

### 3. Results and discussion

The results showed that some types of PAHs were found in water and sediment samples from the Banyuasin river estuary (table 1). The total of PAHs concentration in the water samples were higher than in the sediment. Total concentration PAHs in water samples ranged from 92.341-320 ppb, while the total PAHs concentration in the sediment was found 0-23.28 ppb, respectively. The total concentration and number of types of PAHs vary at each research station. The highest total of PAHs concentration in water sample was found at Station 4 (320.09 ppb) with the number of types of PAHs 5 types, followed by Station 1 (273.845 ppb) with 4 types of PAHs. Station 5 (237 ppb) with 4 types of PAHs, Station 3 (109.87 ppb) with 2 types of PAHs and the lowest were in Station 2 (92.341 ppb) with 2 types of PAHs. Overall, the highest PAHs concentration and the most number of PAH types (5 types) were found at station 4 (figure 2).

The difference in total concentration and the number of types of PAHs found between research stations can be caused by several factors. Edward (2014) states that water current could act as a factor that influencing the PAHs concentration. The direction and speed of the current which is always changing can cause the pattern of PAHs distribution to be uneven at the surface of the sea. Like other chemical components, PAHs in seawater can be dissolved or particles in the water column so that PAHs can be carried elsewhere by the current (Agustine 2008, Edward 2014).

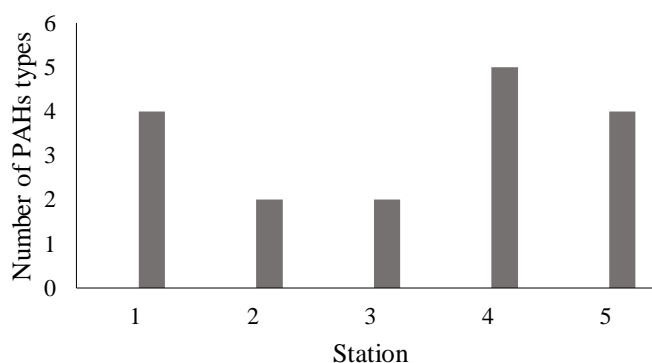
Polycyclic Aromatic hydrocarbons (PAHs) are organic compounds that are widespread in nature. Due to their low water solubility, PAHs are easily adsorbed by particles and colloids when transferred into the water and sediment. This research was found that were 8 types of PAHs in the water column. The type of naphthalene was found in all water samples with range concentration 14.2-16.0 ppt. Likewise 2-Bromonaphthalene (67 ppt), acenaphthene was found ranged from 71.4-71.5 ppt, the type of fluorene was found ranged from 0-90.65 ppt. Furthermore, anthracene was found ranged from 84.2-84.6 ppt, benzo[a]anthracene ranged from 63.9-64.8 ppt, benzo[a]pyrene 77.0-107.5 ppt. For sediment samples, we found only 5 types of PAHs: acenaphthene (3.53 ppt), anthracene (4.23 ppt), pyrene (3.74 ppt), benzo[a]anthracene and chrysene (4.46 ppt). Most of PAHs were found in the water column and small portion of PAHs were found in sediments.

Based on the State Minister for the Environment (2004), the threshold of PAHs for seawater is 3 ppb. Therefore, it can be concluded that the PAHs concentration in the water column in Banyuasin river estuary has exceeded the threshold for the marine organisms. This condition needs further consideration to manage the pollutant problems in Banyuasin river estuary. PAHs may come from natural sources, but anthropogenic activity is generally considered the major source (Baumard *et al* 1998). Anthropogenic PAHs primarily originate from pyrogenic and petrogenic sources. Pyrogenic PAHs are mainly from incomplete combustion of various fossil fuels (such as coal, oil, and natural gas), residential heating, industrial activity, wood, tobacco, and other hydrocarbons (Broman *et al* 1991).

**Table 1.** PAHs concentration in water and sediment sample in Banyuasin river estuary.

PAHs	Station and PAHs concentration (ppb)									
	Water 1	Water 2	Water 3	Water 4	Water 5	Sed 1	Sed 2	Sed 3	Sed 4	
Naphthalene	14.763	15.848	14.279	16.004	16.341	UDL	UDL	UDL	UDL	
Acenaphthylene	UDL	UDL	UDL	UDL	UDL	UDL	UDL	UDL	UDL	
2-Bromonaphthalene	67.07	UDL	UDL	UDL	UDL	UDL	UDL	UDL	UDL	
Acenaphthene	UDL	UDL	UDL	71.529	71.442	3.53	UDL	UDL	UDL	
Fluorene	UDL	UDL	UDL	90.655	UDL	UDL	UDL	UDL	UDL	
Anthracene	84.539	UDL	UDL	UDL	84.629	4.231	UDL	UDL	UDL	
Phenanthrene	UDL	UDL	UDL	UDL	UDL	UDL	UDL	UDL	UDL	
Fluoranthene	UDL	UDL	UDL	UDL	UDL	4.134	UDL	UDL	UDL	
Pyrene	UDL	UDL	UDL	UDL	UDL	3.742	UDL	UDL	UDL	
Benzo[a]anthracene	UDL	UDL	UDL	63.981	64.69	3.172	3.16	UDL	UDL	
Chrysene	UDL	UDL	UDL	UDL	UDL	4.468	UDL	UDL	UDL	
Benzo[k]fluoranthene	UDL	UDL	UDL	UDL	UDL	UDL	UDL	UDL	UDL	
Benzo[a]pyrene	107.473	76.493	95.59	77.924	UDL	UDL	UDL	UDL	UDL	
Indeno[1,2,3-cd]pyrene	UDL	UDL	UDL	UDL	UDL	UDL	UDL	UDL	UDL	
Dibenzo[ah]anthracene	UDL	UDL	UDL	UDL	UDL	UDL	UDL	UDL	UDL	
Benzo[ghi]perylene	UDL	UDL	UDL	UDL	UDL	UDL	UDL	UDL	UDL	
Total	273.845	92.341	109.87	320.09	237.1	23.28	3.16	0	0	

UDL: Under Detection Limit

**Figure 2.** Number PAHs types found at each station.

Furthermore, the concentration and number of types of PAHs in sediment samples lower (ranged from the-23.28 ppb) than water column. PAHs is only found at station 1 (6 types of PAHs) and station 2 (1 type of PAHs). The types found are acenaphthene, anthracene, fluoranthene, pyrene, benzo[a]anthracene and chrysene. As for Station 3 and 4, PAHs are reported under detection limit (UDL). Based on this condition it can be concluded that the PAHs content is lower than the threshold value for marine organism that lives in sediment (45 ppm) (Simpson *et al* 2005).

The Banyuasin river estuary is a ship line area where we can find a lot of fishing boats and ferries there. In addition, several locations in this region are also used as coal stockpiles which can contribute to the presence of PAHs in the waters and sediments. According to Zakaria *et al* (2009) PAHs contamination in water can come from various activities both natural activities (oil seepage, forest fire fumes, volcanic

eruptions) or anthropogenic sources (industrial activities, transportation, and household activities). PAHs molecules with large molecular weights (PAHs > 3 benzene rings) usually originate from incomplete combustion (pyrogenic) while PAHs with small molecular weights (PAHs with 2-3 benzene rings) are very dominant in petroleum (petrogenic) products (Apeti *et al* 2010). Some studies such as in Teluk Klabat (Bangka Belitung, Indonesia) showed that total PAHs levels ranged from 0.375-44.486 ppb with an average of 7.468 ppb in March 2006, while in July it ranged from 1.329-27.826 ppb, average of 15.2 ppb (Munawir 2007). Furthermore, Agustine (2008) obtained 7 types of PAHs in Jakarta Bay ranged from 0.0181 to 1.1551 µg/L. Falahudin *et al* (2011) founded concentration of PAHs in the Timor Sea ranged from 54.46-213.70 ppb (average of 99.75 ppb). Navenka *et al* (2007) in Rijeka Bay, the Adriatic Sea founded total PAHs ranged from 305 ng/L (10 types). Furthermore, Ahmad (2012) explained that PAHs concentration at Jakarta Bay ranged from 201.57 to 474.68 ppb with a total content of 1404.68 ppb.

#### 4. Conclusion

The concentration of PAHs in water samples from the Banyuasin river estuary exceeded the permissible threshold while PAHs in sediment within range of threshold limit value. There are 8 types of PAHs components found in the water samples during the study, naphthalene, 2-bromonaphthalene, acenaphthene, fluorene, anthracene, benzo[a]anthracene benzo[a]pyrene. Whilst, in the sediment samples there were found 5 types, acenaphthene, anthracene, fluoranthene, pyrene, benzo[a]anthracene and chrysene.

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