Concentration of Polycyclic Aromatic Hydrocarbons (PAHs) in the Sediments and Milkfish (*Chanos chanos*, Forsk) at Marunda and Blanakan Ponds, Indonesia

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Abstract The polycyclic aromatic hydrocarbons (PAHs) are pollutants of concern due to their persistence in the marine ecosystem. The aim of the research was to analyse concentration of Polycyclic Aromatic Hydrocarbons (PAHs) in the sediments and milkfish (*Chanos chanos*, Forsk) at Marunda and Blanakan ponds. The PAHs fraction were analysed using GC-MS model Shimadzu QP5000. The results revealed that PAH detected in the surface sediments of Marunda and Blanakan Ponds, were Naphthalene, Benzo(b) fluoranthene, Benzo (k) fluoranthene, Benzo (a) pyrene and Indeno (1,2,3-cd) pyrene with the range concentrations were 27.1–63.0 ng/g and 24.0–64.9 ng/g. Total PAH concentration observed in the meat and gills of *Chanos chanos* at Marunda ponds were 13.3 ng/g and 0.4 ng/g, respectively, while in Blanakan ponds, PAH were not detected. PAHs were detected in Marunda and Blanakan indicates input source petrogenic and pyrogenic both sediment, meat, and gills of *Chanos chanos*, Forskal.

Keywords Polycyclic Aromatic Hydrocarbons (PAHs); Sediments; Milkfish (*Chanos chanos*, Forskal); Marunda; Blanakan

1 Introduction

The polycyclic aromatic hydrocarbons (PAHs) are pollutants of concern due to their persistence in the marine ecosystem, thus it can cause long term adverse effect to the marine life (Elias et al., 2007). These organic contaminants are resistant to degradation, can remain in the environment for long periods, and have the potential to cause adverse environmental effects. Some of them are susceptible to dispersion on a global scale because they are semivolatile, move between the atmosphere and the Earth's surface in repeated, temperature-driven cycles of deposition and volatilisation (Wania and Mackay, 1996). Persistent organic pollutants (POPs) like PAHs, are truly multimedia contaminants which occur in all parts of the environment: atmosphere, inland and sea waters, remote/far away from industrial activities (Neff, 1979). In general, PAHs are occurred in all parts of the environment: atmosphere, water, sediments, soils and vegetation (Wild and Jones, 1995; Wania and Mackay, 1996) not only from places close to industrial areas, but also in remote/far away from industrial activities.

PAHs are formed through natural and anthropogenic processes (Boehm, 2006), for example biosynthesis, diagenesis of organic materials that produce fossil fuel, and incomplete combustion of organic materials (Neff, 1979). According to Nikolaou et al (2009), there are three sources of PAHs: (1) Petrogenic PAHs, including petroleum, with its products such as crude oils, (2) Biogenic PAHs, from biological process or early step of diagenesis on marine sediment (i.e. perylene), (3) Pyrogenic PAHs, from fuel combustion (petroleum and coal) and wood.

PAHs diagenesis is produced naturally when the organic material deposited on the sediment. PAHs which is produced relatively faster (day up to year) at low temperature (< 70 °C) occur on condition with depletion of oxygen and microorganisms involvement such as bacteria. This process is recognized as aromatization reaction and produce aromatic biomarker that was found in the new sediment. The initial diagenesis product is perylene with 5 rings PAHs. Perylene usually found in the river sediment, pond and...
the sea, where there is an oxygen depletion (Boehm, 2006). Organic material diagenesis from the diatom and plant material are source of perylene in anoxic sediment of the sea (Venkatesan, 1998; Boehm, 2006). Tolosa et al (2009) reported that in the Cienfuegos Bay, Cuba, perylene (PAHs natural) was found over in the estuarine areas of Damuji and Salado rivers. PAHs produced in the early diagenesis with a simple biology precursor only include some of PAHs, so that, it differentiated between multispecies complex of PAHs petrogenic and pyrogenic (Boehm, 2006). The objective of the research was to study preliminary analyses concentration of Polycyclic Aromatic Hydrocarbon (PAHs) in the sediments and milkfish (Chanos chanos, Forskal) at Marunda and Blanakan ponds, Indonesia. The results of study will give information regarding with the PAHs contribution in human activity in the environment.

2 Result
2.1 Concentration and characteristic of PAHs on the sediments of Marunda ponds
PAH characteristic which were detected in the surface sediments of Marunda Ponds, Jakarta were Naphthalene, Benzo (b) fluoroanthene, Benzo (k) fluoranthene, Benzo (a) pyrene and Indeno (1,2,3-cd) pyrene. Total PAHs concentrations obtained at the pond surface sediments ranged from 27.1 ng/g to 63.0 ng/g dry weight of Marunda sediment. Highest total PAHs concentrations found in pond M1 while the lowest was in the pond M2. Highest concentration of PAHs components found in Marunda ponds is Benzo (b) fluoranthene (pond M1) with concentration of 28.8 ng/g dry weight sediment (Table 1 and Figure 1).

2.2 Concentration and characteristic of PAHs on sediments of Blanakan ponds
Characteristic of total PAHs found in the sediment of surface sediment at Blanakan ponds were Naphthalene, Benzo (b) fluoranthene, Benzo (k) fluoranthene, Benzo (a) pyrene and Indeno (1,2,3-cd) pyrene. Total PAHs concentrations obtained at the point of sampling ranged between 24.0 ng/g to 64.8 ng/g dry weight of sediment. The highest total concentration of PAHs found in the pond B2 and the lowest B3 ponds. Components with the highest concentration of PAHs compounds are Benzo (b) fluoranthene (30.8 ng/g dry weight of sediment) were found in the pond B2 (Table 2 and Figure 2).

2.3 Concentration and characteristics of total PAHs in milkfish (Chanos chanos, Forsk) at Marunda and Blanakan ponds
Total PAHs concentration observed on meats and gills of Chanos chanos at Marunda pond were 13.3 ng/g and 0.4 ng/g, respectively, while in Blanakan ponds, PAHs were not detected. PAHs compounds in milkfish meat Marunda also detected compounds Naphthalene, Benzo (b) fluoranthene, Benzo (k) fluoranthene, Benzo (a) pyrene and Indeno (1,2,3-cd) pyrene. PAHs compounds in the gills of Milkfish Marunda only detected Naphthalene compound. Component of PAHs compounds in the pond Blanakan is undetectable (Table 3).

2.4 Comparison of total PAHs concentrations in the sediments in the area of aquaculture Marunda, Jakarta Bay and Blanakan, Subang
To analyse the difference between the concentration of PAHs in the sediments Marunda and Blanakan ponds, statistical analysis was used. In general, based on statistical analysis of the results show that in both study sites there was no difference (Table 4).
### Table 1: PAHs concentration (ng/g dry weight) in sediments at Marunda ponds

| Sampling Point | Naphthalene | Benzo (b) fluoranthene | Benzo (k) fluoranthene | Benzo (a) pyrene | Indeno (1,2,3-cd) pyrene | Total PAH concentration |
|----------------|-------------|------------------------|------------------------|-----------------|------------------------|-------------------------|
| M1             | ND          | 28.8                   | 20.4                   | 6.3             | 7.4                    | 63.0                    |
| M2             | 8.4         | 6.8                    | 5.8                    | 4.1             | 2.1                    | 27.1                    |
| M3             | 0.2         | 10.7                   | 9.8                    | 5.5             | 5.7                    | 31.8                    |
| M4             | 6.7         | 12.9                   | 8.9                    | 6.2             | 8.1                    | 42.7                    |

Note: M1-M4=Sampling points at Marunda, ND=Not Detected

### Table 2: PAHs concentration (ng/g dry weight) in sediments of Blanakan ponds

| Sampling points | Naphthalene | Benzo (b) fluoranthene | Benzo (k) fluoranthene | Benzo (a) pyrene | Indeno (1,2,3-cd) pyrene | Total PAH concentration |
|-----------------|-------------|------------------------|------------------------|-----------------|------------------------|-------------------------|
| B1              | 1.0         | 18.6                   | 13.7                   | 3.7             | 4.8                    | 50.6                    |
| B2              | 3.8         | 30.8                   | 21.8                   | 4.4             | 4.1                    | 64.8                    |
| B3              | ND          | 15.4                   | 2.3                    | 2.6             | 3.7                    | 24.0                    |
| B4              | 0.1         | 25.3                   | 18.1                   | 5.2             | 5.4                    | 54.1                    |
| B5              | 5.4         | 20.9                   | 15.1                   | 4.3             | 3.8                    | 49.5                    |
| B6              | 2.4         | 17.0                   | 12.5                   | 3.1             | 3.4                    | 38.4                    |

Note: B1-B6=Sampling points at Marunda, ND=Not Detected

### Table 3: PAHs concentrations (ng/g in dry weight sediment) in the aquaculture of milkfish in Marunda, North Jakarta and Blanakan, Subang

| Sampling Points | Milkfish | Naphthalene | Benzo (b) fluoranthene | Benzo (k) fluoranthene | Benzo (a) pyrene | Indeno (1,2,3-cd) pyrene | Total PAH |
|-----------------|----------|-------------|------------------------|------------------------|-----------------|------------------------|-----------|
| M               | Meats    | 4.7         | 2.6                    | 3.0                    | 1.5             | 1.5                    | 13.3      |
|                 | gill     | 0.4         | ND                     | ND                     | ND              | ND                     | 0.4       |
| B               | Meats    | ND          | ND                     | ND                     | ND              | ND                     | ND        |
|                 | gill     | ND          | ND                     | ND                     | ND              | ND                     | ND        |

Note: M=Sampling points at Marunda, B=Sampling points at Blanakan, ND=Not detected

### Table 4: Levene test dan t-test on PAH concentration (ng/g dry weight) on the sediment at Marunda and Blanakan ponds.

|              | F   | Sig. | T    | Sig. (2 tail) | Conclusion     |
|--------------|-----|------|------|---------------|----------------|
| Naphthalene  | 0.678 | 0.434 | 0.080 | 0.939 | Not significant |
| Benzo (b) fluoranthene | 0.915 | 0.367 | -1.350 | 0.214 | Not significant |
| Benzo (k) fluoranthene | 0.040 | 0.950 | -0.639 | 0.541 | Not significant |
| Benzo (a) pyrene | 0.016 | 0.901 | 2.579 | 0.033 | Significant |
| Indeno (1,2,3-cd) pyrene | 4.557 | 0.065 | 1.416 | 0.194 | Not significant |
| Concentration Total PAH | 0.051 | 0.827 | -0.603 | 0.564 | Not significant |
3 Discussions

3.1 PAHs in Marunda and Blanakan sediments

In Marunda and Blanakan ponds, the components of PAHs consisted of non-branched or non-alkylated PAHs. PAHs that were detected composed of 2, 3 and 4 benzene ring. It showed that sediment at Marunda ponds were already contaminated with petroleum and pyrogenic PAHs resulting from fuel combustion (Zhang et al., 2004; Boehm, 2006; Bouloubassi et al., 2006). The PAHs compounds detected in Marunda and Blanakan ponds were compounds that considered as primary pollutant according to US EPA (Boehm, 2006). The contamination of petroleum at Marunda ponds (located closed to Jakarta Bay), occured because Jakarta Bay is used as cross-nation transportation for fishermen boats, ships and tanker from many offshore rig’s companies under Pertamina Authority of Kepulauan Seribu (Salim, 2000). Oil contamination can reach to the coastal/land areas through the tides action of seawater. In addition, it was also caused by human activities such as the use of leaded gasoline for their vehicles and oil/lubricant that are discharged to the sea. Moreover, industrial activities also contribute for the contamination. Range of total PAHs concentrations in Marunda sediment were lower compared to the result obtained by Zhang et al (2004) at surface sediment on mangrove areas of Deep Bay, China. The range of PAHs found were 238 ng/g up to 726 ng/g dry weight. On the other hand, Gogou et al (2000) found that concentration of PAHs total at sediments of Cretan Sea were 14.7 ng/g up to 161.5 ng/g. This showed that concentration of total PAHs in Marunda ponds were between concentration found in China and Cretan Sea.

PAHs compounds that were detected in Blanakan ponds probably derived from agricultural activities that discharge their wastes to Cilamaya River closed to Blanakan ponds. Other source is coming from fishermen boat using leaded gasoline. Value range of total PAHs concentrations in Blanakan sediment obtained at concentrations lower than obtained by Hu et al (2010) that ranged from 140.6~300.7 ng/g on sediments of Bohai Bay, North China.

Based on statistical analysis, it seemed that in both locations Marunda and Blanakan ponds there were no differences on PAHs concentration. Even though, Blanakan ponds were far away from industrial area, but there are housings and agricultural activities (paddy fields, horticulture and aquaculture). According to Neff (1979), persistent organic pollutants (POPs) like PAHs, are truly multimedia contaminants which occur in all parts of the environment: atmosphere, inland and sea waters, sediments, soils and vegetation (Wild and Jones, 1995; Wania and Mackay, 1996) not only from places closed to industrial areas, but also ones in remote/far away from industrial activities.

3.2 PAHs in the meat and gills Chanos chanos in Marunda and Blanakan

Components with the highest concentrations of total PAHs in the meat and gills of Milkfish in Marunda is Naphthalene. Naphthalene characterized by abenzene ring number 2. This suggests that the meat and gills of Milkfish in Marunda mainly contaminated by petroleum (Zhang et al., 2004; Boehm, 2006; Bouloubassi et al., 2006). Milkfish meat has also been detected by the component PAHs with number of benzene rings 3 and 4, which are derived from petrogenik and pyrogenik. This indicates the influence of high human activity around the location of the research, such as residential, agricultural, industrial and ship activity in the sea.

Concentrations of total PAHs in fish obtained in Marunda generally still low when compared to other research. Other studies have shown that it contains total PAHs in various biota as found by Tolosa et al (2005) in the gulf of Oman and the fish Ephinephelus coioides (the orange-spotter grouper) with a concentration range of 11.8~115 ng/g and Lethrinus nebulosus (Spangled Emperor) with a concentration range of 5.60~43.4 ng/g. Manan et al (2011) also found concentrations of total PAHs in aquaculture fish (red fish, Lutjanus erythropterus; grouper, Epinephelus areolatus and Mycteroperca tigris, promfret, Pampus argentius) at Straits of Malacca, Malaysia ranged 130.26~9610.31 ng/g.

4 Data and Methods

4.1 Sampling time and location

Sediment samples collection was carried out using Ekman Grab in January-March 2012, at Marunda Ponds, North Jakarta and Blanakan, Subang, West Java (Figure 3). Only 5~10 cm of sediment surface taken for PAH analysis. Fish samples were collected from each pond using fish net. Sediments and fishes collected...
from the field location were wrapped with aluminium foil and kept at –20°C until further analysis. Sampling locations were determined using Global Positioning System (GPS).

4.2 Extraction and fractionation

Samples of sediment and fish were freeze dried to eliminate water content. Approximately 10 g dry weight of sediment was weighted in a glass beaker. Sample was added into the soxhlet apparatus and surrogated with Naphtalene-D8 for recovery assessment. The samples were extracted using 250 mL (50:50 v/v) mixture of dichloromethane (DCM) and hexane. After 18 hours extraction, the extracted samples were evaporated under vacuum until 1 mL using rotary evaporator. About 1 mL of extracted sample was fractioned into subfraction using silica-alumina column with 10 g of silica gel, 10 g of alumina, and about 1 cm height of sodium sulphate anhydrous. Hexane (50 mL) was eluted, pass through into the silica-alumina column to elute aliphatic (C12–C34) fraction followed by the 40 ml mixture of DCM and hexane (50:50 v/v) to elute the PAHs fraction. Internal standards of Acenaphthene D8 and Phenanthrene D8 were added, the samples were injected to GC-MS (Prartono and Wolff, 1998; Elias et al., 2007).

4.3 Gas chromatography-mass spectroscopy (GC-MS) analysis

The PAHs fractions were analysed using GC-MS model Shimadzu QP5000 with selective ion monitoring.
mode. PAHs fraction were injected into the GC-MS by using DB-5 silica capillary column (30m × 0.25 mm i.d.; 0.25 μm filmed thickness). The column oven temperature was heated to 50°C for 1 minute, maintained at 25°C/minute up to 195°C held for 1.5 minutes, rise up 8°C/minute up to 265°C, rise up 20°C/minute up to 315°C held for 5 minutes. Helium gas was used as a carrier gas with flow rate at 1.2 mL/min. The PAHs identification and quantification was based on ion fragmentation and retention time compared to that the internal PAHs standard.

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