The Preliminary Study of Organochlorine Pesticide Residues on Sediments of Bivalvia Fishing Ground at Eastern Part of Coastal Semarang

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Abstract. This paper presents the occurrence level of organochlorine contamination in marine sediments of Semarang coastal areas as a fishing ground of Bivalvia. Five compounds (Heptachlor, Aldrin, Endosulfan, Endrin and pp-DDT) of contaminant have been determined in the sediments surface of Semarang coastal waters. The samples were then analyzed by using gas chromatography and followed by using the method of Standard Method Examination. The result showed that the average concentration of organochlorine pesticides Heptachlor, Aldrin, Endosulfan, Endrin and pp-DDT were 25.5, bellow detected, 7.1, 37.2, 28.6 µg/L, respectively. The high concentration of pesticide showed on Endrin (65.84 ppb), pp-DDT (29.53 µg/L), and heptachlor (25.45 µg/L). The low concentrations were detected on aldrin (bellow detected) and endosulfan (0.92 µg/L). The concentration of organochlorine pesticides in these areas might contribute on four rivers which deposited the sediment in these coastal waters.

1. Introduction
Persistent organochlorine compounds including organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) were widely used in industry and agriculture. There are two kinds for OCPs, one is made of benzene including hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT), and another one is cycloidiene including heptachlor, aldrin, dieldrin, and endrin. PCBs were produced as dielectric and hydraulic fluids on an industrial scale since 1929, with particularly large volumes made in the 1950s–1970s [1]. Persistent organochlorine compounds are thought as an important component of xenobiotic chemicals. Their residues were causing the hazard to the environment and had the potential to elicit endocrine disruption in biota [2],[3]. Although organochlorine pesticides (OCPs) such as DDT, HCH, and Aldrin were banned in developed countries over 25 years ago, their continued use has been reported in several Asian countries [4]. The use of such pesticides in tropical countries is often justified for the eradication of disease vectors such as the malaria-carrying mosquito. OCPs are still used in large quantities especially in developing countries for the control of agricultural pests [5]. The bans of PCBs and OCPs were imposed in many countries after their toxicity, and environmental persistence was realized [6]. Due to high toxicity, long environmental half-lives and long scale transportation ability, they are of significant concern and have been studied extensively in the last decades [7]. Organochlorine compounds were detected in many environmental media such as water [8]; [3], sediment [3]; [7], air [9], biota [10] and in bivalve [11]. Organochlorine pesticides are one of the important components of chemical pollutants present in the marine environment. They are toxic to all living organisms [11]. Organochlorine pesticide enters into the marine environment through different sources, more particularly from estuaries [12]. Estuarine and marine sediments are the ultimate global sinks for most of the pollutants. Contamination of soil and sediments of coastal areas with persistent organochlorine compounds may be related to point sources, e.g., industrial discharges and domestic sewage, but more frequently, as in the case of pesticide pollution, it can also be attributed to precipitation, agricultural runoff, etc. [3]. Therefore, the study on...
organochlorine pesticides in sediment which is the bivalve habitat in Semarang coastal areas is very important to be conducted to discover how far the contamination level of those materials in the sediment. Because in the sediment, the bivalve gets the food by filtering the sediment.

2. Materials And Methods

2.1. Samples collection

Sampling points were located on coastal waters areas at the east part of Semarang. Figure 1 shows the sampling sites, the samples of sediments were collected in polyethylene plastic bags bottles from different stations (4 stations). The samples were collected in 3 kg plastic bags. Then, plastic bags were labeled properly and sealed tightly. All the samples were brought to the laboratory for the organochlorine pesticide to be analyzed. The parameters analyzed were psycho-hydrochemical properties of marine waters and organochlorine contents of sediments. The salinity, total dissolved solids, pH, dissolved oxygen, and temperature were measured at the time of samples collection using water quality checker (Horiba Co. Ltd., Japan).

2.2. Sample analysis

The analytical procedure applied was the method of Standard Method [13]. The analytical procedure of Organochlorine Pesticide (OCPs) in sediment samples was modified according to the method described previously [14]; [15]. 15 g of freeze-dried and homogenized sediment sample was placed into a Soxhlet apparatus and extracted with 250 ml of hexane-dichloromethane in n-hexane and capillary columns. One-liter samples were extracted with a solvent mixture and then concentrated in a Kuderna-Danish apparatus. The extracts were cleaned up with Florisil column. The final pesticide extract was obtained in 5 mL of hexane. The samples were then analyzed by using gas chromatography Model Hitachi 163 FPD (Flame Photometer Detector), and nitrogen High Pure (HP) was used as the carrier gas. A 2 in a glass column (3 mm ID) packed with 3% Silicon OV1 on 80-100 mesh Supelcon was used. Gas flow at 30 mL min', column temperature at 160-230°C, detector temperature at 290°C and the injector temperature at 290°C were maintained.

![Figure 1](image)

**Figure 1.** The sampling areas at the eastern part of Semarang Coastal waters

3. Results And Discussion

The eastern part of Semarang coastal waters is a fishing ground area for several biotas such as fish, shrimp, crab, and bivalve. The high activities of fishermen in this area are because in this area the waters is very fertile, some rivers are flowing through this area such as East Banjir Kanal River, Banger, Babon and Sri Mulyo which all of them are flowing the nutrient and pollutant whether in solid, suspension and solution [16]. The high production of fisheries in that area is supported by a good quality of water so it can support the life of sea organisms [16]. It is also proved by the research result on recent water quality that can be seen in table 1. From the table, it can be seen that the water
quality can support the life of sea organisms to live and grow. The range of salinity between (31 – 33 ppt), total dissolved solid between (30.5 – 31.5 mg/L), pH between (7.3 – 7.5), dissolved oxygen (5.6 – 6.4 mg/L) and temperature (29.5 – 29.9 oC).

Table 1. Physico-chemical properties of water samples of marine waters in the sampling areas (Eastern part of Semarang coastal waters)

| Water Quality        | ST 1 | ST 2 | ST 3 | ST 4 |
|----------------------|------|------|------|------|
| Salinity (ppt)       | 33   | 33   | 31.5 | 31   |
| Total Dissolved Solid (mg/L) | 31.5 | 30.5 | 31.5 | 31   |
| pH                   | 7.3  | 7.3  | 7.5  | 7.3  |
| DO (mg/L)            | 5.9  | 5.9  | 6.4  | 5.62 |
| Temperature (°C)     | 29.8 | 29.5 | 29.8 | 29.9 |

The inclusion of nutrient in the waters is also followed by the inclusion of pollutant such as heavy metal, pesticide, bacteria, etc. Several previous researches conducted in the Semarang waters showed that Organochlorine Pesticides such as Heptachlor, Aldrin, Endosulfan, Endrin, and pp-DDT were found in the coastal waters in the West part of Semarang [17]. The research of organochlorine pesticides accumulation in the sea sediment had also been conducted in many countries like India [3], China [15], Singapore [7], Korea [18]. From all of those countries, organochlorine pesticides were found in sediment.

The recent research result by taking the sediment samples in the bivalve fishing ground areas in the east part of Semarang showed that the sediment in that area was found the concentrations of heptachlor, endosulfan, endrin, and pp-DDT exclude aldrin. The range of pesticides residues concentration from the highest to the lowest as followed endrin (8.55 – 65.84 µg/L) detected in two samples, then pp-DDT (27.66 – 50 µg/L) detected in two samples, heptachlor (25 µg/L) only detected in one sample, Endosulfan (0.92 -13.18 µg/L) detected in three samples while Aldrin on the four samples showed the number of below detection. The result can be seen in Table 2 and Figure 2.

Table 2. Range, frequency of occurrence and mean ± standard deviation of organochlorine pesticide residue levels (µg/L) from bivalvia fishing ground at eastern part of coastal Semarang

| Sediment | Heptachlor | Aldrin | Endosulfan | Endrin | pp-DDT |
|-----------|------------|--------|------------|--------|--------|
| ST 1      | bd         | bd     | 1.56       | bd     | bd     |
| ST 2      | 25.45      | bd     | 13.18      | 8.55   | bd     |
| ST 3      | bd         | bd     | 0.92       | 65.84  | 27.66  |
| ST 4      | bd         | bd     | bd         | bd     | 29.53  |
| % detection | 25    | 0      | 75         | 50     | 50     |
| Range     | 25         | 0      | 0.92 -13.18| 8.55 - 65.84 | 27.66 - 50 |
| Mean ± SD | 25.45      | 0      | 5.22 ± 6.9 | 37.2 ± 40.51 | 28.59 ± 1.32 |

Bd = below detection

Evens until now in Indonesia there are no concentration criteria of organochlorine pesticide in the sea sediment for the feasibility of living organisms but OCPs is a persistent material and can be accumulated in the tissues of marine organisms. Moreover, the bivalve from cockles type is normally found in muddy areas near the river mouth [19]. They are sedentary filter feeder, taking in food particulates through their gills when their shells are open [20]. Besides, the sediment in the research location comes from several river currents which flowing through agricultural, residential and industrial areas estimated to still using OCPs. It is estimated later that the higher the OCPs concentration in sediment will also be followed by the increase of the material in bivalve tissue.
4. Conclusion
Some kinds of organochlorine pesticide have been contaminating sediment in the Semarang coastal area which is a fishing ground of bivalve. The OCPs including Heptachlor, Endosulfan, Endrin, and pp-DDT. That was the high concentration of pesticide showed on Endrin (65.84 ppb), pp-DDT (29.53 µ g/L), and heptachlor (25.45 µ g/L). Futher more the low concentrations were detected on aldrin (bellow detected) and endosulfan (0.92 µ g/L).

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6. References

[1] Wang H, He M, Lin C, Quan X, Guo W, Yang Z. Environ Monit Assess. 2007; 133 (1):231–42.
[2] Basheer C, Obbard JP, Lee HK. J. Chromatogr A. 2005; 1068 (2):221–8.
[3] Rajendran RB, Imagawa T, Tao H, Ramesh R. Environ. Int. 2005; 31 (4):503–12.
[4] Kannan K, Tanabe S, Giesy JP, Tatsukawa R. Springer; 1997. p. 1–55.
[5] Pandit GG, Rao AMM, Jha SK, Krishnamoorthy TM, Kale SP, Raghu K. Chemosphere. 2001; 44 (2):301–5.
[6] Feng K, Yu BY, Ge DM, Wong MH, Wang XC, Cao ZH. Chemosphere. 2003; 50 (6):683–7.
[7] Wurf O, Obbard JP. Chemosphere. 2005;58(7):925–33.
[8] Booij K, Hoedemaker JR, Bakker JF. Environ. Sci. Technol. 2003; 37 (18):4213–20.
[9] Jaward FM, Di Guardo A, Nizzetto L, Cassani C, Raffaele F, Ferretti R. Environ. Sci. Technol. 2005; 39 (10):3455–63.
[10] Carlson DL, Hites RA. Environ Sci Technol. 2005; 39 (19):7389–95.
[11] Sundar G, Selvarani J, Gopalakrishnan S, Ramachandran S. Environ. Monit Assess. 2010; 160 (1):593–604.
[12] David B V. 1992. pp. 225–50.
[13] Association APH. 1992.15.
[14] Doong R-A, Peng C-K, Sun Y-C, Liao P-L. Taiwan. Mar Pollut Bull. 2002; 45 (1):246–53.
[15] Yang R, Lv A, Shi J, Jiang G. Chemosphere. 2005; 61 (3):347–54.
[16] Suryono CA, Rochaddi B. Jurnal Kelautan Tropis 2017; 20 (1).
[17] Suryono CA, Rochaddi B, Irwani I. Bul. Ose. Mar. 2017; 5 (2):101–6.

Figure 2. Mean ± SD of occurrence of organochlorine pesticide residue levels (µ g/L) from bivalvia fishing ground at eastern part of coastal Semarang
[18] Hong SH, Yim UH, Shim WJ, Oh JR, Lee IS. *Mar Pollut Bull*. 2003; 46 (2):244–53.
[19] Pathansali D. *I. Malay. Agric. J.* 1963; 44:18–25.
[20] McCoy EW, Tuaycharoen S, Vakily JM, Boonchuwong P. ICLARM. 1988.