Study of copper (Cu) contents in blood cockles (*Anadara* sp.) at Surabaya coastal waters

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Abstract. Heavy metal pollution categorized as harmful effect on the environment. This study aims to determine the content and the rate of accumulation of heavy metals copper (Cu) in the mussel of cockles (*Anadara* sp.) This study uses observation method with descriptive analysis. The test results Cu in sea water was <0.0223 mg/L. The results have exceeded the water quality standard according to state environmental ministerial decree number 51 2004 on marine water quality standards for marine biota maximum limit of Cu in sea water is 0.008 mg/L. Copper concentration in the sediment of 6.16 mg/kg at the Wonokromo station and at the Dadapan station is 4.03 mg/kg. According to the US-EPA in 2004 on the instructions of sediment pollution classification 49.98 mg Cu/kg. The results of shells fur Cu on Wonokromo was 1.833 mg/kg and Dadapan was 1.352 mg/kg. According to the MOH Decree No.0375/B/SK/1989 about Quality Standard Biota Consumption of Metals to the maximum limit of the existing Cu concentrations in marine biota was 20 ppm or 20 mg / kg so that the content of Cu in shellfish feathers still below the limit of existing quality standards.

1. Introduction

Surabaya coastal waters are potential to accumulate anthropogenic burden. Anthropogenic burden is a pollutant that enters the water due to human activities in the form of domestic activities (household), urban activities (cities), or industrial activities [1]. Anthropogenic burden is worsened by the misuse of the river as the waste disposal site. Thus, the pollutant can be distributed up to the estuary, even to the ocean.

The waste that enters the Pamurbaya waters includes solid, gas, and liquid waste. One of the types of wastes that is accumulated highly and pollutes the waters is solid waste including heavy metal pollution. Heavy metal pollution is categorized as pollution that causes dangerous effects to the environment and living organisms. Heavy metals are non-degradable. Heavy metal can be accumulated in the environment like in water column and sediments, and eventually can be absorbed into the marine biota [1]. Heavy metals that pollute the waters are Mercury (Hg), Lead (Pb), Zinc (Zn), Cadmium (Cd) and Copper (Cu). According to the Government Regulation No. 82 Year 2001 class I-IV on Water Quality Management and Pollution Control, the maximum level of heavy metals in the waters are Hg 0.001-0.005 mg/L, Pb ≤ 0.1 mg/L, Zn ≤ 5 mg/L, Cd 0.01 mg/L, and Cu 0.02 – 1 mg/L.

Cu is a heavy metal with essential elements that are needed by plants and animals as the composer of plastocyanin that functions in the transportation of electrons in photosynthesis process [2]. Cu levels that is over 0.5 mg/L would cause LC50 (50 % death concentration) to sea and fresh water’s...
invertebrates [3]. Copper excess in human being may cause diarrhea, nausea, vomiting, anemia, stomach disorder, and kidney failure.

Sea water invertebrates that can be the parameters for the presence of Cu in the waters is, but not limited to, blood cockles. Blood cockles are animals that have a feeding habit by preying on particles that exists in the form of microorganisms or detritus. Blood cockles has a feeding pattern as filter feeder, which filters any type of foods around them, thus they can accumulate microorganisms and other foreign materials, including heavy metals that are absorbed and stored in their digestion system without poisoning the shells themselves [4]. Considering the high demands over blood cockles by the society that is in line with the increase environmental pollution; thus, it is necessary to conduct a research on the copper (Cu) heavy metal content in blood cockles in the east coast waters of Surabaya. The information will be beneficial for water pollution control and food safety.

2. Methodology

2.1. Research time and place

This research was performed in February 2017 at the east coast waters of Surabaya. The blood cockles (Anadara sp.) were taken from two stations. The first one was located in Wonokromo, and the second one was in Dadapan. Analysis of copper in sea water, sediment, and blood cockles was done at laboratory of Badan Riset dan Standarisasi Industri (BARISTAND), Surabaya.

2.2. Tools and materials

The research tools that used were boat, basket, dredges tool, water sampler, cool box, 2 kg plastic bags, refractometer, thermometer, Secchi Disk, pH pen, labeling paper, permanent marker, and GPS. The tools to analyze copper in water, sediment, and blood cockles were analytical balance (0.0001 g precision), 50 mL beaker glass, PVC, 50 mL measuring flask, knife, fume hood, micro pipette, and Atomic Absorption Spectrophotometry (AAS).

The materials used to support this research were the sea water sample, blood cockles, and sediments, concentrated HNO₃, solvent, and ice block.

2.3. Research procedure

2.3.1. Determination of sampling point

Determination of The geographical coordinates of the sampling stations was done with Global Positioning System (GPS).

2.3.2. Blood cockles sampling

Sampling for blood cockles was done in two stations namely Wonokoromo and Dadapan. The sampling process in Wonokromo and Dadapan stations were separated into three points in each station. The blood cockles sampling were repeated twice for every points. Blood cockles sampling was done with dredges, a catching tool that is dragged with a fisherman boat with a speed of 2.7 to 4.6 m/min. Later, the catch is placed in baskets and plastic bags that are labeled according to the sampling station, and finally placed in a cool box. Later, the labeled blood cockles were handled by separating the shell and the meat. The meat was weighed every 50 g and placed in labeled plastic bags before it was brought to the laboratory to be tested for its copper content.

2.3.3. Sea waters sampling

Sampling of sea waters was done at both stations. Sample of sea water was taken with water sampler tool at a depth of 30 cm under sea level for as much as ± 100 mL and it was placed in a bottle. HNO₃ was added into the bottle and the bottle was placed in a cool box with ice blocks in it to ensure that there were no biological and chemical changes. Later, the cool box was transported to the laboratory to be examined.
2.3.4. **Sampling of sediment**

Sampling of sediment was done at every station. The amount of sediment taken was 200 g. The sediment that was taken was placed in plastic bags, and given air-dry treatment so that there won’t be any biological and chemical changes that occurs [5]. Later, the cool box is closed shut and is transported to the laboratory to be examined.

2.3.5. **Copper analysis in blood cockles, sediment, and sea water.**

Copper analysis in water, sediment, and blood cockles sample was performed with Atomic Absorption Spectrophotometry (AAS) based on the Lambert-Beer law principle, which dictates that the amount of light absorbed is directly proportional with the level of the substance [6].

3. **Research Parameters**

The research parameters measured included main parameters and supporting parameters. The main parameters were copper in the water, sediment, and blood cockles from Wonokromo and Dadapan research stations in Pamurbaya Waters. The supporting parameters were water quality including temperature, dissolved oxygen (DO), salinity, water clarity, and pH. Data collected were analyzed with descriptive analysis and reported in the form of graphs, tables, and pictures.

4. **Results and Discussion**

4.1. **General picture of east coast waters of Surabaya**

The general picture of East Coast Waters of Surabaya was reviewed in two stations, namely Wonokromo river station and Dadapan river station, as given in table 1.

| Sampling station | Temperature (°C) | pH | DO (mg/L) | Salinity (ppm) | Clearness (cm) | Suspended Solids (TSS) (mg/L) |
|------------------|-----------------|----|-----------|----------------|----------------|-----------------------------|
| Wonokromo Station | 29              | 8.2| 5.5       | 35             | 40             | 37                          |
| Dadapan Station  | 28              | 8.3| 4.4       | 40             | 60             | 7.5                         |

Table 1 shows the results of water quality measurement including temperature, pH, DO, salinity, water clarity, and suspended solids (TSS). The temperature of East Coast Waters of Surabaya ranged from 28 to 29 °C. Degree of acidity or pH on the East Coast Waters of Surabaya ranged from 8.2 to 8.3. Dissolved Oxygen or DO in the East Coast Waters of Surabaya ranged from 4.4 to 5.5 mg/L. Salinity of the East Coast Waters of Surabaya ranged from 35 to 45 %. The water clarity of the East Coast Waters of Surabaya was 40-60 and the suspended solid or TSS in the East Coast Waters of Surabaya ranged between 7.5 and 37 mg/L.

With dissolved oxygen level of 1.0 - 5.0 mg/L, fish can survive, but their growth will be affected. While DO > 5.0 mg/L is preferred by almost every aquatic organisms [2]. In Dadapan River, it was found that the dissolved oxygen level was 4.4 mg/L, this value shows that the growth of aquatic organisms in the water were disturbed, while the Wonokromo River showed a DO level of 5.5 mg/L, which showed that the aquatic organisms living there were still normal. The water pH of Wonokromo River was 8.2 while water pH of Dadapan River was 8.3. According to Effendi [1] most aquatic biota are sensitive to a change of pH between 7-8.5. The pH levels in both rivers were still within the normal range for aquatic organism.

Salinity at the East Coast Waters of Surabaya ranged between 35 to 40 ppm. Effendi (2000) stated the sea salinity level ranged between 30-40 ppm. Water clarity of the East Coast Waters of Surabaya was 40-60 cm. Clarity is water transparency that is measured visually. It is affected by suspended solid or murk. Suspended solid level in Wonokromo River was 37 mg/L while in Dadapan River the TSS
value was 7.5 mg/L. Loyd (1982) stated that TSS value between 1-25 mg/L does not affect fisheries while TSS value of 25-80 mg/L can mildly affect fisheries. From TSS point of view, the quality of the East Coast Waters of Surabaya was in a good condition.

4.2. Copper in the Sea Waters
Copper content of the sea water of East Coast Waters of Surabaya was analyzed from two research stations: Wonokromo River and Dadapan River and the results are shown in table 2.

**Table 2.** Copper (Cu) heavy metal substances in sea water.

| Testing Parameter | Unit | Level        |
|-------------------|------|--------------|
| Copper (Cu)       | mg/L | <0.0223      |

Level of copper in Wonokromo River and Dadapan River was <0.0223 mg/L. According to the Ministry of Environment Regulation Number 51 year 2004 on Sea Water Quality Standard, for the sea water biota, the maximum Cu is 0.008 mg/L. The concentration of Cu in East Coast Waters of Surabaya exceeded the quality standard. source of copper pollution in the East Coast Waters of Surabaya, allegedly, came from industrial waste, household waste, and shipwrecks. Naturally, copper can come from erosion, rock erosion, or from the atmosphere that was brought down by rain. human activities, industrial activities, mining, or shipyard industry, along with activities in docks, can increase the level of copper in the water [7].

4.3. Level of copper in sediment
Copper level found in the sediment of East Coast Waters of Surabaya is shown in table 3.

**Table 3.** Copper heavy metal substances in sediment.

| Testing Parameter | Unit | Level | Level |
|-------------------|------|-------|-------|
| Copper (Cu)       | mg/kg| Wonokromo | Dadapan |
|                   |      | 6.16   | 4.03  |

The concentration of Cu in the sediment was 6.16 mg/kg in Wonokromo River and 4.03 mg/kg in Dadapan River. Classification of sediment pollution standard guide, the limit of Cu is 49.98 mg/kg, thus the Cu level in Wonokromo River and Dadapan River was still below the existing quality standard. Therefore, the sediment of the East Coast Waters of Surabaya was considered livable as aquatic organism habitat, including for blood cockles.

4.4. Cu level in blood cockles (*Anadara* sp.)
Copper level in the meat of blood cockles was taken from three points at the East Coast Waters of Surabaya: 2000 m, 1750 m, and 1500 m, with the measurement performed twice as shown in table 4.
Table 4. Cu heavy metal substances in the meat of blood cockles in each point with two repetitions.

| Station            | Cu Levels in Shell’s Meat (mg/kg) |
|--------------------|------------------------------------|
|                    | point 1500m | point 1750m | point 2000m |
|                    | 1st     | 2nd     | 1st   | 2nd   | 1st   | 2nd   |
| Wonokromo River    |         |         |       |       |       |       |
| Station            | Repetition | Repetition | Repetition | Repetition | Repetition | Repetition |
| Dadapan River      | 1.44     | 2.05     | 1.79   | 2.64   | 1.92   | 1.16   |
| Station            |           |           |         |         |         |         |

The copper level in blood cockles meat collected in Wonokromo River was 1.833 mg/kg while the blood cockles found in Dadapan River had copper level of 1.352 mg/kg. According to the Health Department of the Republic of Indonesia Regulation No.0375/B/SK/1989 on Standard for Metal in Consumable Biota, the maximum level of Cu in sea biota is 20 ppm or 20 mg/kg.

The concentration of heavy metal found in the meat from blood cockles taken from East Coast Waters of Surabaya did not exceed the existing standard. Results of the measurement of Cu in each point can be seen in table 6 and figure 8 showing that there were differences in concentration of metal found in each station and point. Copper concentration in Wonokromo River was larger than the one in Dadapan River. In Wonokromo River, the highest concentration was found at 1750 m, while in Dadapan River, the highest concentration was found at 1500 m. Concentration of copper decreases as the depth of the water increases [8]. Gulivey (year) stated that the depth sampling location, the lower the copper concentration.

5. Conclusion
Concentration of copper in the meat of blood cockles found in Wonokromo River and Dadapan River was 1.833 mg/L and 1.352 mg/L respectively. This level did not exceed the standard set by the Health Department of The Republic of Indonesia Regulation No.0375/B/SK/1989. However, the level of Cu found in the East Coast Waters of Surabaya showed a number that exceeded the quality standard, thus, efforts should be conducted to decrease the spread of heavy metal pollution in the East Coast Waters of Surabaya.

6. References
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