THE ACCUMULATION OF HEAVY METALS KADMIUM (Cd) IN WATER, SEDIMENTS AND AQUACULTURE BIOTA WHICH CONTAMINATED BY BATIK WASTE IN MULYOREJO VILLAGE PEKALONGAN

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ABSTRACT. This research entitled “The Accumulation of Heavy Metals Kadmium (Cd) in water, sediments and aquaculture biota which contaminated by Batik waste in Mulyorejo village Pekalongan”. Purposes to know the heavy metal concentration Cd in water, sediment and bandeng's flesh, relation between heavy metal concentration Cd in water and sediment with fish's flesh, the pollution status in this aquaculture, and also the consumption properness from the aquaculture station. This study conducted by survey method with stratified random sampling on four stations with four replications. The data then analyzed by descriptive comparative, F-test, regression and correlation, Contamination Factor index, Geoaccumulation index and bioaccumulation factor. The result revealed that the heavy metal concentration in the water 0.003-0.009 mg/L, in sediments 1.272-2.208 mg/kg and fish's flesh 0.087-0.168 mg/kg. The heavy metal concentration (Cd) in the water and sediments with fish's flesh are have positive correlation which strongly (R=0.888 and R=0.906). The pollution status based on the contamination factor index (CF) categorized as very high contaminated and geoaccumulation index is mild contaminated (station III and IV) and mild to severe contaminated (station I and II). The fishes in this station are improper to be consumed except in station IV (distance ±300m from Bremi's river outlet).

Keywords: metals Cd, water, sediment, bandeng fish's flesh
INTRODUCTION

The bandeng (Chanos chanos) pond in Mulyorejo Village, Pekalongan Regency is one of the productive fishpond. Bandeng is a fish that is cultivated in fishponds in the village of Mulyorejo for consumption. Bremi River is one of the tributaries of the Sengkarang River with a length of ± 9 km located in Tirto District. Along the downstream of the Bremi River there are many activities including the batik, textile, screen printing, settlement and aquaculture industries [3]. These industries produce waste containing toxic and dangerous chemicals (B3), one of which is heavy metals.

Cd heavy metal is usually used as a coloring agent in industry, which is toxic and does not decompose in aquatic environments [5]. Heavy metals that are in water over time will undergo a process of sedimentation with mud and settles to the bottom of the water [6]. In addition, heavy metals are known to accumulate in the body of fish for a long time as poisons that have a negative impact on biota [5]. If the fish are consumed by humans, it will endanger human health. The impact of Cd on humans, among others, causes disruption of lung health, bones, liver, reproductive glands, kidneys, heart, which is neurotoxic which results in damage to the sense of smell [4].

Research to determine the Cd metal content that has accumulated in water, sediments, and biota in bandeng ponds in Mulyorejo Pekalongan Village has never been done before, with known Cd levels in water and pond sediments, then the feasibility of the pond as a bandeng aquaculture area. In addition, knowing the level of Cd in bandeng that is cultivated can be determined for its safety for consumption. Therefore, there is a need for research related to the accumulation of heavy metals Cd in these farms.

MATERIAL AND METHODS

The method in this study is a survey method with sampling techniques using the Stratified Random Sampling method. Sampling was conducted at the Bandeng Fishpond in the Village of Mulyorejo, Pekalongan in May 2016. The research location was divided into four stations, sampling was carried out 4 times in a composite manner. Determination of sampling stations based on the distance from the source of freshwater input to the pond (Sungai Bremi). The sampling locations are presented in Table 1.

| Station | Coordinate          | Location                        |
|---------|---------------------|---------------------------------|
| I       | E : 6°52'14.1"     | Bandeng Fishpond I (close to the inflow Bremi River to the pond) |
|         | S : 109°38'58.4"   |                                 |
| II      | E : 6°52'09.8"     | Bandeng Fishpond II (located ± 100m from station I) |
|         | S : 109°38'58.5"   |                                 |
| III     | E : 6°52'05.3"     | Bandeng Fishpond III (located ± 100m from station II) |
|         | S : 109°38'58.6"   |                                 |
| IV      | E : 6°52'00.2"     | Bandeng Fishpond IV (located ± 100m from station III) |
|         | S : 109°38'58.6"   |                                 |

Sampling and Preservation of Samples for Cd Metal Analysis

600 mL of water was taken into a sample bottle, then 0.75 mL concentrated HNO3 was added. ± 250 grams sediment was taken using Ekman Grab at a depth of 15-20 cm. Fish samples are taken using a net, the meat is taken and mashed, then put in a plastic bag. Furthermore, the sample is cooled in an ice box and analyzed in a laboratory (SNI, 2009).

Sample Preparation for Cd Metal Analysis

100 ml sample water is taken, put in an erlenmeyer and shaked. 5ml concentrated
HNO₃ was added, heat it slowly until the volume becomes 15-20 ml and changed in color, after that the sample is cooled and added with 50 ml of distilled water. The sample was put into a 100 ml measuring cup through Whatman No. filter paper. 40 and added distilled water until the volume becomes 100 ml, the sample is ready to be analyzed by AAS (SNI, 2009).

Sediment samples and crystals were first cleaned and dried, then refined in porcelain frying cups. Samples were taken ± 5 grams, embedded in porcelain cups, and then heated in a furnace muffle at 500 °C for 5 hours. The resulting ash was dissolved in aqua regia of 5 mL and heated to a soluble ash, transfer to a 25 mL gauze and add 5 mL of HNO₃ 1 M, and then add aquadest to a volumetric flask incubated with a volume of 25 ml. The solution was filtered with Whatman No. paper. 41 (Muwartiningsih et al., 2015). Filtrates are ready for analysis with AAS (SNI, 2009).

Analysis of Cd

The Cd metal standard solution was made to find out the equation of the Cd metal standard curve by dissolving Cd(NO₃)₂ in 0.1 N nitric acid. Then it was diluted and made in various concentrations of 0.02; 0.50; 1.00; 1.50; 2.00; 3.00; 4.00; and 5.00 mg / L, then absorbance was measured using AAS (SNI, 2009).

Measurement of Cd metal content by the Flame Atomic Absorption Spectrometry method using a set of AAS tools. The prepared filtrate is sucked with a 20 ml respirator tube and put into a Nabulyzer, then atomized and evaporated. The vapors that are formed are burned with a burner flame and followed by an atomization process, then irradiated with cathode rays at a wavelength of 228.8 nm and a strong current of 3.5 mA. The absorbance value of the sample and the Cd standard solution will appear on the AAS screen along with the line equation (SNI, 2009). Calculation of Cd metal content in the sample using the formula:

\[
Cd = \frac{AXB}{C} \text{ mg/l}
\]

ex:  
A= ppm (mg/l)  
B= the final volume of the extracted product  
C= initial sample weight

Calculation of pollution levels based on Contamination factor (CF) index, Geoaccumulation index (Igeo), and Bioaccumulation Factor (BAF).

Contaminant Factor (CF) formula:

\[
CF = \frac{[\text{Cd heavy metal}]}{[\text{Background}]} 
\]

Igeo Calculation Formulas (Geoaccumulation Index)

\[
Igeo = \log^{2} \left[ \frac{[\text{Cd heavy metal}]}{1.5 \ast \text{Background}} \right] 
\]

Bioaccumulation Factor (BAF) calculation formula

\[
BAF = \frac{[CB]}{[CW]} 
\]

ex:  
CB = chemical concentration in organisms  
CW = Concentrated chemistry in sediments (chemical mass / L)
RESULTS AND DISCUSSION

Content of Cadmium (Cd) Heavy Metals in Water

The heavy metal content of each station in the bandeng ponds in Mulyorejo Village is shown in Figure 1.

Figure 1 shows that the Cd heavy metal content between stations was significantly different (P <0.05). This is caused by the distance of the station to the source of pollutants, sedimentation, and salinity. Station I is located closest to the Bremi River inflow to ponds and settlements, so that the highest heavy metal content in water. The source of fresh water in the ponds comes from the Bremi River, the heavy metal content of Cd in water at the source is 0.012 mg / L. The difference in heavy metal content is also caused by sedimentation. Water in ponds at station II, III, and IV is sourced from station I, so that heavy metals carried by the current from station I will experience a process of sedimentation continuously and decreasing. Metals that are difficult to undergo dilution in the water column will eventually descend to the bottom and settle in sediment, so that the metal content in water tends to be small.

At station I to station IV the salinity value increases. The salinity value at station I is the lowest compared to other stations which is 9.75 ppt, then the value has increased from station I to station II and so on up to station IV. Salinity values at stations II, III, and IV are 12.0, 13.2, and 16.2 ppt, respectively. This causes the heavy metal content from I to station IV to decrease. Low salinity will result in a decrease in complexing agent in waters (Cl-), so that more heavy metals will be found in the form of free ions which are more easily entered into the body of biota, and vice versa the higher the salinity value then the complexing agent in waters (Cl-) will increase and bind to heavy metals and settle to the bottom of the waters [2].

The high content of Cd in water affects the health of biota and humans who use the water. The Cd heavy metal content in all research stations is above the threshold value set by KMNHL No.51 of 2004, which is 0.001 mg / L (Figure 1).

Content of Cadmium (Cd) Heavy Metals in Sediments

The heavy metal content of each sediment at the station in the bandeng fish pond of Mulyorejo Village is shown in Figure 2.
Figure 2. Average Cd values in the sediment of each station in bandeng fishponds in Mulyorejo Village, Pekalongan.

Figure 2 shows that the heavy metal content of Cd in sediments between stations was significantly different (P <0.05). Based on further tests of Cd heavy metal content in sediments at station I with stations III and IV were significantly different (P <0.05), while station I with station II were not significantly different (P ≥0.05). The Cd metal content in sediments at stations I to IV has decreased. Heavy metals in sediments are sourced from heavy metals present in water, so decreasing heavy metal content in water will also cause a decrease in heavy metal sources which will settle in sediments (R = 0.893). The R value indicates that the Cd in water with Cd in sediments has a relationship that is directly proportional to the strong closeness. Each increase of 1 mg / L Cd in water was followed by an increase in Cd in sediment of 163,783 mg / kg (y = 0.783 + 163x). The relationship between Cd metals in sediments and Cd metals in water is shown in Figure 3.

COD and TSS values at stations I to IV decreased, so that the content of heavy metals in sediments at stations I to IV also decreased. The average COD values at stations I through IV were 15.60, 14; 82, 9.75, and 7.22 ppm, while the mean TSS values were 1023.67, 862.33, 850.67, respectively, and 786.33 ppm. In addition, the salinity value at station I to station IV has increased, amounting to 9.75, 12.0, 13.2, and 16.2 ppt. The content of heavy metals in sediments between station I and station II is not significantly different because this is due to environmental conditions and the type of sediment that tends to have almost the same characteristics. The environmental conditions at stations I and II have relatively similar COD values which cause the metal content at the two stations is not significantly different. The COD content in the two stations is 15.60 and 14.82 mg / L.
The heavy metal content of Cd in sediments at all research stations was above the threshold value set by CCME [1], which is 0.7 mg / kg (Figure 2). This shows that the condition of aquaculture ponds in all stations has experienced heavy metal pollution and is not suitable as a habitat for aquatic biota, and is at high risk when used as a fishing business area, both for cultivation and capture activities. Cd

**Heavy metal in Bandeng fish (Chanos chanos Forsskal)**

The heavy metal content of each station in bandeng fishponds in Mulyorejo Village is shown in Figure 4.

![Figure 4](image)

**Figure 4. Average value of Cd in fish meat at each station in bandeng fishponds in Mulyorejo Village, Pekalongan.**

Figure 4 shows that the heavy metal content of Cd in fish flesh between stations was significantly different (P <0.05). This is caused by the distance of the station to the source of pollutants, Cd metal content in water, Cd metal content in sediments, and water quality (salinity). The source of fresh water in the ponds comes from the Bremi River, with heavy metal content of Cd in sediments and water at the source (Bremi River) in the amount of 2,380 mg / kg and 0.012 mg / L. Station I is closest to the Bremi River inflow, so the heavy metal content in water and sediment is highest, as is the heavy metal content in bandeng fish (Chanos chanos).

The decrease of heavy metal content in water from stations I to IV will cause the heavy metal content that accumulates in bandeng at stations I to IV to also decrease (R = 0.888). The correlation value (R) shows that between Cd in water and Cd in bandeng has a relation that is directly proportional to the strong closeness. Each increase of 1 mg / L Cd in water was followed by an increase in Cd in bandeng by 12,947 mg / kg (y = 0.047 + 12.9x). The relation between Cd metal in water and Cd metal in bandeng is shown in Figure 5.
Figure 5. Relation between the content of Cd in water and Cd in fish meat.

The content of heavy metals in sediments at stations I to IV has decreased, so that the content of heavy metals in bandeng fish in stations I to IV has also decreased (R = 0.906). A positive correlation (R) value indicates that the Cd in sediments with Cd in bandeng fish has a relationship that is directly proportional to the strong closeness. Each increase of 1 mg / kg Cd in sediments was followed by an increase in Cd in bandeng fish by 0.0479 mg / kg (y = -0.024 + 0.0719x). The relationship between Cd metals in sediments and Cd metals in bandeng fish is shown in Figure 6.

Figure 6. Relation between metal content of Cd in sediments and Cd in fish meat.

Water quality affects the content of heavy metals in the body of bandeng (Chanos chanos). Salinity from stations I to IV has increased, so that the content of heavy metal Cd in bandeng from station I to station IV has decreased. Salinity values at stations I through IV were 9.75, 12.0, 13.2, and 16.2 ppt.

The Cd heavymetal in bandeng (Chanos chanos) fish meat at stations I to III is above the threshold value, while at station IV it is below the threshold value set by SNI [8], which is 0.1 mg / kg (Figure 4). This shows that bandeng in fishponds at stations I to III are no longer suitable for consumption, while station IV is approaching the threshold value. The bandeng that is cultivated in the pond of Mulyorejo Village will have a dangerous health impact if consumed.

**Level of Heavy Metal Cadmium (Cd) Pollution**
Figure 7. Contamination factor (CF) value of Cd heavy metals in the Bandeng pond in Mulyorejo Village.

Figure 7 shows the results of calculating the CF value at each station ranging from 6.360 to 11.040. CF values from station I to station IV belong to the very high contamination category with CF values > 6. This is due to the activity around the Bremi River which is used as a source of fresh water in the bandeng ponds in Mulyorejo Village, which is the waste that is mostly generated from the batik industry. CF values from station I to station IV are decreasing. This is caused by the distance of the station from the pollutant source in the fishpond. Station I is located not far from the existence of settlements, besides that it is located close to the Bremi River inflow to the pond, while in stations II to IV it is further away from the Bremi River inflow. The water from the Bremi River that enters the heavy metal containment ponds at station I is partly heavy metal deposited in sediments, then at station II freshwater is sourced from station I so that the heavy metal content in sediments is less.

Figure 8. Geoaccumulation Index (Igeo) of heavy metal Cd in the bandeng pond in Mulyorejo Village.

Figure 8 shows the results of the calculation of the Igeo value at each station ranging from 1.276 to 2.216. The Igeo values from station I and station II are in the class 3 category, namely moderate to heavily polluted with igeo values of 2-3, while for station III and station IV they are classified in class 2 categories, which are moderately contaminated with igeo 1-2 values. This is due to the station I closest to the source of pollutants, namely the input of water from the Bremi River. Igeo values from station I to station IV are decreasing. Igeo values at stations III and IV are classified as moderately polluted. This is caused by the
distance of the station from the pollutant source in the fishpond. Stations III and IV are very far from the Bremi River inflow, so that the flow will cause the distribution of heavy metal Cd in sediments to be uneven and this station is classified as far from industrial activities so that the accumulation of heavy metals in sediments is low.

Bioaccumulation of Cadmium (Cd) in Bandeng (Chanos chanos) Based on BAF Value

Figure 9 shows the results of the calculation of the BAF value at each station ranging from 0.067 to 0.076. BAF values from station I to station IV belong to the category of organisms lacking in the ability to accumulate metals in their bodies with a BAF value ≤ 1. BAF values are obtained with a contaminant concentration ratio measured in biota in the field or under several exposure conditions with concentrations measured in sediments. This is related to the heavy metal content of Cd in water, the absorption process and the rate of accumulation of heavy metal Cd in bandeng. The low BAF value is influenced by the heavy metal content in the waters. The farther away from the source, the value of BAF in bandeng meat decreases, this is due to the heavy metal content in the media and the pond environment is also decreasing. The accumulation of Cd in bandeng occurs because the absorption of Cd from water is not from sediment. Bandeng is a pelagic fish that is in the water column so it is less able to accumulate heavy metal Cd in sediment and tends to accumulate Cd metal in the water column.

CONCLUSION

Based on the results and discussion of the research it can be concluded that the content of cadmium (Cd) heavy metals in water, sediments, and fish meat ranges from 0.003 to 0.009 mg / L, 1,272-2,208 mg / kg, and 0.087-0.168 mg / kg. The higher the Cd metal content in water and sediments, the Cd metal content in bandeng increased, and vice versa (R = 0.888 and R = 0.906). The level of Cd metal pollution in bandeng ponds in the village of Mulyorejo is categorized as a contamination factor which is classified as very high contaminated, the value of the geoaccumulation index is classified as moderate to severe. The bandeng (Chanos chanos) at stations I to III are no longer suitable for consumption. Based on the value of bioaccumulation factor (BAF), bandeng are less able to accumulate heavy metals in their bodies.

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