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Content of metals of lead and cadmium in water and tilapia (*Oreochromis mossambicus*) and its bioavailability in sediments in Muara Tukad Badung

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Abstract
The Tukad Badung Watershed is densely populated with various activities such as markets, workshops, cottages, industries, and dyeing. The waste from these activities may be the source of metals entering the Tukad Badung River will end at the estuary, which will lead to the accumulation of various discharges from the Tukad Badung watershed in the estuary. The purpose of this study where to determine Pb and Cd contents in water, fish, and sediment and their bioavailability in the sediments at the Tukad Badung estuary. The metal species of Pb and Cd in the sediment were carried out by serial extraction, and the metal content was measured using AAS. The average contents of Pb and Cd in the water is 0,3593-0,4748 mg/L and 0,1698-3709 mg/L, and in fish is 11,6966-16,4734 mg/Kg and 8,2412-13,6261 mg/Kg respectively. Based on the regulation of the Governer of Bali No. 16 of 2016 concerning the quality standard of heavy metal contents in water bodies, those metal contents have exceeded the threshold of 0.03 mg/L for Pb and 0.01 mg/L for Cd. The metal content of Pb in tilapia fish has exceeded the threshold in SNI (2009), 0.3 mg/kg, and the FAO/WHO (2004) quality standard of 0.03 mg/kg. The content of Cd in the fish has also exceeded the quality standard, which is 0.01 mg/Kg. The total contents of Pb and Cd in the sediment are 75,8229-94,2104 mg/Kg and 48,1119-54,0053 mg/Kg, respectively. The bioavailability of Pb metal is dominated by nonbioavailable metals (49,89-55,58%), followed by potentially bioavailable metals (17,37-28,81%), and the smallest metal is bioavailable (3,27-3,90%). The bioavailability of Cd metal is dominated by non-bioavailable metals (61,95-78,50%), followed by potentially bioavailable metals (5,37-23,81%), and the smallest metal is bioavailable (1,18-2,14%).

Keywords: river water, bioavailability, tilapia, heavy metals, sediment

Introduction

Tukad Badung divides Denpasar City into two parts, namely west and east. Around Tukad Badung are dense settlements with various activities such as workshops, markets, cottage industries, and the textile industry. Waste containing heavy metals can come from these activities because they are not processed and enter Tukad Badung. Textile industry waste is the most abundant source of heavy metals such as Pb and Cd and household waste. The river flow will end in the estuary, and this will cause the accumulation of various discharges from the Tukad Badung watershed that crosses the settlements in the estuary (Putra, 2016) [2].

Pb and Cd metals that enter the waters as solutes are deposited and absorbed by organisms. Pb and Cd metals that settle with solids will affect the quality of sediment at the bottom of the water so that it has a destructive impact on aquatic biota such as fish. Pb and Cd metals can enter fish and then reach humans when the fish is consumed.

Based on the research of Kusumadewi *et al*., (2015) [3] found that the Pb content in tilapia fish in Tukad Badung was 0.3 mg/Kg. Other researchers found that the Pb and Cd content in Benoa Bay was 0.0109 – 0.0463 mg/L and 0.0023 – 0.0063 mg/L. Sediments are the final site of various metal compounds that accumulate in waters. In sediments, Pb and Cd are available as free ions or bound to carbonates whose bonds are unstable so that they are quickly released into the waters and absorbed by organisms (Sahara *et al*., 2015). Wijayanti *et al*. (2015) [5] found that Pb's metal content in Tukad Badung's sediment was 4.2669 – 27.9171 mg/Kg, and the percentage of Pb bioavailability in the sediment was 9-70%. Siaka *et al*. (2019) [6] also found that the concentrations of Pb and Cd in the sediment at the Tukad Badung estuary were 286.3344 – 376.1754 mg/Kg and 1.3724 – 7.1725 mg/Kg.

Materials and Methods

Ingredient

The materials used are river water, tilapia fish, sediment, aquadest, lead nitrate, cadmium nitrate, hydrochloric acid, ammonium acetate, HNO3, CH3COOH, H2O2, HONH3.Cl, and reverse aquaregia.

Equipment

The equipment used consisted of SSA, hot plate, analytical balance, spray bottle, set of glassware, blender, sample bottle, filter paper, a plastic funnel, Van Veen Grab Sampler, cool box, centrifuge, pH meter, and magnetic stirrer.

Procedure

Water sampling
River water is taken from 3 different points using plastic bottles that have been washed with HNO3. The water obtained was put in a cooler while being brought to the laboratory and then prepared.

Fish sampling
Tilapia fish are bought from people who fish in the Tukad Badung estuary. The fish obtained were placed in a cooler and stored in the freezer before being prepared in the laboratory.

Sediment sampling
Sediment was obtained with the Van Veen Grab Sampler tool. Furthermore, it is placed in a cooler before being prepared in the laboratory.

Determination of Pb and Cd concentrations in water
25 mL of river water sample was added with 10 mL of 65% HNO3 and heated until transparent in a beaker. Filtered the digestion results, then the volume was adjusted using distilled water in a 25 mL volumetric flask. The absorbance was measured using AAS at the appropriate wavelength.

Determination of Pb and Cd concentrations in tilapia fish
Mujer fish meat samples were mashed using a blender until homogeneous, then weighed 1 gram and destroyed with 10 mL HNO3 and 5 mL H2O2 until transparent. The destruction results were then allowed to cool and filtered, and then the volume was adjusted using distilled water in a 25 mL volumetric flask. Then the absorbance was measured using AAS.

Determined total Pb and Cd concentrations in sediment
one gram of sediment plus 10 mL of 65% HNO3 and heated until transparent in a beaker. The results of the destruction are allowed to cool and then filtered. The volume was adjusted using distilled water in a 25 mL volumetric flask. The absorbance was measured using SSA.

Pb and Cd metal speciation in sediment samples

Extraction Stage I (EFLE fraction determination)
The 1 gram sediment sample was added with 40 mL of 0.1 M CH3COOH and homogenized using a magnetic stirrer for 1 hour. The mixture was centrifuged at 2500 rpm for 10 min. Separate the liquid and solid parts, and then the liquid part is adjusted to the volume using distilled water in a 50 mL volumetric flask. The results of the destruction were analyzed using SSA.

Extraction Phase II (determination of Mn and Fe oxide fractions)
Added the remaining fraction with 40 mL of 0.1 M HONH3.Cl was added with 65% HNO3 to pH 2, then homogenized with a magnetic stirrer for 1 hour. The mixture was centrifuged at 2500 rpm for 10 min. The volume was separated from the liquid and solid parts and then adjusted using distilled water in a 50 mL volumetric flask. The results of the destruction were analyzed using SSA.

Extraction Stage III (organic and sulfide fractions)
The remaining fraction II was added with 10 mL of 8.8 M H2O2 and allowed to stand for 1 hour while shaking occasionally. Then heated in a water bath for 1 hour, allowed to cool, and added 20 mL of 1 M CH3COONH4. Then HNO3 was added to pH two and centrifuged at 2500 rpm for 10 minutes. Separate the liquid and solid parts, and then the liquid part is adjusted to the volume using distilled water in a 50 mL volumetric flask. The results of the destruction were analyzed using AAS.

Extraction Stage IV (resistant fraction)
The remaining fraction III was added with 10 mL of distilled water and 10 mL of reverse aquaria and digested with an ultrasonic bath for 45 minutes, then heated for 45 minutes using a hot plate, and Centrifuged at 2500 rpm for 10 min. Separate the liquid and solid parts, and then the liquid part is adjusted to the volume using distilled water in a 50 mL volumetric flask. The results of the destruction were analyzed using AAS (Davidson *et al*., 1994) [7].

Results and Discussion

The concentration of Pb and Cd in Water
Based on Table 1. The concentration of Pb and Cd in the water at point 3 is the smallest, probably because many plants can absorb Pb and Cd around the sampling location, as stated by Faciu *et al*. (2014) [8].

Table 1: Average Concentration of Pb and Cd in Water at Muara Tukad Badung

Sampling Location	Average Concentration of Pb ±SD (mg/L)	Average Concentration of Cd ±SD (mg/L)
1	0,4049 ± 0,0208	0,3709 ± 0,0002
2	0,4748 ± 0,0362	0,3676 ± 0,0001
3	0,3593 ± 0,0147	0,1698 ± 0,0022

Based on the regulation of the Governor of Bali No. 16/2016, the concentration of Pb and Cd in water is a maximum of 0.03 mg/L and 0.01 mg/L, respectively. Based on this regulation, the concentration of Pb and Cd in the water at the Tukad Badung estuary exceeds the standard set by the government. The presence of Pb and Cd in water comes from cottage industries, dyeing, and workshops around the river area and eventually accumulates in the Tukad Badung estuary. Heavy metals and other solids are insoluble pollutants in water (Rohayati *et al*., 2017) [9]. Apart from textile waste, the presence of heavy metals such as Pb and Cd is mainly produced from motor vehicles, chemical fertilizers, and pesticides (Choirunnisa. *et al*. 2018) [10].

The concentration of Pb and Cd in Fish

Based on Table 2. Concentrations of Pb and Cd in all fish samples had passed the FAO/WHO (2004) quality standards, namely 0.03 mg/kg (Pb) and 0.01 mg/Kg (Cd).

Table 2: Average Concentration of Pb and Cd in Fish in Muara Tukad Badung

Sample Code	Average Concentration of ± SD (mg/Kg)	Average Concentration of ± SD (mg/Kg)
I	15,8654 ± 0,1648	13,6261 ± 0,0052
II	13,9477 ± 0,1008	12,5648 ± 0,1058
III	16,4734 ± 0,1191	12,7663 ± 0,0003
IV	11,6966 ± 0,1956	8,2412 ± 0,0094
V	13,3632 ± 0,2622	13,1773 ± 0,0076

The minor concentrations of Pb and Cd in fish were found in samples IV of 11.6966 mg/Kg and 8.2412 mg/Kg. Probably due to the younger fish age, the time to absorb the metal is less than the other fish samples. The age of the fish obtained by buying from the people who fish in the Tukad Badung estuary cannot be ascertained even though they are almost the same size. The concentration of Pb in fish is higher than that of Cd. It may be due to several factors, such as more Pb pollutant sources entering the waters than Cd. According to Ismarti (2016) [11], the amount of heavy metals absorbed by biota is influenced by metal bonds, sediment size, the presence of microorganisms, and the number of pollutants.

Total Metal Pb and Cd Concentrations in Sediment

Sediment at the bottom of the water will absorb heavy metals and be released in an insoluble form into the soil and then enter the sediment, causing aquatic biota such as fish to be contaminated with heavy metals (Markiewicz Patkowska *et al*., 2005) [12].

Table 3: Average Concentration of Total Pb and Cd in Sediment in Muara Badung Tukad

Sampling Location	Average Concentration of Pb ±SD (mg/Kg)	Average Concentration of Cd ±SD (mg/Kg)
1	90,2327 ± 0,2834	54,0053 ± 0,0179
2	94,2104 ± 0,2456	51,7231 ± 0,3318
3	75,8229 ± 0,2473	48,1119 ± 0,0582

The high presence of Pb and Cd in sediments comes from community activities, especially the textile industry, agricultural fertilizers containing phosphate, and household activities (Puspasari *et al*., 2014) [13]. In general, the presence of Pb and Cd in sediments must be higher than in water and fish, and this is due to the nature of Pb and Cd, which are easier to bind organic matter so that it accumulates in sediments over a long period time.

Speciation and Bioavailability of Pb and Cd in Sediment

The stepwise extraction method can determine the species and bioavailability of Pb and Cd. The metal species bound in each fraction shows that the metal is quickly released, has the potential to be released, and is firmly bound.

Table 4: Speciation and Bioavailability of Pb in sediments at Muara Tukad Badung

Frakction	Average Concentration of Pb ± SD		
	Location 1	Location 2	Location 3
EFLE	6,4846 ± 0,2544	5,2131 ± 0,2737	5,6277 ± 0,0358
Reducible	28,6555 ± 0,4277	25,5236 ± 0,8590	28,2285 ± 0,7268
Organic sulfida	47,5094 ± 0,4237	30,0348 ± 0,7804	36,2130 ± 1,0193
Resistant	82,2756 ± 0,3857	72,9837 ± 0,6211	87,6725 ± 0,2141

Table 5: Speciation and Bioavailability of Cd in sediments at Muara Tukad Badung

Frakction	Average Concentration of Cd ± SD		
	Location 1	**Location 2**	**Location 3**
EFLE	0,5599 ± 0,0129	0,7747 ± 0,0328	0,5810 ± 0,0182
Reducible	4,2064 ± 0,0566	4,3901 ± 0,0084	2,4123 ± 0,0049
Organic sulfida	6,4094 ± 0,0152	8,6321 ± 0,0235	8,5411 ± 0,0118
Resistant	36,3742 ± 0,0981	22,4582 ± 0,0521	33,3904 ± 0,0503

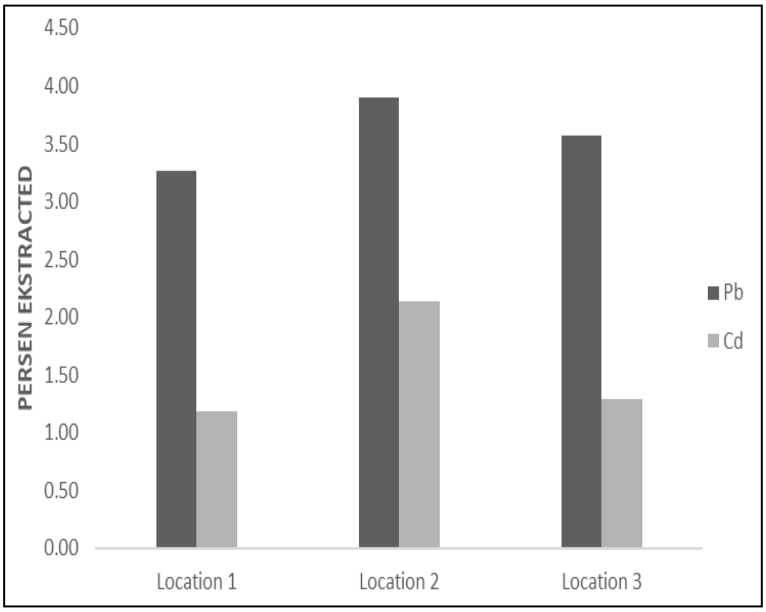

Fig 1: Diagram of Percentage of Pb and Cd of EFLE. Fraction

The first extraction stage is to determine which metals are quickly released, free, easily eroded, and can be exchanged or called the EFLE fraction (easily, freely, leachable, and exchangeable). This first stage of extraction is the fraction which the most unstable bonds, such as ionic bonds, carbonate bonds, and complex ones. Heavy metals in this fraction are bioavailable because they are quickly released.

Fig1 shows the percentage of Pb bound to the EFLE fraction at point 1, which is 3.27%; point 2 is 3.90%; point 3 is 3.57%. The percentage of Cd extracted in the EFLE fraction at point 1 was 1.18%; point 2 was 2.14%; point 3 was 1.29%. Figure 4.3 shows the highest percentage of extracted Pb at point 1 and the highest percentage of extracted Cd at point 3. The percentages of Pb and Cd extracted in the EFLE fraction are small, so they are not too harmful to the environment because they are less than 10% (Siaka *et al*., 2020) [15].

The second stage of extraction is the reducible fraction. In the reducible fraction, Pb and Cd are bound to Fe-Mn oxide and can be reduced by acid at low redox conditions to released the metal into ions or molecular ions. In this fraction, metals that are bound to Fe-Mn are potentially bioavailable and can turn into bioavailable when reduced by acids or potent reducing agents (Gasparatos *et al*., 2005) [14].

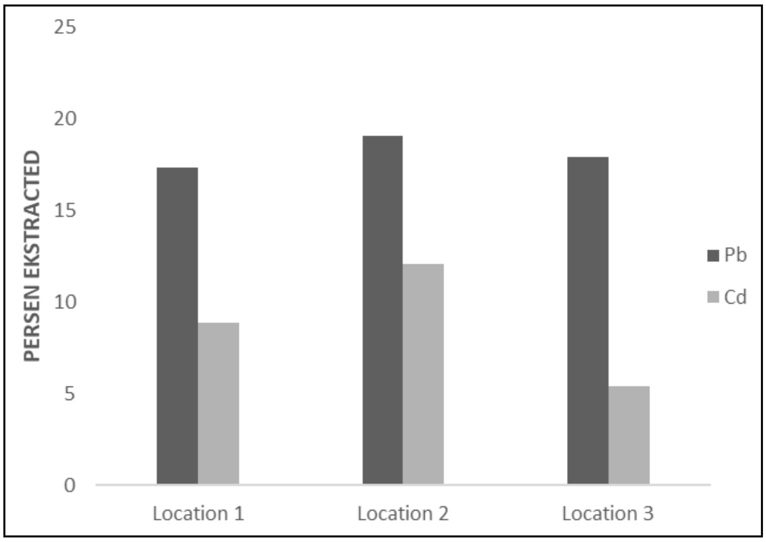

Fig 2: Percentage Diagram of Pb and Cd Reducible Fractions

The percentage of Pb bound to Fe-Mn oxide at point 1 is 17.37%; point 2 is 19.08%; and point 3 is 17.90%, while for Cd at point 1 is 8.85%; point 2 is 12.11%; point 3 is 5.37%. Figure 4 shows that the percentage of Pb and Cd bound to Fe-Mn is large at point 2. The metal bound in this fraction is quite significant because it is more than 10% except for Cd at points 1 and 3. Nevertheless, the extracted metal in this fraction is not harmful. Aquatic environment because of the nature of the bond, which is more stable and not easily separated into ions.

The third step is to extract Pb and Cd, which are bound to organic compounds or sulfides. The organic sulfide fraction is obtained by extracting sediment using a potent oxidizing agent such as H2O2 so that can release the Pb and Cd bonds with organic compounds and sulfides (Siaka *et al.*, 2020) [15].

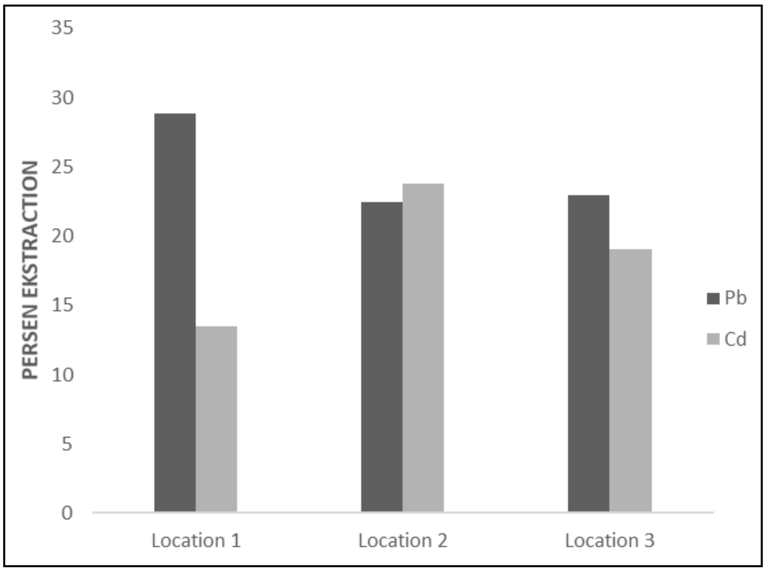

Fig 3: Percentage Diagram of Pb and Cd Organic Sulfide Fractions

The percentage of Pb extracted in this fraction at point 1 was 28.81%; point 2 is 22.46%; and point 3 is 22.96%, while for Cd at point 1 is 13.48%; point 2 is 23.81%; point 3 is 19.01%. In Figure 5 can see that the highest percentage of Pb and Cd extracted in this fraction was at points 1 and 2. The metal bonded in this fraction was relatively high at more than 10%, except for Cd metal at point 1. Pb and Cd bound to organic compounds or sulfides in the water are not dangerous because of their more substantial bonding properties than the EFLE fraction.

The fourth stage of extraction is to determine the resistant fraction. This fraction is a metal group with stable properties and is firmly bound to primary minerals found in sediments.

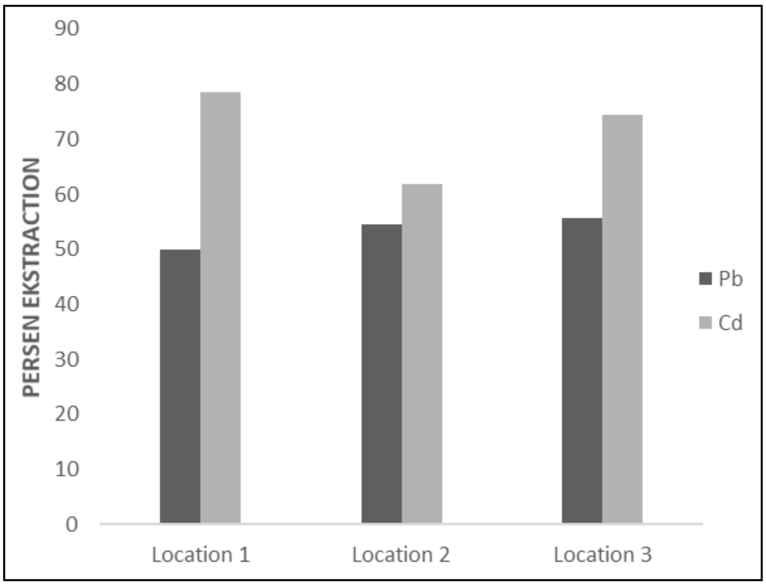

Fig 4: Diagram of the Percentage of Metal Pb and Cd Fraction Resistant

The percentage of Pb extracted in this fraction at point 1 was 49.89%; point 2 is 54.56%; and point 3 is 55.58%, while for Cd at point 1 is 76.50%, point 2 is 61.95%; point 3 is 74.32%. The percentage of metal bound in this fraction is very high, but it is not harmful to the environment because it is nonbioavailable. The metals in this species come from natural contamination, including weathering, the destruction of rocks, or the decomposition of silicate crystals in rocks.

Conclusion

The average concentrations of Pb and Cd in water were 0.4130 ± 0.0239 and 0.3028 ± 0.0008 mg/L, respectively, in tilapia fish were 14.2692 ± 0.1685 and 12.0752 ± 0.0257 mg/Kg. The average concentrations of total Pb and Cd in the sediments were 86.7555 ± 0.2588 and 51.2802 ± 0.1360 mg/Kg, respectively. The bioavailability of Pb is dominated by nonbioavailable metals (49.89 – 55.58%), followed by potentially bioavailable metals (17.37 – 28.81%), and the tiniest metal is bioavailable (3.27). – 3.90%). The bioavailability of Cd is dominated by nonbioavailable metals (61.95 – 78.50%), followed by potentially bioavailable metals (5.37 – 23.81%), and the tiniest metal is bioavailable (1.18). – 2.14%

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