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## Heavy Metals in Maninjau Lake, Indonesia: water column, sediment and biota

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### Abstract

Heavy metals (Cd, Cu, Fe, Pb, Zn) concentration in water column, sediments, and fish were analyzed from Maninjau Lake in January and June 2015. The heavy metal concentration in water was Cu>Pb>Zn>Cd > Fe, in sediments Cu>Fe>Pb>Zn>Cd. Two fish species, *Oxyeleotris marmorata* demersal fish and *Rasbora lateristriata* pelagic fish were collected from the lake and analyzed to know heavy metal content of muscle. The heavy metal concentration profile in *Oxyeleotris marmorata* fish followed the sequence of Zn>Fe>Cu> Cd >Pb, whereas the heavy metal concentration profile in *Rasbora lateristriata* fish followed the sequence Fe>Zn>Cu>Cd>Pb which was not similar to the sequence of heavy metal concentration in sediments. However, the heavy metal concentration in the fish did not exceed standar of FAO/WHO.

**Keywords:** Water quality, heavy metals, water column, sediment, biota, Maninjau Lake.

### Introduction

In the province of West Sumatra, Republic of Indonesia, there are four lakes i.e Maninjau Lake, Singkarak Lake, Diatas Lake and Dibawah Lake. One of them, Maninjau Lake is being badly contaminated and threatened by heavy metals. The lake had a water-surface area of 9997.5 ha, average depth 105 m, volume of water 10,226,001,629.2 m<sup>3</sup>, and water retention time 25.04 year, and the lake was located at altitude of 461.50 m above sea level [1]. Maninjau Lake catchment areawas13, 260 ha with the proportion of land use was 2,518 ha of paddy fields, dry land was 3,606 ha, settlement was 869 ha, forest was 6,951 ha and others were 96 ha [2]. The lake was used as a hydroelectric power plant with an installed capacity of 64 MW, tourism, fisheries and as an aquaculture with floating net cages [3,4]. In the lake, fifteen species of fish lived with tropic level of food that was herbivore, omnivore and carnivore [1]. The number of floating net cages in Maninjau Lake in 2014 were 16,280 units, and farmed-fish were *Cyprinus carpio*, *Tilapia sp* which produced organic waste from 2001 to 2013 was 111,899.84 ton [5], and the number of people living around the lake were 33,784 individuals [2]. In aquatic systems, heavy metals had been considerably paid attention due to their toxicity and accumulation in biota [6, 7, 8, 9]. Heavy metals generally flew into the aquatic environment through atmospheric deposition, erosion of the geological matrix, and it was due to anthropogenic activities caused by industrial effluents, domestic sewage, mining wastes, motorization, urbanization [10, 7] by agricultural waste, population density and industrial activities [6] and by waste floating net cages [11,12]. Therefore, the objective of this study was to examine the pollution level of Maninjau Lake by determining the accumulation of Cd, Cu, Fe, Pb and Zn in the water column, sediment and some tissues of the demersal fish *Oxyeleotris marmorata* and pelagic fish, *Rasbora lateristriata*.

### Materials and Methods

#### Sampling sites and sample collection

Sampling sites were purposefully selected based on the research objectives (Fig. 1). The four sites, Maninjau Lake, Sungai Batang, Koto Kaciek, Sigiran, and Muko-Muko were locations of the sample collection (Table 1). Two replicate water and sediment samples were collected from each of the four sampling sites during each sampling occasion. Samples were collected between June and Auguts 2015. A total of 32 samples of water and sediment (2 replicates x4 sites x4 sampling occasions) were collected during the period. Additionally, 32 fish for each of

the selected fish species were collected during the period. The sampling occasions were intended to capture the hydrologic variations experienced in the study area and thus enabled us to

capture the spatial and temporal variations in heavy metal concentrations in water, sediment and fish.

**Table 1:** Description of the sampling sites in Maninjau Lake

Sampling site	Geographical Position	Description
(1) Sungai Batang	S : 00°21'31.1" E: 100°12'50.6"	Littoral waters were ramps, mud and sand substrate, the location was also the floating net cages farming of tilapia, and the riparian lakes were human settlement area and hotels.
(2) Koto Kaciek	S: 00°16'37.15" E: 100°12'07.41"	Littoral waters is ramps, muddy substrate, the area for floating net cages farming of tilapia, overgrown by <i>Eichhornia crassipes</i> , and the riparian area was agricultural site.
(3) Sigiran	S: 00°18'21.58" E: 100°11'18.98"	Littoral waters were steep area, little aquatic vegetation, and substrate dominated by rocks, and the area for floating net cages farming of tilapia, and human settlement area.
(4) Muko-Muko	S: 00°17'58.5" E: 100° 09' 47.3"	It was an outlet for hydroelectric power plant intake, conservation area, and tourist area.

## 2.2 Sampling and analysis of heavy metals in water samples

Water samples were collected using trace metal clean procedures [13]. All equipment used for sample collection, storage and analysis of heavy metals were pre-cleaned using high-purity nitric acid (GFS Chemicals Inc.) and rinsed with copious amounts of Milli-Q water to ensure that they were trace-metal free. After rinsing, the bottles were stored in double-bagged zip-lock polyethylene bags. Such cleaning and storage procedures ensured that there were no detectable metal contaminants in the sampling equipment [14]. The samples were collected in polypropylene bottles and filtered immediately through 0.45 µm and acidified with ultra-pure HNO<sub>3</sub> to pH<2 and stored at 4 °C prior to heavy metal analyses. Other water quality physico-chemical variables known to affect dissolved metals were measured (i.e., dissolved oxygen pH, total dissolved solids, electric conductivity) in the field according to [13]. Heavy metals in the filtrate (0.45 µm) were here operationally defined as “dissolved”. The study focused on the dissolved fraction as this fraction was more likely to have measurable biological effects on aquatic organisms.

In addition, the dissolved metals had been shown to be similar to the exposure conditions used in toxicity tests [14], allowing for comparisons between standard toxicity tests and field community surveys. Metal concentrations were determined by the atomic absorption spectrophotometer (AAS). In brief, 15 mL of sample were transferred into a vial into which an internal standard containing 40 µg/L <sup>6</sup>Li, <sup>75</sup>Ge, <sup>115</sup>In and <sup>209</sup>Pb was added. 40 µg/L of <sup>196</sup>Au was added to the sample solutions to stabilize Hg. A standard calibration curve for all the analyses was established on standards prepared in a linear range from 0.001mg/L to 0.1 mg/L. National Institute of Standards and Testing Reference material (NIST 1640) and procedural blanks were analyzed for all selected heavy metals.

## Sediment sampling and heavy metals analysis

Sediment sampling and handling was performed following methods described in [13], USEPA [15]. Two sediment samples were collected from each sampling site using a Sediment grab sampler (Hydro Bios Kiel) from the top 10 cm of the sediment.

All samples were immediately stored at 4 °C and transported to the laboratory for analyses. In the lab, the sediment samples were processed in similar way as the fish samples described above.

## Fish sampling and heavy metals analysis

Gillnets and fish traps were used to capture fish for the study. Fish traps were constructed at the selected sampling sites with the help of local fishermen. A total of 32 samples of fish (2 replicates X 4 sites X 4 sampling occasions) were collected for each species by the end of the study. Weight and total length-measurements for two kinds of fishes for each of the selected species were recorded immediately after sampling. Thereafter, a 50-g sample of muscle tissue from each fish sample was taken based on methods described in [16]. Samples were wrapped in aluminum foil and stored in ice before transferring into a freezer. Heavy metal analysis on the sampling-fish was performed in a clean-room laboratory at the Chemistry Laboratory of Bung Hatta University Padang, West Sumatra Province, Indonesia. Heavy metals in fish tissue samples were determined by digesting 50 mg of sample in ultra-pure nitric acid (HNO<sub>3</sub>) and Hydrofluoric acid (HF) and brought to a final volume of 100 mL in 2% ultrapure HNO<sub>3</sub>. Metal concentrations in the sampling-fish were measured using the AAS. Standards were prepared in a linear range from 1 µg/L to 1000 mg/L. An internal standard consisting of Li-6, Ge, In, Tm and Bi was added to each of sampling-fish. To ensure quality control and assurance, procedural blanks and analytical reference materials USGS-SDO-1 and USGS-SGR-1 were analyzed. All equipment and glassware used in processing the sampling-fish were HNO<sub>3</sub> which was washed and rinsed using Milli Q water.

## Statistical analyses

The data were analyzed by applying the analysis of variance (ANOVA), followed by comparisons of means by Least Significant Differences (LSD). Data of water quality parameters, heavy metals in waters, sediments, and fish samples were analyzed statistically using the SPSS, version 17.

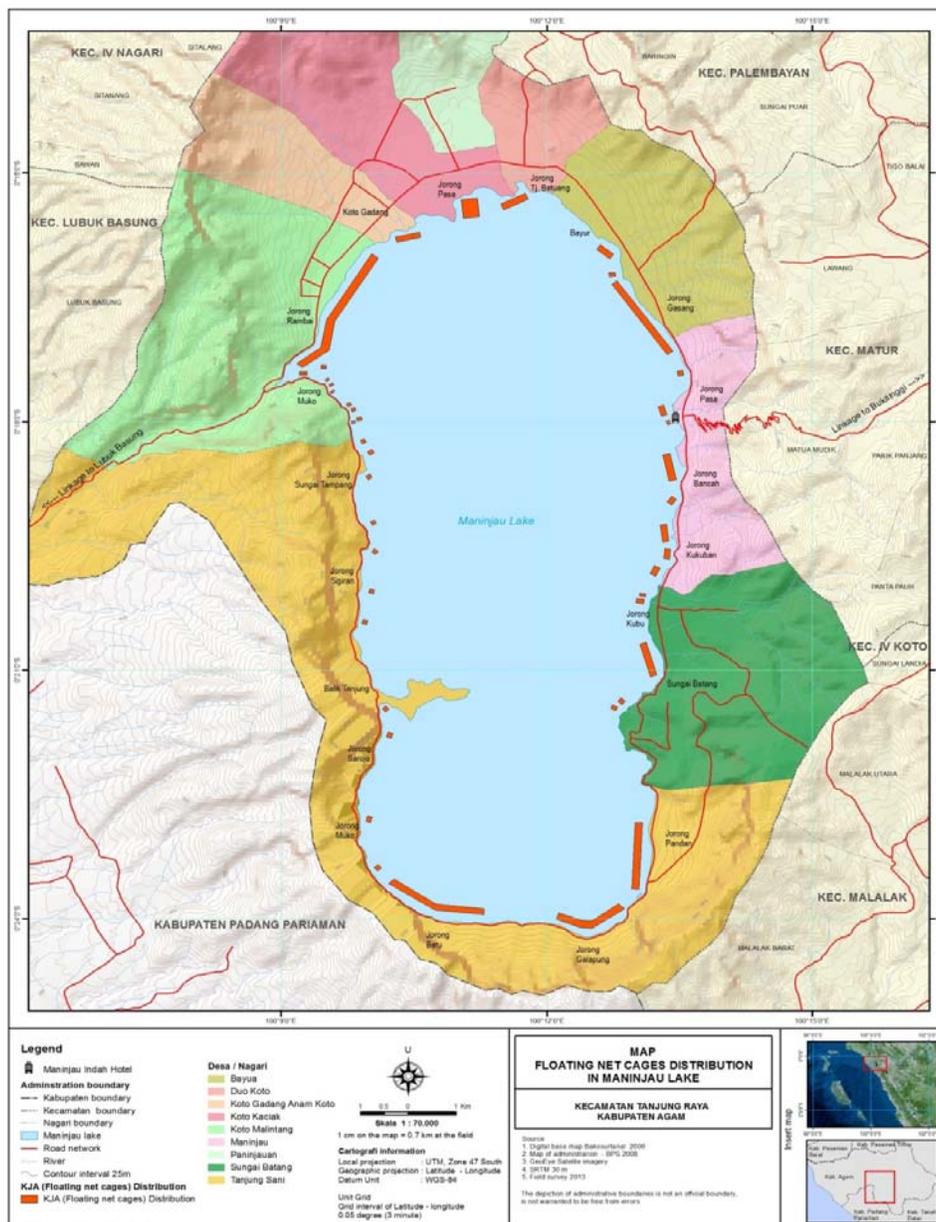


Fig 1: Map of Maninjau Lake showing sampling-sites

**Results and Discussion**

**3.1. Water quality parameters**

No significant differences were observed in water temperature, water transparency, and in pH concentrations between the sampling-sites in Maninjau Lake. Total dissolved solid in Sungai Batang and Koto Kaciek sites was significantly different from that of Sigiran and Muko-muko sites. Dissolved

oxygen in Koto Kaciek was significantly different from that of Sungai Batang, Sigiran and Muko-Muko (Table 2). Heavy metal levels in water column depended on the physico-chemical parameters of water such as temperature, pH, and electrical conductivity [17]. The levels of heavy metals depended on ionic strength, pH, temperature, dissolved oxygen and hardness [18].

Table 2: Means (±SE) of various physico-chemical variables in water samples collected from Maninjau Lake

Parameters	Sampling Site			
	Sungai Batang	Koto Kaciek	Sigiran	Muko-Muko
Temperature (°C)	28.00±1.00 <sup>a</sup>	28.33±1.15 <sup>a</sup>	27.66±0.57 <sup>a</sup>	27.33±0.83 <sup>a</sup>
pH	6.63±0.23 <sup>a</sup>	6.56±0.20 <sup>a</sup>	6.66±0.28 <sup>a</sup>	6.80±0.20 <sup>a</sup>
Dissolved Oxygen (mg/L)	6.25±0.58 <sup>a</sup>	5.08±0.17 <sup>b</sup>	6.49±0.35 <sup>a</sup>	6.11±0.37 <sup>a</sup>
Total Dissolved Solids (mg/L)	20.46±2.34 <sup>a</sup>	22.84±1.48 <sup>a</sup>	14.66±1.05 <sup>b</sup>	12.44±0.13 <sup>b</sup>
Water transparency (m)	2.10±0.36 <sup>a</sup>	1.56±0.40 <sup>a</sup>	1.76±0.25 <sup>a</sup>	1.70±0.10 <sup>a</sup>
Electrical Conductivity (µSm/cm)	0.2294±0.01 <sup>a</sup>	0.2370±0.03 <sup>a</sup>	0.2585±0.02 <sup>a</sup>	0.2401±0.02 <sup>a</sup>

Information: Average ± SD (n=4) with different superscript letters indicating significant differences (p<0.05).

**Table 3:** Heavy metal concentrations in mg/L (Mean±SE) in water samples collected from Maninjau Lake

Heavy metals	Sampling Site			
	Sungai Batang	Koto Kaciek	Sigiran	Muko-Muko
Cadmium	0.5733±0.015 <sup>a</sup>	0.1267±0.006 <sup>b</sup>	0.2520±0.002 <sup>c</sup>	0.5683±0.010 <sup>a</sup>
Copper	0.8127±0.074 <sup>a</sup>	1.1283±0.019 <sup>b</sup>	0.6480±0.041 <sup>c</sup>	1.1300±0.018 <sup>b</sup>
Iron	0.0267±0.006 <sup>a</sup>	0.0700±0.010 <sup>b</sup>	0.0700±0.010 <sup>b</sup>	0.0533±0.006 <sup>c</sup>
Lead	0.6553±0.007 <sup>a</sup>	0.9027±0.046 <sup>b</sup>	0.5823±0.007 <sup>c</sup>	0.9310±0.006 <sup>b</sup>
Zinc	0.4337±0.042 <sup>a</sup>	0.7567±0.009 <sup>b</sup>	0.4090±0.012 <sup>a</sup>	0.7567±0.009 <sup>c</sup>

**Information:** Average ± SD (n=4) with different superscript letters indicating significant differences (p<0.05).

**3.2. Heavy metals in waters**

An analysis of variance resulted in that there were significant temporal differences in heavy metal concentrations in water samples collected in Maninjau lake. A similar pattern was observed for the remaining sampling sites (p<0.05). Pooled together, the concentrations of Cd in water column ranged from 0.12 to 0.57 mg/L, Cu ranged from 0.64 to 1.13 mg/L, Fe ranged from 0.02 to 0.07 mg/L, Pbranged from 0.58 to 0.93 mg/L, and Zn ranged from 0.40 to 0.75 mg/L respectively (Table 3). Comparatively higher metal concentrations were recorded in the anthropogenically impacted sites such as agricultural runoff, household waste, and floating net cages activity. In Ciratareservoir, West Java Province, the concentration of Cdand Pb (mg/L) in water at 0.032 and 0.036, heavy metals weresources such as household and industrial waste [11]. According to [19] heavy metals from natural and anthropogenic sources such as industrial effluents, agricultural runoff, transport, burning of fossil fuels, geochemical structure and mining activities were continually released into aquatic ecosystems. Whereas [20] the high levels of heavy metals were attributed to the riparian land use practices such as uncontrolled agriculture, urban runoff and mining activities around the lake.

Water of Maninjau Lake could not be used asa source of drinking waterandbathing because it causeditching disease. Heavy metals such as copper, iron, chromium and nickel were essential metals since they played an important role in biological systems, whereas cadmium and lead were non – essential metals, as they were toxic, even in trace amounts [21]. Cd was considered as the most toxic element to human life. It caused itai-itai, a bone disease similar to rickets, and cardiac enlargement, anemia, gonadal atrophy, kidney failure, and pulmonary emphysema [7]. Whereas Cu was a vital element necessary for normal organism growth and metabolism, and its uptake was regulated by physiological mechanisms according to nutritional demand. At high concentrations, Cu became toxic to the body [9]. Pb was toxic and a major hazard to man and animals. Poison by lead causes anemia, encephalopathy, weight and coordination loss, abdominal pain, vomiting, constipation, and insomnia [22]. Cd, Cu, Pb were present in water samples from all sites, but they were at levels above the

WHO guidelines. WHO drinking water standards (HDL) were Cd = 0.01 mg/L; Cu = 0.05 mg/L; Pb = 0.05 mg/L [23]

**3.3. Heavy metals in sediments**

The concentrations of Cd, Cu, Fe, Pb and Zn (in mg/kg) in sediment ranged from 0.15 to 0.39, 5.79 to 18.69, 5.14 to 11.13, 1.51 to 2.58 and 0.69 to 1.54, respectively. All sediment samples were significantly (p<0.05) different from the sites (Table 4).The highest levels for cadmium, copper, iron, lead and zinc were recorded in samples collected from Sungai Batang and tended tobe lower in Muko-Muko sites. Cadmium, Copper, Lead, and, Zinc concentrations from Sungai Batang, Koto Kaciek, Sigiran and Muko-Muko sampling sites exceeded the WHO limits for sediment at 0.0006, 0.016, 0.031 and 0.12 mg/kg, respectively. Sungai Batangand Koto Kaciek were major of source of heavy metals flowing into the lake. Sungai Batangand Koto Kaciek were area of settlements, agriculture, animal husbandry, and floating-nets cages. The farming areas were source of pesticides, animal waste, and waste deriving from the floating-net cages of which the number in 2013 were 15,860 units [1]. According to [5] organic load of waste-floating net cages from 2001 to 2013 was 111,889.84 tons with an average of 9,324.98 tons/year. The sources of heavy metals at Muko-Muko could be attributed to tourismarea and sport fishing. The metal levels in sediments in the current study were however significantly lower than those measured by [12] in Maninjau Lake in a study area characterized by similar anthropogenic activities. It was therefore likely that sediment dwelling organisms at these sites will be adversely impacted in terms of their growth, survival and reproduction.

Finally, benthic organisms in Maninjau Lake are likely to be impaired by copper since its levels exceeded the WHO recommended guideline values. Such elevated concentration of copper is bound to impact negatively on the macro invertebrates and by extension their predators. Sediments of waste floating net cages, fish feed have been a negative impact on *Corbiculat moltkiana* population on Maninjau Lake [12, 1]. Elevated metal concentrations have been shown to adversely affect macro invertebrates in terms of reproduction, growth, abundance and diversity [9].

**Table 4:** Heavy metal concentrations in mg/kg (Mean±SE) in sediment samples collected from Maninjau Lake

Heavy metals	Sampling Site			
	Sungai Batang	Koto Kaciek	Sigiran	Muko-Muko
Cadmium	0.3910±0.002 <sup>a</sup>	0.3587±0.002 <sup>b</sup>	0.1470±0.001 <sup>c</sup>	0.3050±0.023 <sup>d</sup>
Copper	18.6990±0.540 <sup>a</sup>	13.0833±0.493 <sup>b</sup>	10.6843±0.551 <sup>c</sup>	5.7927±0.039 <sup>d</sup>
Iron	11.1353±0.004 <sup>a</sup>	10.4483±0.266 <sup>b</sup>	8.2853±0.031 <sup>c</sup>	5.1450±0.010 <sup>d</sup>
Lead	2.5863±0.122 <sup>a</sup>	2.4430±0.020 <sup>b</sup>	1.4470±0.002 <sup>c</sup>	1.7110±0.003 <sup>c</sup>
Zinc	1.5433±0.015 <sup>a</sup>	1.1227±0.003 <sup>b</sup>	1.2617±0.114 <sup>c</sup>	0.6933±0.025 <sup>d</sup>

**Information:** Avarage ± SD (n=4) with different superscript letters indicate significant differences (p<0.05).

### 3.4. Heavy metals in *Oxyeleotris marmorata* and *Rasbora lateristriata*

The concentrations of Cd, Cu, Fe, Pb and Zn (in mg/kg) in *Oxyeleotris marmorata* demersal fish samples ranged from 0.0050 to 0.3910, 0.985 to 1.4823, 5.1450 to 35.3697, 1.4470 to 2.5863 and 0.6933 to 42.1500, respectively. Whereas the concentrations of Cd, Cu, Fe, Pb and Zn (in mg/kg) in pelagic fish samples ranged between 0.0240 to 0.0427, 0.9150 to 1.2873, 32.7183 to 51.4410, 0.0040 to 0.0093, 36.0167 to 71.7787 respectively. All heavy metals samples were significantly ( $p < 0.05$ ) different between the sites (Table 5 and 6). The highest levels for Cd, Cu, Pb and Zn were recorded in *Oxyeleotris marmorata* demersal fish and *Rasbora lateristriata* pelagic fish samples and collected from Sungai Batang. Cd, Cu, Pb and Zn concentrations from Sungai Batang, Koto Kaciek, Sigiran and Muko-Muko sampling sites exceeded the FAO/WHO limits for fish samples. The heavy

metal concentration profile in *Oxyeleotris marmorata* demersal fish samples followed the sequence,  $Zn > Fe > Cu > Cd > Pb$ , whereas the heavy metal concentration profile in *Rasbora lateristriata* pelagic fish samples followed the sequence  $Fe > Zn > Cu > Cd > Pb$  which was no tsmilar sequence in heavy metal concentration in sediments. Concentrations of heavy metal levels in fish depended on different factors such as ecological needs, fish species, season of capture and physico-chemical parameters of water [8]. However, the heavy metal concentration in fish did not exceed [25]

In general, heavy metals contained in the water and sediment were also found on the species of fish that live in those waters such as *Channa marulius* in Madivala Lakes in Kartanaka [24], *Cyprinus carpio* in Mogan Lake, Turkey [26], *Cyprinus carpio* in Işikli Lake, Turkey [27], *Sander lucioperca* in Lake Karataş Turkey [8], and *Cyprinus carpio* in Lake Naivasha, Kenya [9].

**Table 5:** Heavy metal concentrations in mg/kg (Mean±SE) in *Oxyeleotris marmorata* demersal fish samples collected from Maninjau Lake

Heavy metals	Sampling Site				Limits (mg/kg)	
	Sungai Batang	Koto Kaciek	Sigiran	Muko-Muko	WHO Guidelines	Indonesian National Standard
Cadmium	0.0127±0.002 <sup>a</sup>	0.0103±0.001 <sup>a</sup>	0.0050±0.001 <sup>c</sup>	0.0273±0.002 <sup>d</sup>	0.100	0.100
Copper	1.4823±0.028 <sup>a</sup>	1.4020±0.007 <sup>a</sup>	1.0723±0.054 <sup>a</sup>	0.985±0.01 <sup>a</sup>	2.000	2.000
Iron	35.3697±1.149 <sup>a</sup>	35.1530±0.257 <sup>a</sup>	32.0547±0.032 <sup>c</sup>	30.0583±0.014 <sup>d</sup>	43.00	43.00
Lead	0.0093±0.001 <sup>a</sup>	0.0080±0.001 <sup>a</sup>	0.0040±0.001 <sup>c</sup>	0.0060±0.001 <sup>d</sup>	0.200	0.200
Zinc	42.1500±0.655 <sup>a</sup>	40.5423±0.919 <sup>b</sup>	40.2680±0.616 <sup>c</sup>	36.0167±0.416 <sup>d</sup>	100	100

**Information:** Avarage ± SD (n=4) with different superscript letters indicate significant differences ( $p < 0.05$ ).

**Table 6.** Heavy metal concentrations in mg/kg (Mean±SE) in *Rasbora lateristriata* pelagic fish samples collected from Maninjau Lake

Heavy Metals	Sampling Site				Limits (mg/kg)	
	Sungai Batang	Koto Kaciek	Sigiran	Muko-Muko	WHO /FAO Guidelines	Indonesian National Standard
Cadmium	0.0427±0.002 <sup>a</sup>	0.0370±0.001 <sup>a</sup>	0.0240±0.003 <sup>c</sup>	0.0277±0.001 <sup>d</sup>	0.100	0.100
Copper	1.2873±0.016 <sup>a</sup>	1.1253±0.005 <sup>a</sup>	1.0163±0.005 <sup>a</sup>	0.9150±0.005 <sup>a</sup>	2.000	2.000
Iron	51.4410±0.614 <sup>a</sup>	49.6517±0.677 <sup>a</sup>	36.3867±0.596 <sup>c</sup>	32.7183±0.561 <sup>d</sup>	43.00	43.00
Lead	0.0267±0.002 <sup>a</sup>	0.0260±0.001 <sup>a</sup>	0.0140±0.001 <sup>c</sup>	0.0147±0.003 <sup>d</sup>	0.200	0.200
Zinc	39.1500±0.655 <sup>a</sup>	71.7787±1.178 <sup>b</sup>	59.0750±0.875 <sup>c</sup>	46.0167±0.416 <sup>d</sup>	100	100

**Information:** Avarage ± SD (n=4) with different superscript letters indicate significant differences ( $p < 0.05$ ).

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