

## **Copper, Lead and Zinc Concentration in Water, Sediments and Catfish (*Clarias macrocephalus* Gunther) from Butuanon River, Metro Cebu, Philippines**

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**Abstract:** Copper, lead and zinc contamination is a serious hazard. In this study, the concentration of these metals were determined by Atomic Absorption Spectroscopy in the water, sediment and in the muscle, liver and gills of catfish (*Clarias macrocephalus*) collected from three sampling stations of Butuanon River, Metro Cebu, Philippines. Water analysis results showed that no station exceeded the Philippines DAO 34 Series of 1990 standard at 0.05ppm both for Cu and Pb. Both Cu and Zn concentration in sediments showed no significant difference but Pb concentration tends to increase from upstream to downstream station without exceeding the Klocke's Maximum Allowable Limit at 100ppm. The Pb concentration in *C. macrocephalus* from downstream station exceeded Europe's Maximum Allowable Limit in fishes set at 2ppm. All metals are concentrated in the organs in this order liver>gills>muscle. The Biota-Sediment Accumulation Factor (BSAF) values for organisms are within noncritical range of 0.270 to 1.819. Using regression analysis, metal concentrations in the sediment were found to positively affect the metal concentration in catfish opposite to that of the water. Organic matter negatively affects Cu concentration. Results indicate that Zn is naturally abundant in Butuanon River, while Pb and Cu are introduced through industrial and agricultural activities.

**Keywords:** Butuanon River, *Clarias macrocephalus*, contamination, trace metals, water quality

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### **I. Introduction**

Trace metals naturally occur in low concentrations in a given system [1,2] but anthropogenic activities such as unregulated industrialization saturate these in the water, air and soil [2,3]. An abnormal increase in metal concentration in these spheres could disrupt ecosystem function [1] and the dynamic equilibrium between environment and the organism [1]. Bioaccumulation occurs when organisms are exposed to polluted environment or through contaminated food [3,4]. Contaminants may accumulate in the bodies of organisms once they are taken up and stored faster than they are metabolized or excreted [1]. Once concentrated in the body of an organism they may be passed on through trophic transfer and could eventually reach the top of the food chain such as humans. Bioaccumulation of trace metals may lead to various diseases among different organisms including death [3,5].

Butuanon River is one of Metro Cebu's major water bodies [6,7]. Due to its status and importance to the island, it was among the sites under the United States-Asia Environmental Partnerships Program from 1996-1999 that initiated a management plan to rehabilitate the Butuanon Watershed in collaboration with local organizations. However, recent studies show that it is heavily polluted being the sink of domestic and industrial wastewater of the city [8,9] and metals are present in its water and sediment on considerable amounts [6,7]. Specifically the highest concentrations recorded were that of copper (Cu), lead (Pb) and zinc (Zn) [6,7].

The potential accumulation of these metals in the organisms inhabiting the Butuanon River [10] has never been assessed. People fish along the Butuanon River for household consumption [9] and for commercial purposes. Using the catfish (*Clarias macrocephalus*) as a bioindicator [4], it is the aim of this study to determine if this fish has accumulated Cu, Pb and Zn from its ambient environment and if it is safe for human consumption.

### **II. Materials and Methods**

#### **21. The Study Site and the Sampling Stations**

Butuanon River starts at Brgy. Sirao, Cebu City passing through adjacent Manduae City and eventually opens to the Mactan Channel. The headwaters of the Butuanon River originated from the upland areas of Cebu City that is characterized by extensive farming of large scale mango production and cutflower cultivation, patches of grassland and thin secondary forest [9]. It is a channel of slow moving water of about 5-10 m in width that stretches as far as 10 km. with some portions of the river drying up during the dry season. If the upstream portions of Butuanon River is characterized by agricultural activities, its midstream and downstream

portion is characterized by intensive urban sprawl such as residential, commercial and industrial establishments. These industries discharge their wastewater into the river, however not all of these employ a wastewater treatment facility and even those with the wastewater treatment facility, some are ill-managed [9].

Three stations were established for this study based on the water quality as indicated from previous studies which used BOD, DO and metal concentration in the water as parameters [8,9]. These three stations also differ in terms of elevation and land use. Upstream is the least polluted and is a residential area although it is preceded with agricultural land. Midstream has a deteriorating water quality [8,9] has high industrial activity such that 6 out of the 10 furniture industries discharging waste in the river are situated within the midstream station. Near this station is also a paint and thinner production facility, 2 gas stations and 2 oxygen-acetylene production facilities. The rest of the industries concentrate in the downstream area as it moves toward the mouth of the river. Downstream has the most deteriorated water quality and as of 2010, the downstream station has 13 food and feed production facilities, 4 galvanized iron producers, 3 aluminum production facilities, 3 concrete mix facility, and 2 each of the furniture industry, gas station, car service station, supermarket and 1 used oil treatment facility [http://mandauacity.gov.ph]. All of these facilities, except for the food and feed industries, have the potential to discharge metals [11].

Water, sediments and *C. macrocephalus* were sampled for two consecutive months particularly on December 2010 and January 2011. The pH, organic matter content and grain size of sediments were also determined since these could affect the solubility and mobility of trace metals [11,12].

## 2.2 Water Sampling and Analysis

Water samples were collected using 10% (v/v) HNO<sub>3</sub> acid washed polyethelene plastic bottle. About 1 gallon of water samples were collected from each station. The samples were added with 5mL nitric acid and were transported to the laboratory for digestion and analysis. About 500mL of the sample were transferred to a beaker added with 3ml nitric acid, pH adjusted to less than 2, heated and evaporated to a volume between 10 to 15mL before precipitation occurs. Samples were then filtered using Whatman #5. The filtrate was placed in a 25mL volumetric flask which was diluted to volume. The solution was then exposed to Flame Atomic Absorption Spectroscopy (FAAS) (Shimadzu) for the determination of Cu, Pb and Zn concentration [6,13].

## 2.3 Sediment Sampling and Analysis

On site analysis of the pH of the sediment was conducted using a soil pH meter. Core samples of at least 1 meter depth were collected using an auger. The inclusion of subsoil horizons is the ideal depth for a study on elemental leaching [2]. A total of 15 core samples were collected covering the middle of the stream and both sides of the riverbanks. The composite sample from each station was packed in polyethylene bags, chilled and transported within the day to the laboratory for analysis. Samples were homogenized, air dried and oven dried at 110°C for three hours. The samples were divided into three for three types of analysis namely, grain size analysis, organic matter content analysis and metal content analysis [14,15,13] respectively. The samples were sieved using a sieve plate (0.002mm) as sediments at this particular size and lower are considered silt [14]. The dried samples were weighed ( $W_1$ ) and exposed to 600°C muffle furnace to obtain pure inorganic matter. This was weighed ( $W_2$ ) and the computation was made to determine the organic matter content (OM) content [15]:

$$(1) \quad OM = \frac{(W_1 - W_2)}{W_1} \times 100\%$$

Approximately 1 gram of sediment samples were placed in a preweighed Teflon vessel and was added with analytical grade reagents, 7ml 65% HNO<sub>3</sub> and 1ml 30% H<sub>2</sub>O<sub>2</sub> and digested using a microwave (Milestone ETHOS labstation) set at the following parameters: 1000 watts 10 mins. at 200°C then 20 min at 20°. After digestion samples were diluted to volume of 25ml and exposed to FAAS for the determination of Cu, Pb and Zn concentration.

## 2.4 Catfish Sampling and Analysis

Ten catfishes (*Clarias macrocephalus*) were randomly collected from each sampling station per sampling, a total of 60 catfishes were collected across sampling periods in all stations. Specimens were properly labeled, packed in an aluminum foil, chilled and transported to the laboratory for analysis. Initial weight and length of the samples were measured. Samples were pooled into two groups of five. This was necessary to obtain the minimum required weight for digestion which is 1g. Samples were dissected to separate the gills, liver and muscle [16]. Length and weight measurement were likewise recorded. The organs were placed in a petri dish to dry at 120°C until reaching constant weight. Samples were placed in a preweighed Teflon vessel added with analytical grade reagents, 7ml 65% HNO<sub>3</sub> and 1ml 30% H<sub>2</sub>O<sub>2</sub> and digested using a microwave (Milestone ETHOS labstation) set at the following parameters: 1000 watts 10 mins. at 200°C then 20 min at 20°. Digested samples were diluted to volume of 25ml and exposed to FAAS for the determination of Cu, Pb and Zn concentration.

Computation was made to obtain the actual metal concentration in all samples using the following equation [6]:

$$(2) \quad \mu\text{g metal/l} = C \times F$$

where:

C = metal concentration as read directly AAS

F= Dilution Factor

## 2.4 Data Analysis

The Cu, Pb and Zn loads in the water and sediments were compared with the Philippines' Department of Environment and Natural Resources Administrative (DAO) 34-1990 standard [http://www.denr.gov.ph] while that of the sediments were compared with the Kloke's Values [14]. Copper, lead and zinc concentration in the catfish (*C. macrocephalus*) was compared with international standards particularly that of Europe to conclude if it is safe or toxic for human consumption [17]. Metal concentration in sediments and fishes had to be compared with international standards due to the unavailability of such standards in the Philippines.

The Minitab Statistical software was used to process all data. The MANOVA was used to determine if there were statistically significant differences on the heavy metal loads of the water, sediments and organisms among the different sampling periods and stations and as well as among the different organs of the catfish (*C. macrocephalus*). The Tukey's HSD was used as post hoc test.

To determine the predictive bioaccumulation levels of *C. macrocephalus*, two assessment methods were employed; namely the computation of the Biota-Sediment Accumulation Factor (BSAF) and through regression method. The BSAF is an expression of the relationship between sediment and tissue. It was computed to determine the degree of accumulation of Cu, Pb and Zn of the organism in comparison to the sediment through the equation [18]:

$$(3) \quad \text{BSAF} = \frac{\text{metal concentration in the organism}}{\text{metal concentration in the sediment}}$$

The BSAF values were calculated for each pair of observations and then averaged. It is interpreted to mean that the higher the BSAF, the higher is the degree of accumulation. Additionally, this study having more than one independent variable, multiple regression was used to establish the best predictor variables in the concentration of Cu, Pb and Zn in the *C. macrocephalus* which could be utilized by future studies focusing on the Butuanon River as these equations would provide the relationship of metal concentration in the organism with several independent variables. Multiple regression is a straightforward way to accommodate ancillary variables [20].

## III. Results

The bioavailability of metals once introduced to the water and sediments particularly in a river ecosystem are affected by several factors such as pH, siltation and organic matter. Sediments sampled from Butuanon River have pH values consistently neutral across the three sampling stations and registered no significant difference ( $p > 0.05$ ) (Table 1). Both the percentage silt and percentage organic matter follows an increasing trend from upstream to downstream portions. The values of percentage of silt registered a significant difference ( $p < 0.05$ ) across stations. On the other hand, percent organic matter content registered a significant difference ( $p < 0.05$ ) between upstream and downstream stations while midstream station has neither a significant difference with upstream and downstream stations.

**Table 1.** Physical parameters of sediments from Butuanon River

Sampling Stations	Key Industry	pH	% Silt	% Organic Matter
Upstream	None but preceded with agricultural areas	7.1±0.3	31.46 ±0.42	3.365 ±0.505
Midstream	Furniture, Paint-thinner, Gas Station	7.0 ±0.1	39.19 ±2.26	4.692 ±1.470
Downstream	Food and Feeds, Galvanized Iron, Aluminum	7.1 ±0.2	45.25 ±0.87	5.375 ±0.526

Notes: Values are Mean±Standard Deviation

The Department of Environment and Natural Resources Administrative Order 34-1990 sets the maximum allowable limits for natural waters in the Philippines. This guideline has established the regulatory standards for Cu and Pb but not for Zn for a Class C Body of water. Butuanon River however belongs to the Class D and has no established standards for physico-chemical and biological properties. This difference in classification is based on water use. Class C is intended for fishery production, boating and industrial supply while Class D is intended for agriculture, irrigation, livestock watering and industrial supply. In the case of river sediments, comparison was made with the standards established by Kloke [14].

The Cu concentration in the water of Butuanon River is confirmed to be within the acceptable standard at 0.05 ppm and no significant difference ( $p>0.05$ ) was noted among stations. On the other hand, Cu concentration in the sampled sediments of Butuanon River has exceeded the natural content interval at 20 ppm but not in terms of maximum allowable limit set at 100 ppm. In terms of Pb concentration, the results indicate that the water from downstream station is significantly higher ( $p < 0.05$ ) than that of upstream and midstream stations. The Pb content of water in all stations in Butuanon River passed the standard set by DENR at 0.05 ppm. However, the Pb concentrations in sediments of Butuanon River were found to have exceeded the natural content interval at 20 ppm though is still within the maximum allowable limit at 100 ppm. Comparing the three stations, Pb concentration in the sediments indicated that downstream station is significantly higher ( $p < 0.05$ ) compared upstream but not with the midstream station. The station midstream likewise is not significantly different upstream. The Zn concentration in the water and sediment sampled from Butuanon River has no significant difference ( $p < 0.05$ ) among the stations (Table 2). Zinc in water for Class D bodies of water has no established standard but its load in the sediment indicates that there could potentially be an anthropogenic introduction since it has exceeded the natural background level at 50 ppm. It has been observed, however, that Zn concentration values in the sediments of Butuanon River is still within the maximum allowable limit at 300 ppm set by Klope [14].

If an ambient environment is contaminated with metals, there is a huge chance that an organism would likewise accumulate the metals [3]. Given that Cu, Pb and Zn are present in the Butuanon River, results of this study confirm that the catfish from this river, *C. macrocephalus* has accumulated these metals in its organs, liver, gills and muscle at varying concentrations. Table 2 shows that the Cu concentration in the liver, gills and muscle of *C. macrocephalus* from Butuanon River is within the European standard at 20 ppm (17) and following this order liver > gills > muscle. Only the liver among the organs showed a significant difference ( $p < 0.05$ ) among the stations such that samples downstream is significantly lower compared to samples taken upstream and midstream. Lead was not detected in the organs of *C. macrocephalus* from stations upstream and midstream. This however will not prove if the fish sampled upstream and midstream has passed the European standard at 2 ppm [17] since the method detection level is at 2.7 ppm. Sampled fish from downstream station clearly indicate though that it has exceeded the allowable limit and is therefore not safe for consumption. In terms of Zn, no significant difference ( $p < 0.5$ ) among the fish organs were observed although the concentration is in this order liver > gills > muscle.

An implicit assumption of the BSAF approach is that there is a proportional relationship between the concentrations in sediment and tissues of living organisms. That is, if the sediment contaminant concentration doubles, the tissue contaminant concentration is also expected to double [20]. Table 3 shows that BSAF of metals in *C. macrocephalus* is in the following order, Zn > Cu > Pb.

**Table 2.** Metal concentration of water, sediments and in liver, gills and muscle of *C. macrocephalus* from Butuanon River

Metal	Samples	Standard	Upstream	Midstream	Downstream	
Cu (ppm)	Water	0.05ppm <sup>a</sup>	0.0044± 0.0010	0.0476± 0.0016	0.0069± 0.0016	
	Sediment	20ppm <sup>b</sup> / 100ppm <sup>c</sup>	53.85± 8.06	55.14± 0.14	56.98± 1.66	
	<i>C. macrocephalus</i>	Liver	20ppm <sup>d</sup>	18.50±6.58	15.72±0.21	7.89± 0.69
		Gills	20ppm <sup>d</sup>	6.46± 2.02	5.91±0.62	5.60±0.85
		Muscle	20ppm <sup>d</sup>	2.50± 0.10	2.75±0.52	2.05± 0.12
Pb (ppm)	Water	0.05ppm <sup>a</sup>	0.0100± 0.0015	0.0075± 0.00185	0.0151± 0.00256	
	Sediment	20ppm <sup>b</sup> / 100ppm <sup>c</sup>	27.65± 1.28	33.99± 6.10	49.25± 4.99	
	<i>C. macrocephalus</i>	Liver	2ppm <sup>d</sup>	<MDL	<MDL	4.25± 0.65
		Gills	2ppm <sup>d</sup>	<MDL	<MDL	3.58± 0.33
		Muscle	2ppm <sup>d</sup>	<MDL	<MDL	3.32± 0.47
Zn (ppm)	Water	None <sup>a</sup>	0.0648± 0.0312	0.0499± 0.0403	0.0527± 0.0190	
	Sediment	50ppm <sup>b</sup> / 300ppm <sup>c</sup>	100.45± 6.08	96.52± 3.60	111.30± 7.63	
	<i>C. macrocephalus</i>	Liver	50ppm <sup>d</sup>	62.83± 10.97	87.92± 3.76	54.47± 2.34
		Gills	50ppm <sup>d</sup>	56.01± 0.70	61.69± 5.14	54.98± 2.75
		Muscle	50ppm <sup>d</sup>	20.87± 1.08	20.70±1.04	20.17± 0.66

Notes: Values are Mean±Standard Deviation

a Philippines' DENR DAO 34 Series of 1990

b Klope's Guideline Values for the Soil (Normal Background Levels)

c Klope's Guideline Values for the Soil (Maximum Allowable Limit)

d Maximum Allowable Limit for Trace Metals (Europe)

MDL = Method Detection Limit

**Table 3.** Biota-Sediment Accumulation Factor (BSAF) of *C. macrocephalus* from Butuanon River.

Stations	Cu	Pb	Zn
Upstream	0.453	n.c.	1.440
Midstream	0.442	n.c.	1.819
Downstream	0.270	0.228	1.210

n.c. = not computed as it is below MDL

The bioavailability of metals is often affected by a variety of parameters; among considered in this study are the metal concentration in water, sediment, organic matter content and percent silt. Using these variables, analysis was employed to determine what greatly affects the bioconcentration of Cu in the *C. macrocephalus* from Butuanon River. The derived regression equation ( $R = 89.9$ ) affecting copper concentration in *C. macrocephalus* is shown below:

$$(4) \quad Cu_{(Fish)} = 1.36 + 0.00800 Cu_{(Sediment)} - 67.1 Cu_{(Water)} - 0.0288_{(Organic\ Matter)}$$

Moreover, due to the unavailability of data on Pb values of the upstream and midstream stations, a regression equation could not be established. Regression was run for Zn but neither of the parameters tested is a good predictor of Zn concentration in Butuanon River.

#### IV. Discussion

A higher pH value promotes the precipitation of metals, which subsequently settles to the sediments [21] in fact when the pH values of soils ranged from 5.0 to 7.0, the mean values of extractable metals are approximately the same [22]. Since there is no significant difference across stations and the pH are neutral, pH is not a factor in the bioavailability of metals in the case of Butuanon River.

Sediments have a general downhill tendency moving towards floodplains, deltas and eventually delivered to the sea.[22] and this is shown in Butuanon River (Table 1). Siltation in Butuanon River though is aggravated by a number of human activities that increase sedimentation rate. These are run off are due to poor agricultural practices, channel straightening, overgrazing of river and stream banks, and clearing of streamside vegetation, construction and construction related activities such as dredging and quarrying [23].

Butuanon River shows a typical distribution of organic matter (Table 1). Organic matter is usually carried along with the silt in a downhill direction and could be increased by the effluents from the residences and from food and feed manufacturing facilities [24] that are notably abundant at midstream and downstream stations. The organic matter can actually be both beneficial and detrimental. Detrimental in such a way that it may increase BOD since more organisms would require oxygen to proceed with the process of decomposition [2]. On the other hand, it could be beneficial in such a way that organic matter can sorb trace elements and reduce contamination in the water and organisms [2].

The result clearly suggests the occurrence of anthropogenic introduction of Cu in Butuanon River (Table 2). The likely major source of Cu in Butuanon River could be at the headwaters of Butuanon River as no statistical difference were observed among the three sampled stations. The above findings could be attributed to the widespread use of fungicides in the mango plantations and other agricultural crops that abound the upper portions of Butuanon River. There is a heavy use of fungicides with copper oxychloride and copper hydroxide as active ingredients in the Philippines [25]. These pesticides come in different trade names and may be widely used among mango plantations located prior to the upstream station. Major diseases that affect mango crop production in the Philippines are all caused by fungi and are more often treated with copper based fungicides [26].

Findings as shown in Table 2 suggest that there is a source of Pb even before the upstream station and is further aggravated at midstream and downstream stations. Non-point sources in the upstream could have contributed to the Pb load such as the deposition from the atmosphere from petrol or industrial sources and old paints [6]. This could be further amplified by anthropogenic activities midstream and downstream. These activities are caulking, soldering and use of paints and pigments that are common among furniture industries. The paint-thinner production facility near midstream station may also contribute to the Pb concentration in the river [12]. In addition, the concrete mix facilities present along the Butuanon River may also have contributed since Pb is naturally present in cements [27]. Gas stations and car service stations found midstream could have also contributed to Pb concentration in the river. Lead in this type of industry is usually from battery electrolytes, paints and thinners [28]. Furniture industries and gas stations are also present downstream in addition to the used-oil treatment facility that could be a unique source of Pb as opposed to other sampling stations. Used oil may contain metals particularly Pb [29]. Adjacent potential sources of Pb may be present midstream but it was found to have smaller Pb concentration both in water and sediment. This is primarily because once a metal is discharge into the river, it is usually carried by the water and it settles several kilometers downstream [30]. This process could explain why Pb concentration is significantly higher downstream.

Potential sources of Zn such as galvanized metal production and brass and bronze alloy production in the furniture industries [12] are all present midstream (Table 2). However no significant difference across the sampling stations were noted although a slight increase is observed downstream possibly caused by four galvanized iron facilities where zinc is used as a coating to prevent corrosion [31]. Additional sources could be through the settlement of Zn metal transported by the water [34]. Overall, results of this study indicate that Zn is a natural component in the sediment of Butuanon River since it is fairly abundant upstream at 96.157 ppm despite the absence of identified source in the area. In a study [21], Zn was found to be an abundant trace metal in all aquatic ecosystems that could range at varying concentrations even as high as 261 ppm. This is further supported by a separate study by [2] claiming that Zn may exist naturally between 25 to 200 ppm.

Contaminants are usually discharged at low levels but long-term partitioning to the sediment could result to the accumulation of high load of pollutants [35]. This process explains why heavy metal concentration in the water is extremely low in contrast to that of the sediments. The fate of metals is also affected by other parameters such as silt and organic matter concentration.

Cu and Zn are essential for the metabolism of organisms but can become toxic in high concentrations due to their influence in the redox balance of the cell while Pb has no clear biological function and exposure to them can impair enzymatic activity, reproductive capacity and development [4].

The concentration for Cu in catfish (*C. macrocephalus*) across stations is within the European standard at 20ppm but it shows a decreasing trend for samples downstream (Table 2). An earlier study shows that 90% of Cu is immobilized as it is adsorb in the surface and forms complexes with organic matter [20] and this could explain the decrease in Cu concentration in fishes sampled from an organic matter rich downstream station. While, the detection of Pb only in catfishes sampled downstream is a clear indication that this station has a higher degree of contamination consistent with the trend of Pb concentration values in the water and sediment of Butuanon River. The sampled fish downstream clearly accumulated Pb from its ambient environment making it unsafe for human consumption. The Zn concentration across stations passed the European standard at 50ppm likewise did not differ significantly which is consistent with the Zn concentration values of water and sediment as well. This further indicates that Zn may be naturally present in the Butuanon River. However, among the three organs of the *C. macrocephalus*, muscle is found to be significantly lower ( $p < 0.05$ ) as compared to gills and liver. The Zn concentration values in the muscle of *C. macrocephalus* are within the 50 ppm standard of Europe but both liver and gills have failed. Though Zn concentration in fish organs is indicative of the contamination level in Butuanon River, the threat it poses is less serious as liver and gills of *C. macrocephalus* are rarely consumed.

In all metals and sampling stations, the order of concentration in the organs follow this trend liver > gills > muscle (Table 2). It should be pointed out that the liver of the fish plays a primary role in the metabolism and excretion of xenobiotic compounds with morphological alterations occurring in some toxic conditions [33]. The concentration of these metals in the gill tissues of catfish (*C. macrocephalus*) could possibly be related to the fact that they are the main sites for pollutant uptake due to the large surface that is in contact with environment and the very thin barrier separating the external and internal media of the animal [34]. On the other hand, the muscles of the catfish having contained the lowest levels of heavy metals could be due to being an inactive site in accumulating metals [35].

As shown in Table 3, the BSAF values obtained in this study are in an expected order since Zn and Cu are both essential metals while Pb is a non-essential metal [36]. The BSAF values for Cu and Zn obtained in this study follow in the same order with another carnivorous fish, *S. thumbergi* [37]. However, the BSAF values are relatively smaller compared to other studies implying that the degree of accumulation in the *C. macrocephalus* is not that high as compared to other polluted aquatic ecosystems [37,38]. In a previous study [43,8], Pb and Zn had a BSAF value of 1.72 and 4.96 respectively for *Chrysichthys* sp. and 2.59 and 7.48 respectively for *Tilapia* sp. BSAF value for Cu could also reach as high as 11.2 [37]. Measured BSAFs above or below 1 to 2 are entirely reasonable for fish [39] as there are solid mechanistic reasons why fish should not be in equilibrium with their sediments. The fish BSAF values incorporates wide ranges of influences including biomagnification due to the trophic level of the fish, sediment-water column chemical disequilibrium, the diet of the fish and its underlying food web, the fish's foraging range and chemical metabolism within the fish and its food web [42].

The regression equation established in this study confirms that an increase in the Cu content in the sediment will increase Cu concentration in the *C. macrocephalus* that could be explained by the ecology of the fish being a burrower and a bottom feeder [4]. The water and percentage organic matter with its negative values suggest that it reduces Cu in the fish. Copper tend to bind on the surface area of organic matter instead of becoming bioavailable to the organism [14]. Overall, this equation further supports why Cu concentration in sampled fish downstream is significantly lower. A regression equation could not be established for Zn since its concentration in the tissues does not necessarily follow a positive relationship with the metal in the soil [40]. Furthermore, it should be noted that Zn is potentially naturally present in Butuanon River as confirmed by this

study. Zinc exists as a residual fraction means that bioavailability and remobilizability may take time under normal conditions [6].

## V. Conclusion

Anthropogenic introduction of Cu and Pb in Butuanon River could be attributed to industrial and agricultural activities rampant in the area while Zn may be naturally present in Butuanon river since this is within the normal level for an aquatic ecosystem. The introduction of these metals into the water and sediments has definitely led to the accumulation of these metals in *C. macrocephalus*. It is clear that the *C. macrocephalus* fished downstream is not safe for human consumption due to the toxic concentration of Pb. It is recommended therefore that catfishes caught downstream should not be consumed. Further, it is recommended that continuous monitoring of Butuanon River should be established to control an increased loading of pollutants into the water and sediments and in effect prevent further accumulation of metals in fishes especially in the less polluted, elevated areas of the river.

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