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The Effect of Pulang-Bato Spring on the Levels of Copper and Zinc at the Zone of Impact of the Spring and a Section of Butuanon River

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Abstract

Butuanon River, one of the geographically important rivers in Cebu province is highly contaminated with copper and zinc metals. Different environmental samples including water, sediments, umbrella plant, guppy fish, and earthworms have been collected over the years and all have been found to be contaminated with these metals. A possible tributary that may contribute to the river's metal contamination is the spring in Barangay Pulang-Bato, Cebu City, which is suspected to be one of the sites for copper mines but was abandoned because of the low amount of copper and instead a spring was uncovered. The spring consequently is assumed to feed the river with solids containing copper and zinc. It highly notable that Cebu is known to be rich in copper and usually zinc co-exist in copper ores. Sediment and suspended solids were sampled at three sites; at the location of the spring, at the zone of impact (ZOI) of the spring with the river and another section of the river which is 20m downstream from the ZOI. Composite samples from each site were taken for six months representing the dry and wet seasons and analyzed for copper and zinc by Flame Atomic Absorption Spectroscopy (FAAS). Correlations and relationships were found between the concentrations of copper and zinc in sediments and suspended solids and among the stations. Contamination factor (Cf), Pollution Load Index (PLI) and Geoacumulation Index (Igeo) were determined to assess the metal contamination in the sediments only. All three sampling sites exhibited relatively high levels of copper and zinc in sediments and suspended solids. Copper and zinc in suspended solids range from 0.02 to 0.67% and 2.79 to 23.52 %, respectively. In sediments, copper and zinc range from 83.88 - 242.2 ppm and 55.24 to 174.8 ppm respectively for the six-month sampling duration.

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Generally, higher concentrations of these heavy metals were recorded during the dry season compared to the wet season. Statistical data revealed varying degrees of significant relationship between the copper and zinc levels at different stations. In the spring, the concentrations of the two metals present in sediments exhibit significant relationship which suggests similarity in geochemical behavior of the two metals at the site. In the same manner, significant relationships were found to exist between the copper in sediments and in suspended solids; zinc in sediments and in suspended solids; and, copper in suspended solids and zinc in suspended solids at the zone of impact. Meanwhile, at the site 20-meters away from the ZOI, the amounts of copper and zinc in sediments are considerably correlated and has significant relationship with each other which was also the case for the copper and zinc in suspended solids. Interestingly, the correlations of copper and zinc concentrations between stations are promising. The three stations are positively correlated and have significant relationships in terms of copper and zinc concentrations in suspended solids. On the contrary, the stations are less correlated in terms of heavy metal contents in sediments. These results suggest that the effect of the spring on the river is determined more by the suspended solid due to its relative mobility compared to sediments. All three assessments *Cf, PLI*, and I_{geo} revealed that the sediments are more heavily contaminated with copper than zinc.

Keywords: Pulang Bato Spring; Butuanon River; Copper; Zinc; Sediments; Suspended Solids; Contamination factor; Pollution Load Index; Geoaacumulation Index.

1. Introduction

Contamination of rivers is a common problem in many developing countries. In the Philippines, most urban rivers are already highly contaminated. In Metro Cebu, the fast growing urbanization and industrialization have led to increased disposal of untreated urban wastes and effluents from various industries. Runoff from agriculture and mining activities are also prevalent in several areas of the metropolis. Since there is no wastewater treatment at the household, municipal and/or city level in Metro Cebu, all of these wastes drain directly into the rivers. Butuanon River, running through the cities of Cebu and Mandaue, is highly contaminated with copper and zinc [1,2,3,4,5,6]. A range of environmental samples including water (surface and pore water), sediments (surface and rhizosphere), umbrella plant and guppy fish have been collected over time and has been established to be heavily contaminated with these two metals. A possible tributary that may contribute to the copper and zinc contamination in Butuanon River is the spring in Pulang-Bato, Cebu City. According to the residents in Pulang-Bato, the spring was discovered some ten years ago when people made several diggings and earth moving in search of copper mines. These activities eventually hit the head of the spring causing water to be released. The spring and its surrounding areas where several diggings were made was apparently not an economical source of copper, and hence it was abandoned. Since water is continuously overflowing from this site, the owner of the property made narrow channels to guide the water to drain into a certain portion of the river passing through Barangay Pulang-Bato, Cebu City. In 2015, the Mandaue CENRO investigated this area which the locals now call as “copper spring” and they found red-colored sediments after a long spell of the dry season (no rain). The spring waters were sampled and analyzed, and traces of copper and zinc were detected. Yet, the sediments which are considered the true sink of the contaminants [7,8,9] remained undisturbed and untapped for scientific and research studies. Since this site where the spring was discovered were possible sites for mining copper, it is assumed that the spring waters are gradually draining and continuously feeding the river with copper and possibly zinc which usually co-exist in copper ores. This project sought the study of the sediments and suspended solids for copper and zinc contamination in the “copper spring” and a particular section of the Butuanon River where the spring waters come in contact with the river. Since the spring is continuously draining its waters into the river, suspended solids will also be a possible mode of transfer for the metals from the spring to the river sediments, an apparent storage of these contaminants. It is important therefore to validate this hypothesis and confirm if the waters of the spring have indeed contaminated the river with copper and zinc.

2. Materials and Methods

2.1. Description of the Study Area

Two areas were identified in this study. The first location was the natural spring at Pulang-Bato, Cebu City. It is situated at approximately 10^{o}19’54”N 123^{o}53’51”E of the Cebu province. Elevation at these coordinates is estimated at 111.7 meters or 366.5 feet above mean sea level. The second location was the Butuanon River at Brgy. Pulang-Bato area. It has 34.5-kilometer distance, starting from Brgy. Malubog, Cebu City passing through adjacent Manduae City and eventually opens to the Mactan Channel. The part of the river at Pulang-Bato which was subjected to the study is only about 20-30 meters long.

2.2. Sampling Stations

Three sampling stations were established for this study: one was the natural spring of Pulang-Bato (10^{o}19’54”N 123^{o}53’51”E, elevation 111.7-m above sea level), and two in the river. Station 1 was the natural spring; Station 2 (10^{o}19’54”N 123^{o}53’50”E) was the immediate area where the spring waters come in contact with the river, and Station 3 (10^{o}19’54”N 123^{o}53’50”E) was 20 meters away after the zone of impact of the natural spring and the river.

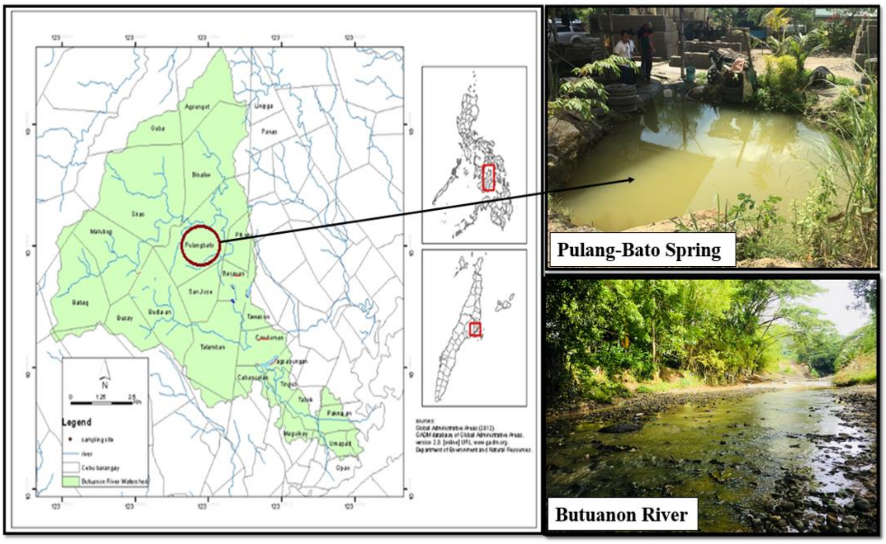


Figure 1: Natural spring at Pulang-Bato and Butuanon River

2.3. Reagents and Instrumentation

All chemicals and reagents used for the analyses were analytical reagent grade. Concentrated HNO3, concentrated HCl, and Whatmann filter paper #42 µm were used in the digestion. Standard solutions for copper and zinc were used. For 100-ppm Cu and Zn standard stock solution, an aliquot of 25-mL was taken from 1000-ppm stock solution, transferred into a 250-mL volumetric flask and was diluted to the mark with distilled water. The pH, dissolved oxygen (DO) and stream flow was measured using Orion pH meter, Milwaukee DO meter and twig-method for stream flow, respectively [2,10,11]. Moisture determination was conducted using the Ehret TK 4067 oven. The analyses of total copper and zinc were done using the AA-3600 Shimadzu Flame Atomic Absorption Spectrophotometer using air-acetylene flame [1,2,3,4,5,6].

2.4. Physico-chemical Parameters

pH, dissolved oxygen (DO) and stream flow were measured immediately prior to sample collection. The pH was measured directly on both the spring and river water. The concentrations of dissolved oxygen (mg/L) in the spring and the river were measured by taking 100 to 200-mL of water samples and placing it in a stable container thereby reducing the disturbance in the water which may cause instability of the digital readings. To determine the stream flow, a modified procedure was done. A twig of about 2-inches long was allowed to float along with the current in a 10-m stretch of the river. Furthermore, the width and the depth of the stretch were also measured to determine the total volume of the water. The stream flow values were presented as cm3/s. All measurements were done in triplicates to ensure reliability of the results. Collection and Analyses of Sediments and Suspended solids. The collection of sediment and suspended solid at three stations were done in November, December, and January representing wet season; and February, March, and April representing dry season. The sediment and suspended solid samples were collected within the 5 m x 5 m stretch of the river per station. Three (3) random sampling for each station were done to enhance the reliability of the results. Analyses of these samples for copper and zinc were done in triplicates using External Calibration (EC) [2,10,11,12].

2.5. Sediments and Suspended Solids

Surface sediments were collected using a small shovel, stored in plastic bags and transported to the laboratory. These sediments were immediately air-dried for 3-5 days, screened through a sieve shaker at an aperture of 180-um and was homogenized further. The air-dried samples was oven dried and its moisture content was determined. Oven-dried sediment samples were digested using the method by ISO standard 11466 where aqua regia was used instead of 30% H_2O_2. The resulting sediment digest (SD) was filtered again and the filtrate was placed in a 100-mL volumetric flask which was diluted to the mark. This was labeled as Water Digests (WD). External calibration standards of 0.10-, 0.20-, 0.30-, 0.40, 0.60, 0.80, 1.0-ppm were prepared. All calibration standards and WD were subjected to Shimadzu Flame Atomic Absorption Spectroscopy (FAAS) for the determination of Cu and Zn concentration [2,10,12,13]. Suspended solids were collected from the water sample taken from the spring and river. The water sample was filtered using a previously oven-dried and weighed micro filter paper. The filter paper together with the residue was then oven-dried and weighed; and from its total weight, the weight of the residue was determined. The filter paper with the residue was then digested using the method by US-EPA #3050B. The resulting suspended solid digest (SD) was filtered and collected in 50-mL volumetric flasks, diluted to mark and ran in the FAAS together with the freshly prepared calibration standards [2,11].

2.6. Limit of Detection and Method Validation

The Limit of Detection (LOD = 3s) was determined by running the reagent blank and a 0.20-ppm copper and zinc standards 30 times in the FAAS. Percentage recoveries for water samples will be determined and calculated using Equation 1.

$$\% \text{ recovery} = \frac{AWD + X_{standard} - AWD}{A\, x_{standard}} \times 100 \qquad \text{(Equation 1)}$$

where: $AWD + X_{standard}$ = absorbance of $WD + X_{standard}$

AWD = absorbance of WD only

$A\, x_{standard}$ = absorbance of $X_{standard}$ only

X/x = Cu or Zn

2.7. Data Analysis

The concentrations of Cu and Zn in the river sediments and suspended solids were compared with the Philippines' Department of Environment and Natural Resources Administrative (DAO) 34-1990 standard and Criteria for the Assessment of Freshwater Sediment by [14]. Correlation coefficient using Pearson's r was calculated to determine the relationships between the concentrations of Cu and Zn in sediments and suspended solids at three sampling stations. The data of the mean of the replicates and the evaluation of significance differences among stations, seasonal variation and by interaction were processed using multiple analyses of variance (MANOVA), followed Tukey-Post Hoc analyses using Microsoft Excel 2013 and SPSS 16.0 [2,10,12,13].

3. Results

3.1. Physicochemical Parameters

The average pH, dissolved oxygen, and stream flow values from November to April are presented in Figure 2. The pH of the water ranges from slightly acidic to slightly basic (6.56 – 8.03). Based on the DENR Administrative Order no. 34, the pH range of Class D waters like Butuanon River should range from 6.00-9.00. The results showed that the pH values of water in the river and the natural spring are within the DENR standard value. There was an irregular trend for DO values for dry and wet seasons. In natural spring (Station 1), the DO values range from 2.63 to 3.33 mg/L with the lowest value observed in the month of April (dry season) while the highest was on November (wet season). The same is true for Stations 2 and 3 where the lowest and highest

DO values fall in April and November respectively. The DO values range from 5.40 to 7.77 mg/L and 5.23 to 7.27 mg/L in Station 2 and 3 respectively. Generally, the concentrations of dissolved oxygen are lower in the natural spring water (Station 1) compared to the river water (Stations 2 & 3). There was a fluctuating stream flow values for dry and wet seasons. In Station 2, the values range from 260.26 to 26,391 cm^3/s while in Station 3 stream flow measurements range from 1,651.7 to 35,657.14 cm3/s. The lowest value was observed on the month of April (dry season) while the highest was on January (wet season). Meanwhile, there is no measured stream flow in the natural spring (Station 1) since the water is only withdrawn to the river through a small man-made gutter or channel.

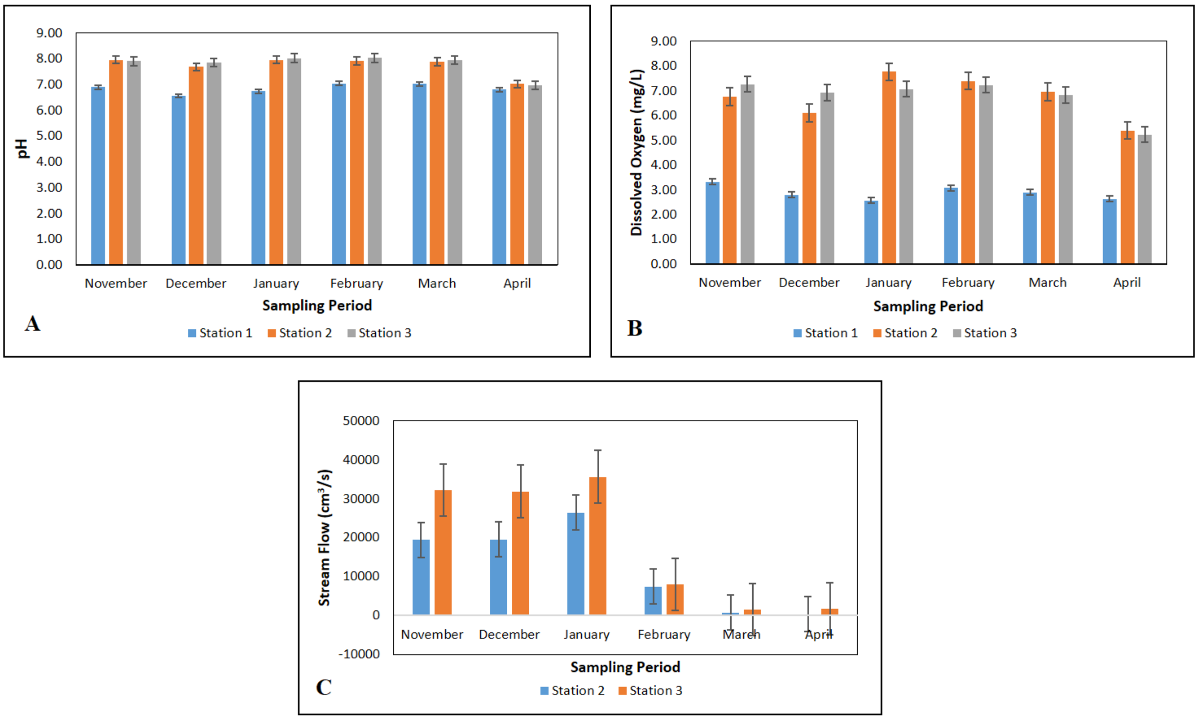


Figure 2: Physicochemical parameters pH (A), Dissolved Oxygen (B), and Stream Flow (C) of the three stations.

3.2. Concentrations of Copper and Zinc in Suspended Solids

The levels of copper in the natural spring (Station 1) alone fluctuated throughout the wet and dry seasons. The highest copper concentration was recorded on the month of March (Dry) and lowest on December (Wet). Significant differences in the copper levels occurred between the different months; higher levels in November, January, and March compared to December; and February exceeding the levels in November. In the zone of impact of the spring and the river (Station 2), there is no observed significant differences throughout the six-month sampling duration except for the month of March which has higher copper level than the rest of the months.

The 20-meter site from the ZOI (Station 3) exhibits significantly higher copper levels in February, March, and April compared to November, December, and January. Furthermore, in the natural spring (Station 1), the concentrations of zinc range from 12.53 to 23.52% in the whole six-month sampling duration. The lowest and highest levels were recorded during December (wet season) and March (dry season) respectively. This range is considerably higher than the zinc levels observed in both Stations 2 (3.35 to 20.96%) and Station 3 (2.79 to 22.48%). The considerable margin of difference indicates the abundance of the said metal in suspended solids of the natural spring. All zinc concentrations in the natural spring are more or less similar in all six months and large fluctuation in the data is not observed except for the month of March which exhibits a significantly higher amount compared to the other months. In Stations 2 and 3, the higher amounts of zinc are observed in the months representing dry season which exceed significantly the concentrations in the months representing wet season. The lower levels of copper and zinc in wet season than in dry season is due to the heavy downpour of rain which washed away the waters containing the suspended solids to the lower zone of the river. In the case of the natural spring, the increase in the amount of water in rainy season contributes to the lower concentrations of the copper and zinc [2].

The presence of phytoplankton activity can also decrease the levels of the metals; phytoplankton consume copper and zinc and high density of these organisms are observed during wet monsoon which leads to high consumption of copper thereby depleting its concentrations [15]. In addition, the concentrations of heavy metals like copper and zinc in suspended solids generally depletes in rainy season.

This is due to the fact that the rate of flow increases and the enrichment of heavy metals in water particulates like suspended solid decreases [16]. This also supports the findings that there are relatively higher concentrations of copper and zinc in suspended solids during the dry season. The prevalence of the heavy metals in the suspended solids of natural spring may be due to its proximity to the old copper mining site. In the report published by the author in [17], continuous weathering and erosion of the land masses in mining areas contribute significantly to the levels of heavy metals like copper and zinc in the bodies of water near it. Consequently, these heavy metals can be stored in water particulates like suspended solid [16,17,18,19]. In addition, the predominantly higher pH (slightly basic to basic) in this site, results to formation of copper and zinc metal complexes in aerated natural waters and subsequently stored in the suspended solids [20].

According to the data available in the local government, Brgy. Pulang-Bato’s land is not primarily used for agricultural and industrial purposes; hence, waste discharges from this anthropogenic activities were very minimal and there is no strong link that these are the sources of the elevated concentrations of these heavy metals in suspended solids. The similarity in the distribution pattern of the two heavy metals is due to the fact that zinc co-exist in copper ores. The variation of copper and zinc concentrations in suspended solids for wet and dry seasons is presented in Figure 3.

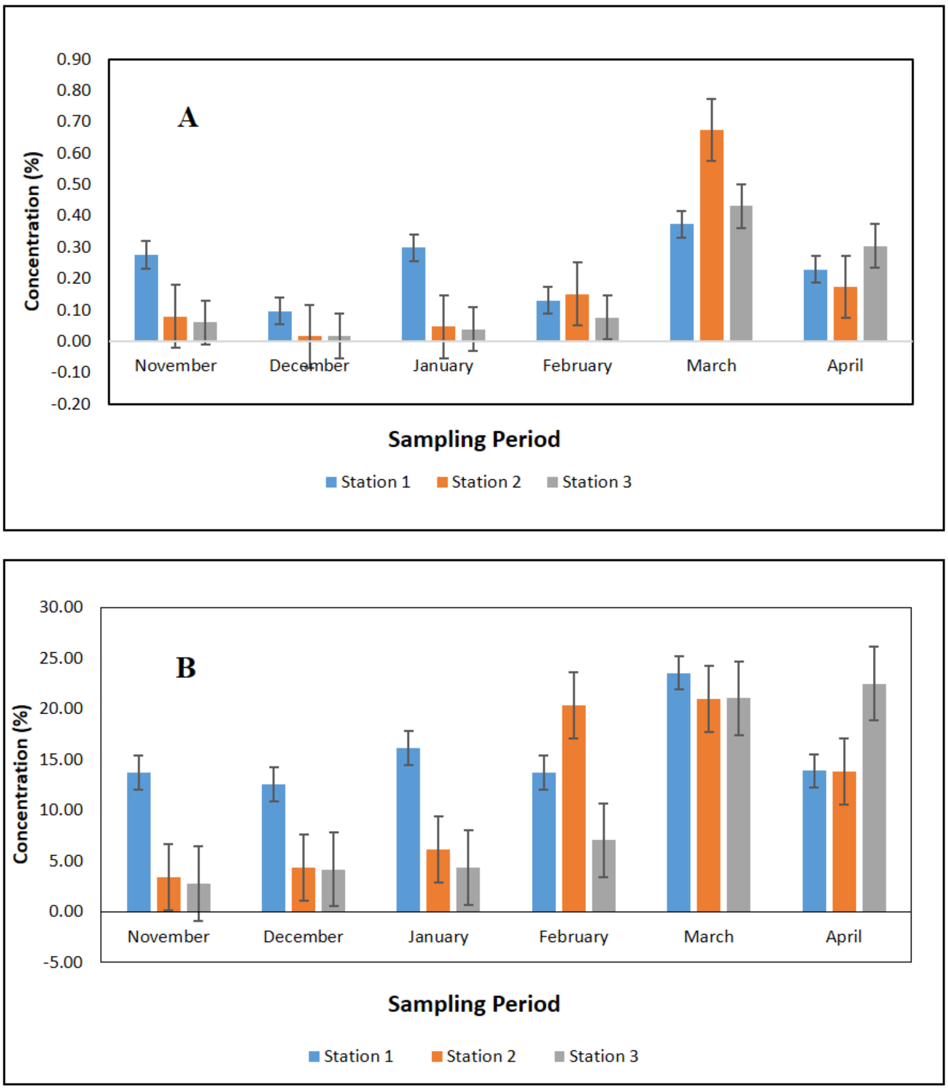
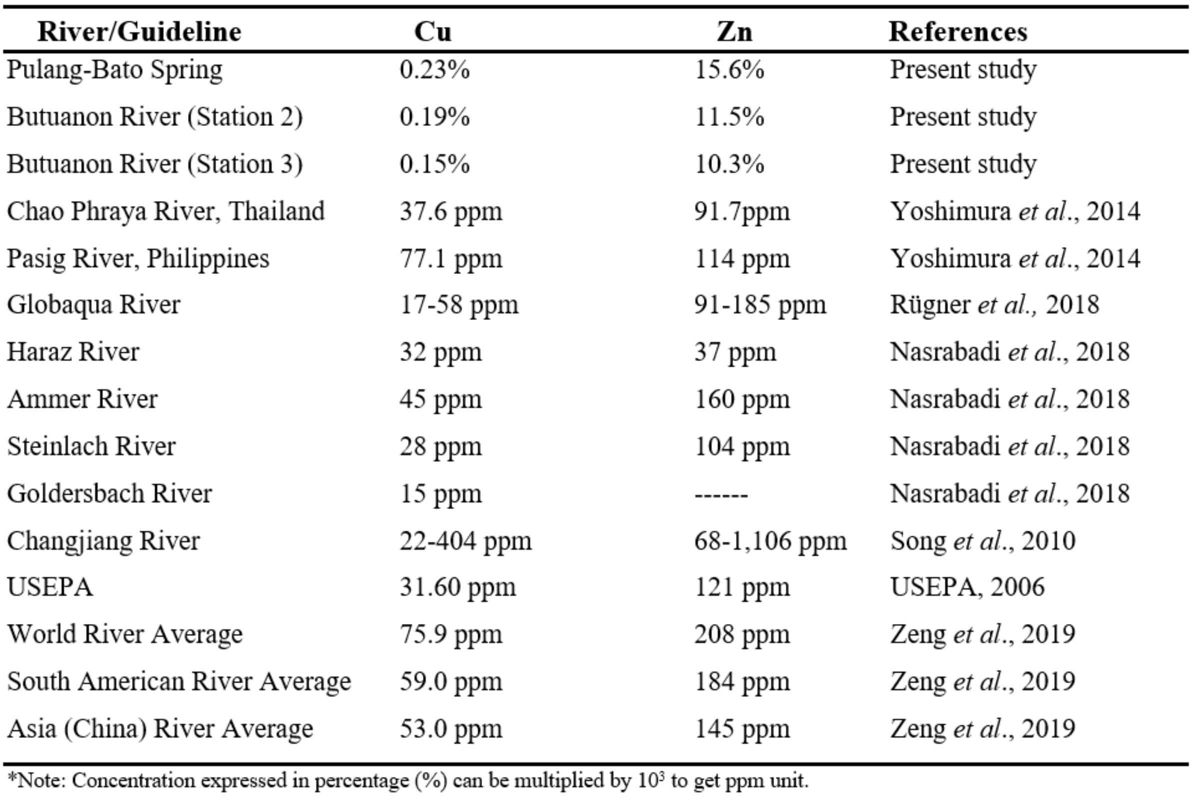


Figure 3: Copper (A) and Zinc (B) concentrations in Suspended Solids solids per sampling period at three stations. Computed as % (ppm/10,000).

3.3. Comparison of Copper and Zinc in Suspended Solids of the Present Study with other World Rivers and Guidelines

Several studies on the concentration of copper and zinc in suspended solids have been done in both international and local settings. The average concentrations of copper and zinc in the suspended solids of Pulang-Bato spring and the two stations at Butuanon River (ZOI) are considered abnormally high as it exceed greatly the findings of other related studies conducted on different world rivers. In addition, the concentrations are way above the standard concentrations set by USEPA Screening Benchmark, World River System Average, and Asian River Average for suspended solids. The comparison of Pulang-Bato spring and Butuanon River heavy metal contamination in suspended solids with other world rivers and guidelines is presented in Table 1.

Table 1: Comparison of Average Heavy Metal Concentration in Pulang-Bato Spring and Butuanon River Suspended Solids with other World Rivers and Guidelines



River/Guideline	Cu	Zn	References
Pulang-Bato Spring	0.23%	15.6%	Present study
Butuanon River (Station 2)	0.19%	11.5%	Present study
Butuanon River (Station 3)	0.15%	10.3%	Present study
Chao Phraya River, Thailand	37.6 ppm	91.7ppm	Yoshimura *et al*., 2014
Pasig River, Philippines	77.1 ppm	114 ppm	Yoshimura *et al*., 2014
Globaqua River	17-58 ppm	91-185 ppm	Rügner *et al.,* 2018
Haraz River	32 ppm	37 ppm	Nasrabadi *et al*., 2018
Ammer River	45 ppm	160 ppm	Nasrabadi *et al*., 2018
Steinlach River	28 ppm	104 ppm	Nasrabadi *et al*., 2018
Goldersbach River	15 ppm	------	Nasrabadi *et al*., 2018
Changjiang River	22-404 ppm	68-1,106 ppm	Song *et al*., 2010
USEPA	31.60 ppm	121 ppm	USEPA, 2006
World River Average	75.9 ppm	208 ppm	Zeng *et al*., 2019
South American River Average	59.0 ppm	184 ppm	Zeng *et al*., 2019
Asia (China) River Average	53.0 ppm	145 ppm	Zeng *et al*., 2019

*Note: Concentration expressed in percentage (%) can be multiplied by 10^3 to get ppm unit.

3.4. Concentrations of Copper and Zinc in Sediments

The copper concentration in the natural spring (Station 1) throughout the six-month sampling period range from 143.97 to 242.18 ppm with the months of November and February exhibiting the lowest and highest levels respectively. However, there is no great variation in the copper level readings across the six-month sampling period as there is no observed significant differences with one another except for the months of February and November. Furthermore, copper level in February (dry season) exceeds significantly that of November (wet season). The copper levels at the zone of impact (Station 2) throughout the six-month sampling period range from 83.88 to 224.35 ppm with the months of March and April exhibiting the lowest and highest levels respectively. In this station, the copper levels are significantly different with one another in all months with some exceptions; results in November has no significant difference with that of March as well as between December and February. Lastly in Station 3, the copper concentrations in six-month sampling period range from 88.92 to 196.60 ppm with the months of March and December exhibiting the lowest and highest levels respectively. The copper levels are significantly different with one another in all months with some exceptions; concentrations in November has no significant difference with that of March as well as between December and April. The amounts of zinc in the natural spring (Station 1) range from 94.09 to 174.82 ppm from November to April. Furthermore, statistical findings reveal that there is no significant differences in the zinc concentrations throughout the six-month sampling period. The relative stability of the readings may be due to the fact that the spring is an enclosed body with only a narrow channel connecting it to the river; thus, it is less affected by flow rate, rapid changes in the volume of water, oxygen uptake, and anthropogenic discharges which contributes greatly to the concentrations of metals like copper and zinc [2,7,8,9]. On the other hand, an irregular trend on the concentrations of zinc across the six-month sampling period is observed in Stations 2 and 3. At the zone of impact (Station 2), the zinc levels in the month of January significantly exceeds all the other sampling months. In Station 3, the zinc level in sediments is distinctly higher in December than all the other sampling months. Similarly, the average zinc concentration in dry season (90.81 ppm) outweighs the measurements in wet season (87.53 ppm). This follows similar findings with the copper in sediments since literature suggests that both metals co-exist in the same ore. Hence, factors like frequency of raining, amount and type of sediments, and the proximity to a mining site that control the distribution of copper in sediments are most likely the same factors that affect the amounts of zinc in sediments [2,7,16,17,18,19]. The relatively high concentrations of copper and zinc in sediments in both seasons reveal that the surface water is highly contaminated as the sediments are the depositories of these heavy metal contaminants [21]. These findings show that the sediments in both the spring and river is highly contaminated with these heavy metals and may be alarming in the future for the river's ecosystem. In similar studies for heavy metals in sediments, it has been found that the average copper concentration was 124.15-ppm at a different site in Butuanon River [2] and in other world rivers; 11.74-ppm at Ghaghara, 49-ppm at Ghazipur, 58-ppm at Buxar, and 56-ppm at Ganga [22,23,24,25]. These results from other studies reveal that the concentrations of copper in the sediments of the natural spring in Pulang-Bato and the section of Butuanon River highly exceed the copper levels in many other world rivers. Meanwhile, the World Average concentration for copper in sediments which is 45-ppm [26] and the World River System which is 100-ppm [27] are still much lower compared to the values recorded in the present study. This only magnifies the high degree of copper contamination in the three sites. In addition, all copper concentrations exceed the threshold effect and occasional effect levels (TEL and OEL) based on Guideline Values by [14] for the freshwater sediments which is 36-ppm and 63-ppm respectively. This guideline is one of the most recent standards for allowable copper levels in sediments. In past reviews, the average value of zinc (Zn) concentration in the sediment of the other World Rivers was recorded as 230.4-ppm at Yangtze, China; 13.26-ppm at Katerniaghat, India; 502.3-ppm at Buriganga, Bangladesh; 110-ppm at Amazon Mouth, Brazil; 67.8-ppm at Ganga, India; 14.29-ppm at Dohrighat, India; and 18.11-ppm at Chhapra, India [22,23,24,25,28,29]. The average concentration of zinc in the sediments of natural spring at Pulang-Bato (127.3-ppm) is slightly above the permissible limit proposed by [30] (121-ppm) and World Average (95-ppm) [26]; however, the concentrations of zinc in the sediments at the section of Butuanon River were below the USEPA (1999) and World Average concentrations. On the contrary, the zinc concentrations at all sites are lower than the maximum value set by World River System [27] which is 350-ppm. These comparative analyses also reveal that zinc concentrations in the sediments of the natural spring and the section of Butuanon River do not exceed greatly the international sediment standards and within the range of the findings of other similar studies. Furthermore, the average concentration of zinc in Station 1 are above the threshold effect level (80-ppm) but below the occasional effect level (170-ppm) except for February (174.82-ppm) based on Guideline Values by [14] for the Freshwater Sediments. Meanwhile, all zinc concentrations in Stations 2 and 3 are below both TEL and OEL. This guideline is one of the most recent standards for allowable zinc concentrations in sediments. The variation of copper and zinc concentrations in sediments for wet and dry seasons is presented in Figure 4.

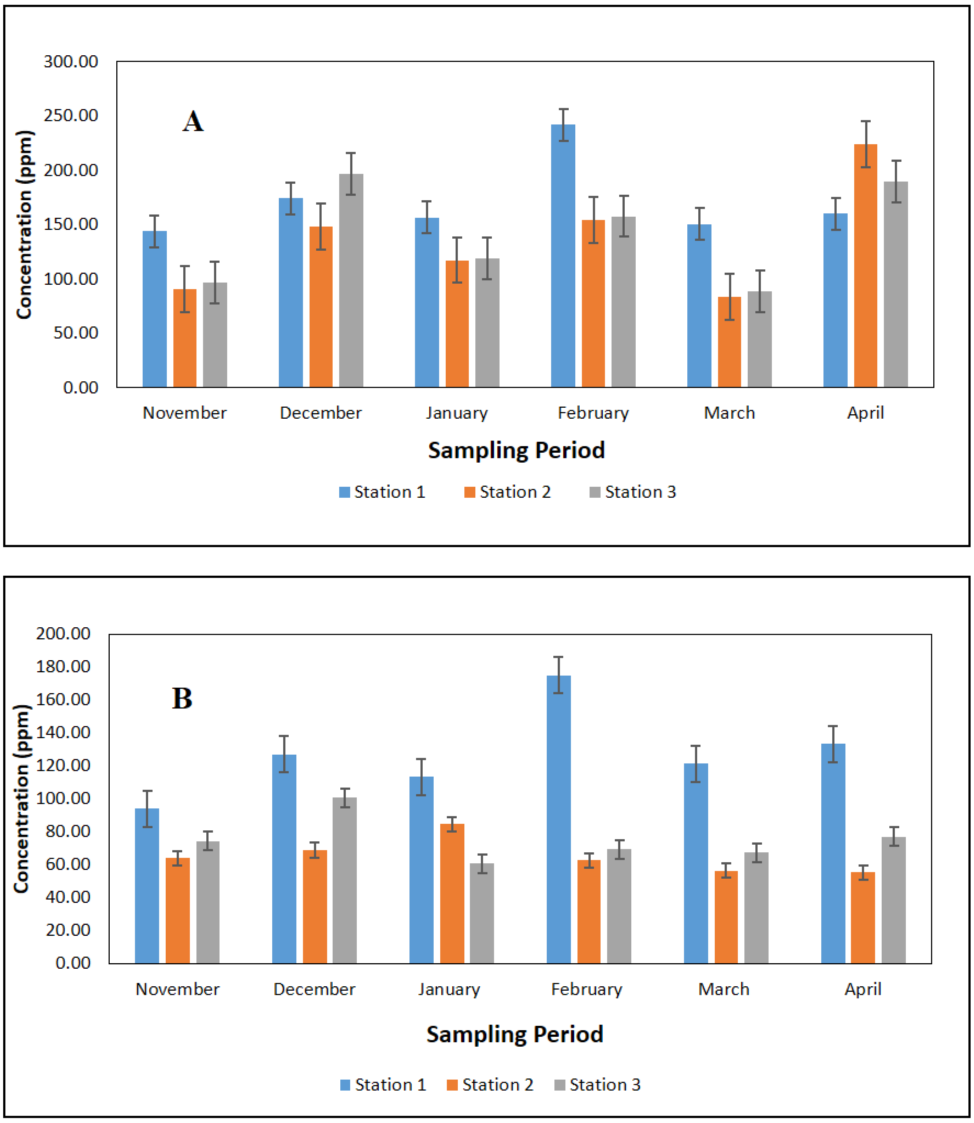


Figure 4: Copper (A) and Zinc (B) concentrations (ppm) in Sediments per sampling period in three stations.

3.5. Correlations between Copper and Zinc Concentrations in Sediments and Suspended solids

Correlations are evaluated as: Very low (*0.00 – 0.19); Low (0.20 – 0.39); Moderate (0.40 – 0.59); High (0.60 – 0.79); and Very high (0.80 – 1.00). The correlations in copper and zinc concentrations in sediment and suspended solids are each determined in every station. Positive and negative correlations reveal some significant and non-significant relationships between the heavy metal concentrations. In the natural spring (Station 1), a very low negative correlation (r = -0.159, p = 0.252) and no significant relationship is found between the copper concentrations in sediments and suspended solids. Furthermore, there is also no significant relationship with very low positive correlation (r = 0.002, p = 0.988) between the zinc concentrations in sediment and suspended solid showing a similarity in behavior with that of copper. In the study of [16], similar results were obtained showing that although there is a common geochemical sources of copper and zinc in sediment and suspended solid, no further relationship was revealed. This may indicate the differences in the characteristics of these heavy metals in sediments and suspended solids as well as the factors that control the individual concentrations in the spring [16]. Similarly, statistical results gave an r = 0.178 and p = 0.198 between the concentrations of copper and zinc in suspended solids showing that there is no existing significant relationship between the two. In contrast, a very high positive correlation (r = 0.909, p = 0.000) and a significant relationship is observed between the concentrations of copper and zinc in sediments showing that as copper increases, zinc also increases. This high correlation suggests that the heavy metals have same geochemical behaviors or sources and more or less affected by similar factors [16,17,18]. In the Zone of Impact of the spring and Butuanon River (Station 2), a different relationship between the concentrations of copper in sediment and suspended solid is observed. Statistically, a low negative correlation (r = -0.302, p = 0.027) and with significant relationship occurs between the concentrations suggesting that as copper in sediment slightly increases, the copper in suspended solid slightly decreases. Similar correlation is observed between the zinc concentrations in sediment and suspended solids but with moderate negative correlation (r = - 0.592, p = 0.000). This follows that as zinc in sediment moderately increases, the copper in suspended solid moderately decreases. One of the most probable contributing factors to these findings is sedimentation, it is commonly described as settling of the suspended particles present in surface water [31]. When suspended particles carrying the heavy metals and entrained by the turbulence of moving water is removed in the surface by sedimentation, the amounts of copper and zinc increase in the sediments thereby decreasing its concentration in the suspended solids [31,32]. Interestingly, this correlation between the sediment and suspended solid concentrations is not observed in the natural spring. Several factors may affect this difference, the course of sedimentation in the spring may be more dynamic and complex compared in the river because of its relative depth (6 feet and 1 inch), the absence of stream flow, and its enclosed system (with a diameter of approximately 3 meters); hence, a correlation between sediments and suspended solids is harder to take place. However, the concentrations of copper and zinc in sediments shows no significant relationship with a low negative correlation (r = -0.208, p = 0.132) while the concentrations of the metals in suspended solids exhibits a moderate positive correlation and has significant relationship (r = 0.574, p = 0.000). These results suggest that the concentrations of the heavy metals in the sediments in this station are independent of one another while in suspended solids, as the copper level moderately increases, the zinc moderately increases too. Generally in this station, significant relationship is observed more between the amounts of copper and zinc in suspended solids compared to sediments. Station 3 is the site 20 meters away from the Zone of Impact. In this area, a low negative correlation with no significant relationship (r = -0.211, p = 0.126) occurs between the copper concentrations in sediments and suspended solids. Similarly, the zinc concentrations in sediments and suspended solids shows a moderate negative correlation with no significant relationship (r = -0.519, p = 0.100). In contrary to the relationship found in the Zone of Impact, this result may suggest that sedimentation or settling process in this area is more irregular than in Station 2 [31,32]. The difference in the sedimentation process may be brought about by the difference in the volume of water and stream flow between the two sites [33]. Meanwhile, a moderate positive correlation and a significant relationship (r = 0.499, p = 0.000) appears to be the case between the concentrations of copper and zinc in sediments while there is a very high positive correlation and a significant relationship (r = 0.890, p = 0.000) between the heavy metal concentrations in suspended solids. This clearly indicates that as the amount of copper in sediments and suspended solids increase, the amount of zinc in sediments and suspended solids increases as well. This relationship shows the likeness in geochemical behaviors of the two heavy metals in this area [16]. These correlations are shown through a scatter graph in Figure 5.

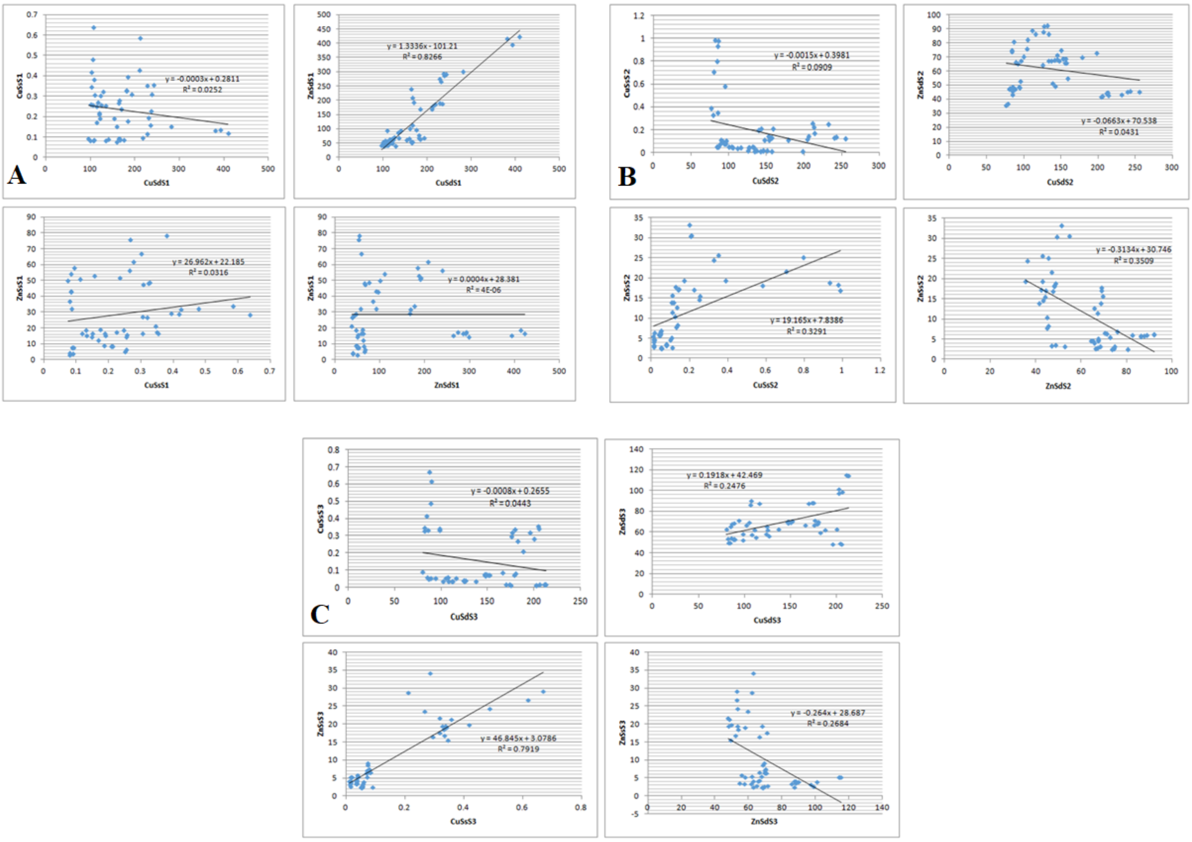


Figure 5: Scatter Graph Summary for Station 1 (A), Station 2 (B), and Station 3 (C) for the six-month sampling period. Note: Ss – Suspended Solids; Sd – Sediments; S3 – Station 3..

3.6. Correlations between Copper and Zinc Concentrations in the Three Stations

The effect of the Pulang-Bato spring on the copper and zinc content at the zone of impact of the spring and the river is determined through the correlations of the three stations in terms of copper and zinc concentrations present in sediment and suspended solid. The concentrations of copper in sediment between the spring (Station 1) and zone of impact (Station 2) shows a very low correlation and exhibits no significant relationship (r = 0.170, p = 0.220) with one another. The same is true between Stations 1 and 3 (r = 0.170, p = 0.220) showing no significant relationship. Nevertheless, a very high correlation and significant relationship (r = 0.814, p = 0.000) is found between the sediment copper content of Stations 2 and 3. Meanwhile, the concentrations of zinc in sediment between the spring (Station 1) and zone of impact (Station 2) shows a very low correlation and has no significant relationship (r = -0.174, p = 0.208). The same is observed between Stations 1 and 3; a very low correlation and no significant relationship (r = 0.133, p = 0.339). Furthermore, a positive correlation and significant relationship (r = 0.323, p = 0.017) exists between the sediment zinc content of Stations 2 and 3. Generally, the correlations of the three stations in terms of heavy metal contents in sediment are similar for both copper and zinc. These statistical findings reveal that the concentrations of the two heavy metals in the sediments of the spring have no significant effect on the sediments of both Stations 2 and 3. This also shows that as the sediment concentrations of copper and zinc in Station 2 increase, the concentrations in Station 3 also increase. The lack of significant effect of copper and zinc present in the spring's sediment on Stations 2 and 3 could be attributed to the topography of the spring. The combined depth (6 feet 1 inch), lack of stream flow and turbulence in the spring enhances the settling process, stability, immobility, and heavy metal storage in the sediments thereby reducing its effect on the heavy metal contents at Station 2 and 3 sediments. In the report published in the Environment Agency Flood and Coastal Erosion Risk Management R&D Programme entitled, "Sediment Transport and Alluvial resistance in rivers" it mentioned that sediment movement and its materials is highly influenced by structural features and affected by geological constraints, more enclosed systems slow the movements of the sediments as well as the components there within [31,34]. The close similarity of Stations 2 and 3 in terms of geological features, physico-chemical characteristics as well as the proximity of the two stations improved the high correlation and significant relationship to be established [34]. The scatter graph analyses for the three stations in terms of heavy metals in sediments are shown in Figure 6.

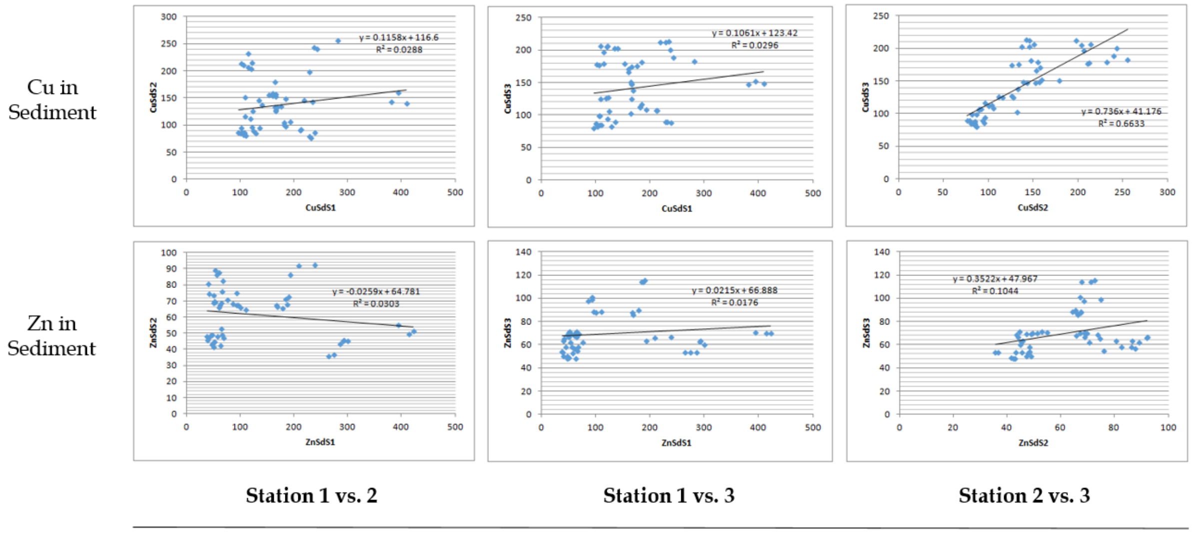


Figure 6: Scatter Graph Analyses for the three stations in terms of copper and zinc contents in sediments. Note: Sd – Sediments; S1 – Station 1; S2 – Station 2; S3 – Station 3.

On the other hand, higher correlations and more significant relationships are found among the three stations in terms of heavy metal contents in suspended solids. The relative mobility of solid particulates in water compared to sediments makes an ideal medium for heavy metals like copper and zinc to be distributed more efficiently [35,36,37,38]. A moderate positive correlation and a significant relationship (r = 0.560, p = 0.000) exist between the spring (Station 1) and the zone of impact (Station 2), a higher correlation compared to what is observed between Station 1 and Station 3 which exhibits a low positive correlation with significant relationship (r = 0.338, p = 0.000). The higher correlation observed between Station 1 and Station 2 could be attributed to the proximity between the two stations and the fact that Station 2 is where the contact of the spring water and the river takes place. In addition, Stations 2 and 3 exhibit a high positive correlation and significant relationship (r = 0.650, p = 0.000) which is expected to take place due to its proximity, similarity in topography, and physico-chemical characteristics. In the same manner, high correlations among the three stations are observed in terms of zinc concentrations in suspended solids. A low positive correlation and significant relationship (r = 0.385, p = 0.004) exist between the spring (Station 1) and the zone of impact (Station 2), a slightly higher correlation compared to what is observed between Station 1 and Station 3 which also exhibits a low positive correlation with significant relationship (r = 0.355, p = 0.008). Lastly, Stations 2 and 3 exhibit a moderate positive correlation and significant relationship (r = 0.537, p = 0.000). The comparability in the correlations exhibited by both copper and zinc in suspended solids among the stations proves the similarities of geochemical behaviors of these heavy metals [16]. However, the correlations among the stations are higher and more definite in copper than in zinc. These results reveal that suspended solids contribute more on the effect of Pulang-Bato spring on the copper and zinc contents at the zone of impact of the spring and Butuanon River. The high surface area and reactivity of suspended particulate matter or suspended solids, makes it ideal for dissolved heavy metals in the water to be easily adsorbed by it; thus, the bulk of the heavy metal concentrations are distributed through the suspended solids [39,40,41]. Furthermore, copper and zinc in the water tend to accumulate in suspended solids because of its direct interface with water, and the deposition of metal-adsorbed suspended solid is the primary process for the accumulation of copper and zinc in sediments [40]. Accordingly, the contaminated surface sediments might become re-suspended because of continuous water flow disturbance or turbulence [39,40,41]. To show the graphical relationships between the stations in terms of heavy metals in suspended solids, the scatter graph analyses are shown in Figure 7.

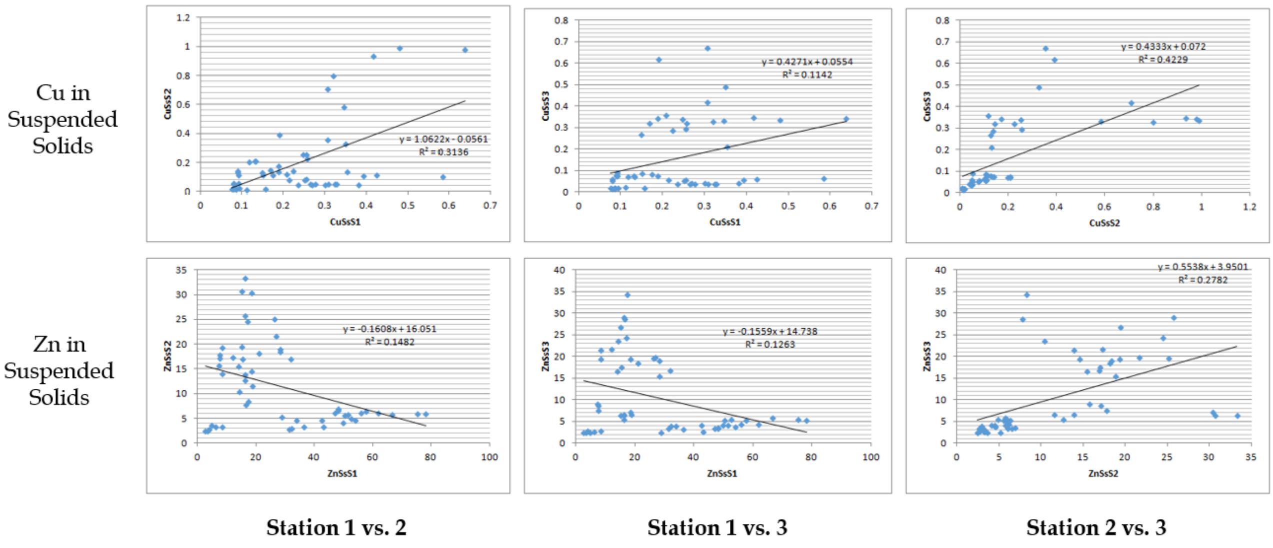


Figure 7: Scatter Graph Analyses for the three stations in terms of copper and zinc contents in suspended solids. Note: Ss – Suspended Solids; S1 – Station 1; S2 – Station 2; S3 – Station 3.

3.7. Concentration Factor, Cf

The contamination factor was calculated with respect to the world surface rock averages [27,42,43]. The contamination factor (*CF*) was used to determine the contamination status of sediments in the three stations. The level of contamination of sediment by metal is expressed in terms of a contamination factor (*CF)* as summarized in Table 2.

Table 2: Concentration Factor (*CF*) Summary of the Three Stations for the Six-month sampling duration.

Month	Station 1 (Pulang-Bato Spring)		Station 2 (Zone of Impact)		Station 3 (20-m away from ZOI	
	Copper	Zinc	Copper	Zinc	Copper	Zinc
November	4.50	0.74	2.82	0.50	3.03	0.59
December	5.45	1.00	4.64	0.54	6.14	0.79
January	4.89	0.89	3.67	0.67	3.73	0.48
February	7.57	1.38	4.82	0.49	4.93	0.55
March	4.71	0.96	2.62	0.44	2.78	0.53
April	5.00	1.05	7.01	0.43	5.94	0.61

The assessment of sediment contamination was carried out using the contamination factor, based on four classification categories described by [44] is given in Table 3.

Table 3: Contamination factor categories and terminologies.

CF Categories	Terminologies
$CF < 1$	Low *CF* indicating low contamination
$1 \leq CF < 3$	Moderate *CF*
$3 \leq CF < 6$	Considerable *CF*
$CF \geq 6$	Very high *CF*

The overall contamination of sediments at the three sites, based on the *CF* values indicate that the contamination range from moderate to very high for copper and low to moderate for zinc. In Station 1, *CF* values range from considerable to very high contamination. The highest values for both copper and zinc was observed in the month of February while the lowest for both metals was on November. These months that exhibit the extremes of *CF* values represent the dry and wet seasons respectively. However, lower *CF* values are observed in Station 2 in comparison to Station 1. Copper *CF* values range from moderate to very high with the months of March and April exhibiting the lowest and highest values respectively. A much lower *CF* values for zinc compared to copper are observed in this area. In Station 3, copper contamination factor values range from moderate to considerable while zinc still shows low *CFs* for six months. It should be noted that higher *CF* values for copper metal are recorded in all stations for the six-month sampling duration. This suggests that the sediments at the three sites are extensively contaminated with copper than it is with zinc. Also, the average *CF* values for each station demonstrates that the sediment of the natural spring (Station 1) has higher level of copper and zinc contamination compared to both stations at the river. The *CF* values for copper and zinc are documented in other related studies. Contamination factors for copper in other rivers range from 0.04 to 0.26 [45]; 0.70 to 1.81 [46]; 0.02 to 0.61 [47]; and 0.2 to 1.8 [48]. The results in the present study are significantly higher than those observed in other similar studies; nevertheless, the values are comparable to the findings of the author in [43] which reported an average copper *CF* value of 6.36 in a study that determined the degree of contamination around a Copper-Nickel Mine in the Selebi Phikwe Region, Eastern Botswana. The relative comparability of the average *CF* values suggests that mining activities have significant contribution on heavy metal concentrations like copper on surface sediments thereby increasing its contamination level. In the same manner, the *CF* values for zinc at Station 1 (0.74 to 1.38) are somehow comparable to the results gathered in other related studies like that of [46] (1.11 to 2.79); [48] (0.4 to 1.7); and [43] (1.21), while Stations 2 and 3 are more likely similar to the findings of [45] (0.19 to 0.19); and [47] (0.05 to 0.48). Hence, it could be drawn out that zinc is a common heavy metal contaminant that accumulates in the surface sediments of rivers.

3.8. Pollution Load Index, PLI

The pollution load index, *PLI* was calculated using the equation proposed by [50] and summarized in Table 4.

Table 4: Pollution Load Index (*PLI*) summary of the three stations for the six-month sampling duration.

	Station 1		**Station 2**		**Station 3**	
	Cu	**Zn**	**Cu**	**Zn**	**Cu**	**Zn**
November						
CF	4.50	0.74	2.82	0.50	3.03	0.59
PLI	*1.826*		*1.194*		*1.332*	
December						
CF	5.45	1.00	4.64	0.54	6.14	0.79
PLI	*2.333*		*1.586*		*2.206*	
January						
CF	4.89	0.89	3.67	0.67	3.73	0.48
PLI	*2.090*		*1.565*		*1.335*	
February						
CF	7.57	1.38	4.82	0.49	4.93	0.55
PLI	*3.228*		*1.543*		*1.641*	
March						
CF	4.71	0.96	2.62	0.44	2.78	0.53
PLI	*2.121*		*1.078*		*1.213*	
April						
CF	5.00	1.05	7.01	0.43	5.94	0.61
PLI	*2.290*		*1.746*		*1.899*	

The PLI is able to give an estimate of the metal contamination status and the necessary action that should be taken. Table 5 shows the pollution load index and pollution grade summary [49]. Furthermore, the author in [50] emphasized that *PLI* values equal to 1 means that only baseline levels of pollutants are present while those that exceeds 1 would indicate deterioration of the site quality.

Table 5: Pollution Load Index and Pollution Grade Summary.

PLI	Category
$0 < PLI \leq 1$	Unpolluted
$1 < PLI \leq 2$	Unpolluted to Moderately
$2 < PLI \leq 3$	Moderately polluted
$3 < PLI \leq 4$	Moderately to highly polluted
$4 < PLI \leq 5$	Highly polluted
$PLI > 5$	Very highly polluted

Pollution load index values in Station 1 range from 1.826 to 3.228 with the months of November and February exhibiting the lowest and highest values respectively. While *PLI* values in Stations 2 and 3 are lower than that of Station 1, the values are still greater than one which suggests that the sites' qualities are deteriorating due to heavy metal contamination [50]. In the study of [43], it was suggested that a *PLI* value of ≥1 indicates an immediate intervention to remediate pollution; $0.5 \leq PLI < 1$ suggests that more studies are needed to monitor the site, while a value of < 0.5 indicates that there is no need for drastic rectification measures to be taken. Since all stations exhibit *PLI* values of more than 1, then immediate action is needed to decrease the heavy metal contamination to at least baseline levels at these sites.

3.9. Geoaccumulation Index, I_{geo}

The Geoaccumulation Index, I_{geo} was calculated using the equation proposed by [51] and summarized in Figure 8.

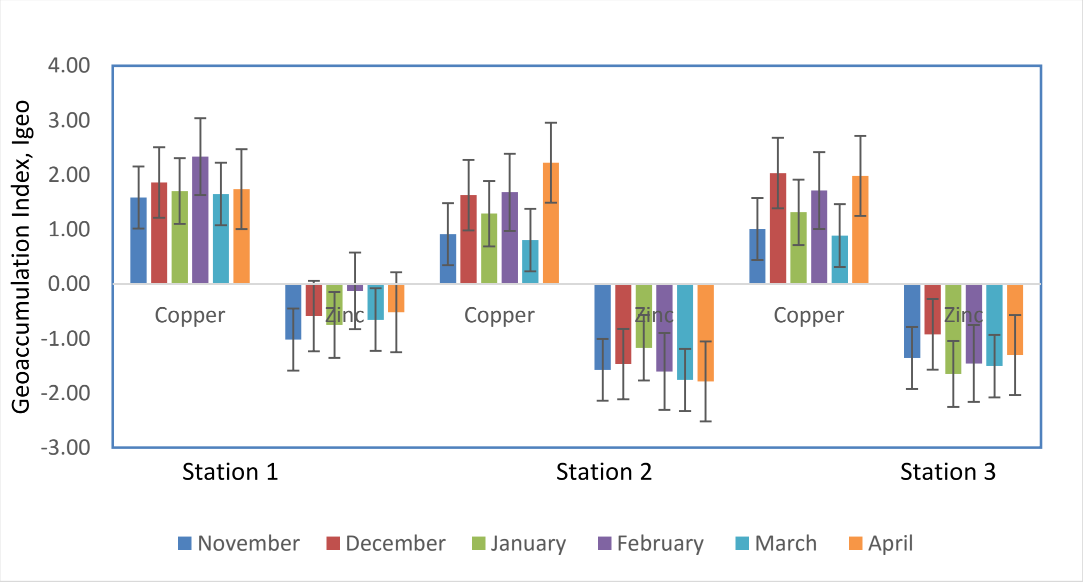
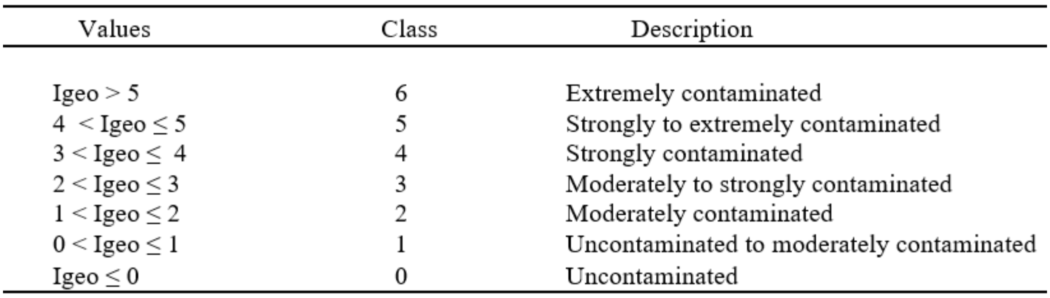


Figure 8: Geoaacumulation Index, I_{geo} summary of the three stations for the six-month sampling period.

The Geoaccumulation Index was evaluated based on the seven descriptive classes for increasing I_{geo} values proposed by [51] as shown in Table 6.

Table 6: Geoaacumulation Index, Igeo values, classification, and description.



Values	Class	Description
Igeo > 5	6	Extremely contaminated
4 < Igeo ≤ 5	5	Strongly to extremely contaminated
3 < Igeo ≤ 4	4	Strongly contaminated
2 < Igeo ≤ 3	3	Moderately to strongly contaminated
1 < Igeo ≤ 2	2	Moderately contaminated
0 < Igeo ≤ 1	1	Uncontaminated to moderately contaminated
Igeo ≤ 0	0	Uncontaminated

The calculated geoaccumulation index values were used to successfully assess the copper and zinc contaminations at the three stations by comparing it to the original pre-industrial concentrations in the sediments. The effect of the spring near the old copper mine to the zone of impact between the spring and Butuanon River was assessed. Data presented in Figure 15 reveal uncontaminated sediments in terms of the heavy metal zinc. All I_{geo} values of zinc fall below zero from November to April which indicates deficient to very minimal enrichment and/or relatively low levels of zinc contamination in sediments [22,43,51]. On the other hand, I_{geo} values for copper range from 1.58 to 2.34 at Station 1; 0.81 to 2.22 at Station 2; and 0.89 to 2.03 at Station 3. These geoaccumulation indexes depicts a moderate to strong contamination of copper in the sediments at all sampling sites [51]. The high degree of I_{geo} values for copper shows the deteriorating effect of the old copper mine to both the spring and the portion of Butuanon River. The geoaacumulation indices gathered in other related studies reported rivers which fall under uncontaminated category ($I_{geo} \leq 0$) for both copper and zinc metals [22,47,48]. However, the authors in [43,45] reported that the I_{geo} values for copper are higher than zinc in the sediments of Swarnamukhi River and Ghaghara River, India. Such is the case in the present study where the sediments in the natural spring, and the section of Butuanon River have higher geoaccumulation indices for copper than for zinc indicating a relatively stronger contamination for copper than for zinc.

4. Conclusion

High concentrations of copper and zinc metals were observed in both seasons. Generally, the two heavy metals exhibited higher amounts during dry season than in wet season in both sediments and suspended solids. The difference in the concentrations could be attributed to many factors like the variations in the volume of water present in the spring and the river, stream flow and or turbulence, pH, and dissolved oxygen. These factors could affect the rate of mobility, complexation, deposition, degradation, and solubility of copper and zinc which may either increase or decrease their respective concentrations. Correlations in copper and zinc concentrations between sediments and suspended solids; and between stations were determined for the six-month sampling period. This is to determine if there are significant relationships between varying concentrations of the heavy metals and to assess the effect of the spring on the copper and zinc content at the zone of impact of the spring and the portion of Butuanon River. Statistical data revealed varying degrees of significant relationship between the copper and zinc levels at different stations. In the spring, the concentrations of the two metals present in sediments exhibit significant relationship which suggests similarity in geochemical behavior of the two metals at the site. In the same manner, significant relationships were found to exist between the copper in sediments and in suspended solids; zinc in sediments and in suspended solids; and, copper in suspended solids and zinc in suspended solids at the zone of impact. Meanwhile, at the site 20-meters away from the ZOI, the amounts of copper and zinc in sediments are considerably correlated and has significant relationship with each other which was also the case for the copper and zinc in suspended solids. Interestingly, the correlations of copper and zinc concentrations between stations are promising. The three stations are positively correlated and have significant relationships in terms of copper and zinc concentrations in suspended solids. On the contrary, the stations are less correlated in terms of heavy metal contents in sediments. These results suggest that the effect of the spring on the river is determined more by the suspended solid due to its relative mobility compared to sediments. Furthermore, the degree of contaminations at the three sites were determined by calculating the contamination factor (*CF*), pollution load index (*PLI*), and geoaccumulation index (I_{geo}). The overall contamination of sediments at the three sites, based on the *CF* values indicate that the contamination was higher for copper than for zinc in all stations for the six-month sampling duration. The PLI values was able to give an estimate of the metal contamination status and the necessary action that should be taken. All stations exhibit *PLI* values of more than 1, suggesting that immediate action is needed to decrease the heavy metal contamination to at least baseline levels at these sites. Lastly, the geoaccumulation index values were used to successfully assess the copper and zinc contaminations at the three sites by comparing it to the original pre-industrial concentrations in the sediments. Data revealed uncontaminated sediments in terms of zinc concentrations while Igeo values for copper depicts a moderate to strong contamination in the sediments at all sampling sites. This study reveals that Pulang-Bato spring in Pit-os, Cebu City is contaminated significantly with copper and zinc metals. This could be due to its geological position and proximity to the old copper mine. As a result, it is continuously contributing to the heavy metal contamination in Butuanon River since it is draining its waters into the river's portion for the past ten years.

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