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Heavy metal concentration and contamination assessment in soils along Gibong Riverbanks in Prosperidad, Agusan Del Sur, Philippines

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Key words: Contamination index, Gibong riverbank, Heavy metals, Physicochemical, Soil

Abstract

The study aimed to analyze the physicochemical characteristics and heavy metal concentrations of soil along the Gibong Riverbanks in Prosperidad, Agusan del Sur, Philippines. The study found no significant differences in soil pH, electrical conductivity, soil salinity, total dissolved solids, soil temperature, moisture, or organic matter values between the three sampling sites. The concentrations of seven heavy metals, copper, lead, manganese, nickel, and cadmium in the soil samples from the Gibong riverbank do not reflect any environmental threats or concerns. However, the significant traces of chromium and borderline levels of cobalt in all three stations pose an alarming threat worthy of further investigation and intervention. Copper concentrations in the soil samples from the three statins revealed significant differences, while chromium concentrations were higher than the standard or permissible value. Lead concentrations were also significantly higher than the standard or permissible value, but the values were lower than the standard or permissible value. Cobalt concentrations were at a borderline level of reaching the standard or permissible level (50ppm) in agricultural soils, and further investigation is needed for appropriate environmental interventions. Manganese concentrations were also found to be equivalent, while nickel concentrations were below the standard or permissible value. Cadmium concentrations were also significant, but lower than the standard or permissible value. The findings can be used to establish data on the presence and contamination of heavy metals in the soils of the Gibong riverbank in Agusan del Sur, Philippines, providing data on the status of physicochemical parameters present in the soils. The data presented in the study can be used as a baseline for environmental protection programs and policies.

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Introduction

The 21st century is marked by a rapid industrial revolution, resulting in new technology, discoveries, and innovations. However, this has also led to increased use of natural and man-made resources, causing health and environmental problems such as soil nutrient overload, eutrophication, increased chemical burdens, water quality declines, and climate change (Road National Research Council, 2012). The use of organic and inorganic chemicals in manufacturing has led to numerous solutions to industrial, economic, and health problems in the 21st century. Heavy metals, such as cadmium, are essential for semiconductors, electronics, thin films, and various applications. Cobalt, a heavy metal, is used in alloys for aircraft engine parts, corrosion and wear resistance, batteries, and electroplating. Other inorganic compounds, including heavy metals, are essential nutrients for physiological and biochemical functions in animals and humans, potentially causing deficiency diseases or syndromes if not in adequate amounts (Persistence Market Research, 2020; Chemicool, 2020; Engwa *et al.*, 2019).

Heavy metal and industrial waste have become a global problem due to the accumulation and spread of dangerous substances in terrestrial and aquatic ecosystems, agricultural lands, human-inhabited urban and rural areas, and the atmosphere. Common anthropogenic sources contributing to heavy metal contamination include automobile exhaust, smelting, insecticides, and burning fossil fuels. Soil contamination can negatively impact terrestrial plants and animals' health and behavior, causing habitat destruction and environmental imbalances. Heavy metal contamination can lead to fatal illnesses in animals and humans, including anemia, emaciation, anorexia, depression, and weakness in livestock. Efforts are being made to eliminate the use of heavy metals and other hazardous raw materials in industrial production (Masindi & Muedi, 2018; Shen *et al.*, 2019).

Soil is a mixture of organic and inorganic materials, including disintegrated rocks and humus, which provide a medium for plant growth. It undergoes diverse environmental pressures and varies in texture, proportions, and organic and mineral compositions. Soil type, temperature, moisture, pH, texture, electrical conductivity, organic matter content, and salinity are factors that affect soil quality and its ability to support habitats, agricultural and industrial developments, and the ecosystem (Byju's The Learning App, 2020). Different soil types favor plant growth, with sandy soils being the poorest due to low nutrients and poor water holding. It is good for drainage systems and is formed by the breakdown or fragmentation of rocks like granite and limestone. Silt, a smaller type, is smooth and fine and is fertile, making it useful to improve soil fertility in agricultural lands. Clay, the smallest particle type, is dense and heaviest, but it does not drain well and does not provide space for plant roots to flourish. Loam, a combination of sand, silt, and clay, retains moisture and nutrients, making it suitable for agricultural use. It also contains hummus and has higher calcium and pH levels due to its inorganic origins (Stivers, 2017).

Many small and large manufacturing and mining companies are subjected to environmental regulations for environmentally favorable modifications in their procedures and clearing their perimeters. Research and development programs of non-government and government agencies emphasize remediation and removal of heavy metal contaminants. Preliminary actions, such as tracing and establishing data on the presence and contamination of heavy metals in different habitats, are popular actions worldwide, particularly in areas of human habitation (World Health Organization, 2011; Yhols, A., Richard, 2012; United Nations Industrial Development Organization, 2018).

The province of Agusan del Sur is known to have had several mining companies operating for many years. Some of which are big exporters of gold, minerals, and ores. Small-scale mining is also evident in some municipalities and barangays. Agricultural industries such as farming, small-scale poultry, and livestock farming are also popular throughout the province

(Egirani, 2014). Human activities, aquatic effluents from industrial, agricultural, and household run-offs, transported animal and human excretions, and domestic waste are known to be major contributors to heavy metal and synthetic compound wastes in the neighboring provinces of Agusan del Sur and Agusan del Norte (Velasco *et al.*, 2016). The Gibong River, a tributary of the Agusan River that passes through the provinces of Agusan del Sur and Agusan del Norte, was previously noted to have been contaminated with some heavy metals. Traces of heavy metals such as mercury, lead, and cadmium were detected upstream of the Gibong River (Roa *et al.*, 2011). There is also a high level of mercury contamination in tilapia fish from the Gibong River (Cui, 2016).

The available data to establish the severity and extent of heavy metal contamination along the Gibong River and Gibong Riverbanks is quite limited, especially since previous research only analyzed water contamination with selected heavy metals and contamination in tilapia species found in the river. Heavy metal contamination in the Gibong River could originate from big and small mining operations, poultry and livestock industries, agricultural farms, and other anthropological sources in the areas where the river runs through and eventually becomes a catchment. The river, as the main basin of streams and rainwater flowing from the nearby upper lands, can substantially catch any possible contamination nearby. The accumulation of heavy metals in riverbank soils imposes a great threat, not only to the aquatic and terrestrial plants and animals in the area but also to the human residents.

Heavy metals can accumulate in aquatic and terrestrial plants, including food crops that are consumed by humans and grass that is consumed by land animals daily. The metals can also accumulate in many food sources, such as aquatic and terrestrial animals, including fish, poultry, livestock, etc., through direct exposure or through consumption of contaminated vegetation. There have been no studies conducted yet to ascertain heavy metal contamination and pollution along the Gibong Riverbank soils.

Thus, this study aims to establish preliminary data on the presence and contamination of heavy metals in the soils along the riverbank of the Gibong River, one of the longest tributaries of the Agusan River in Agusan del Sur, Philippines. This study is undertaken to: (a) How do the soil qualities from the three riverbank locations along Gibong River compare in terms of the value of selected physicochemical parameters? (b) How do the soil qualities from the three riverbank locations along Gibong River compare in terms of the concentrations of the selected heavy metals? and, (c) How well do the soil qualities comply with the concerned set values of permissible limits of the Philippine and other countries' agricultural soil standards for selected heavy metal concentration?

Materials and methods

This study uses a descriptive research design to determine contamination and pollution levels in Gibong riverbanks by analyzing soil samples, physicochemical characteristics, and heavy metal concentrations from three sampling stations.

Research Locale

The study examined the soil profile, physicochemical characteristics, and heavy metal concentration in soil samples from three sampling stations on the Gibong riverbanks. These areas are popular agricultural and farmland areas for crops like corn, cassava, coconut, and vegetables. The river is a source of irrigation for 6,000 hectares of rice fields in three municipalities in Agusan del Sur. The Gibong River, a tributary to the Agusan River, extends from the northern part of Prosperidad to San Francisco and drains into the Agusan River at Brgy. Novele in Rosario The river extends approximately 33 kilometers from the north to the south end of Prosperidad, a first-class municipality and capital of the province of Agusan del Sur, Philippines.

Sampling Scheme

Non-composite, grab soil sampling was used in this study. In the first station, three substations were established by drawing a triangular pattern with 100-meter distance from one another. The pattern was drawn from one side of the riverbank, crossing the river to the other side and back, forming a triangle. There were two substations on one side and one substation on the other side of the riverbanks. The identified soil sampling points were dug at about 20 centimeters before 1-kilogram soil samples were dug and taken from each substation. The soil samples were immediately placed in a zip-lock bag and assessed of its physicochemical characteristics and stored in an ice bucket.

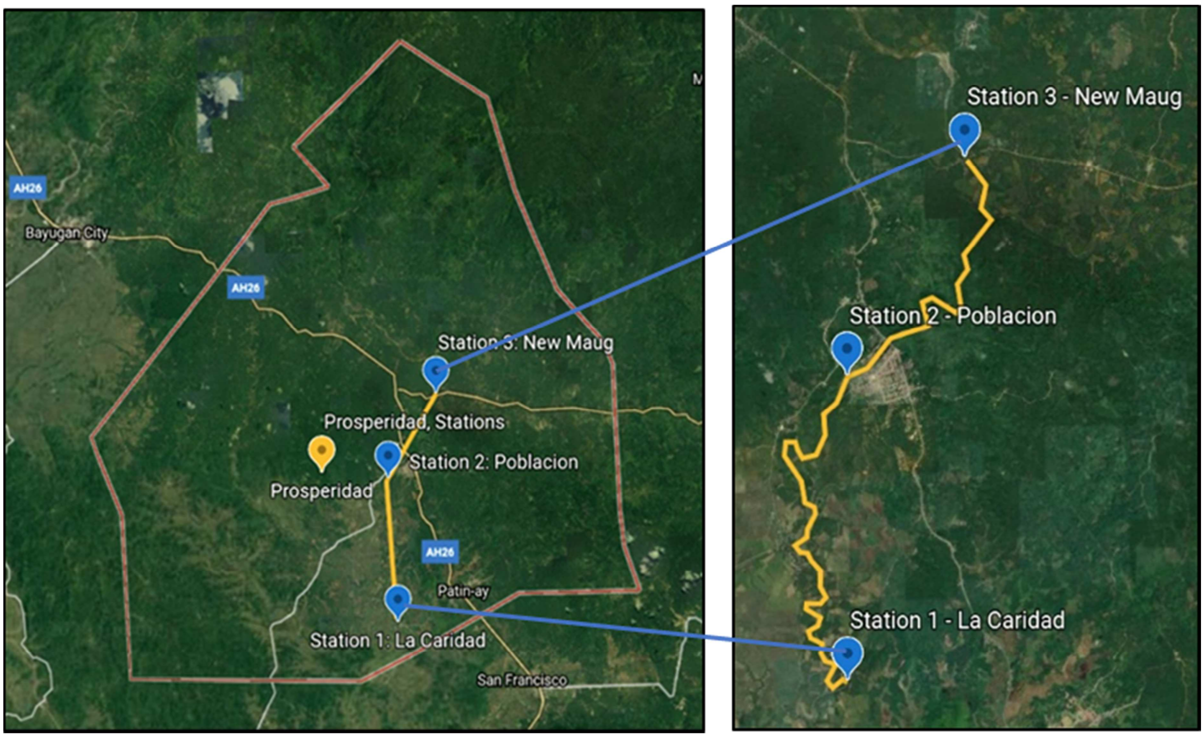

Fig. 1. Prosperidad Sites Map.

Station Profile

The location coordinates of the sites were taken using a mobile GPS tracker application, and light intensity was measured using a portable light (lux) meter from the University of Science and Technology of the Southern Philippines Chemistry Laboratory.

Physicochemical Parameters

The physicochemical parameters such as soil conductivity, salinity, pH, and temperature were tested onsite using the Soil Conductivity Meter HI 993310. The soil samples were prepared by removing foreign matter and slightly softening them with hands. 100g of soil was filled into a bottle with 1 L of distilled water, shaken, and settled before measuring. Soil moisture was measured using an XLUX soil moisture meter onsite. To further test for organic matter in the soil, soil samples stored in plastic containers were sent to the Instrumentation and Analysis Laboratory of the University of Science and Technology of the Southern Philippines in Cagayan de Oro City within 24 hours, following the university's protocols. The soil organic matter test was done by measuring the weight lost by an oven-dried (105 degrees Celsius) soil sample heated at 400 degrees centigrade, or the "loss on ignition" method.

Heavy Metal Concentrations

Within 24 hours of sampling, the samples were taken to the Instrumentation and Analysis Laboratory of the University of Science and Technology of the Southern Philippines in Cagayan de Oro City for analysis using the university's protocol. The soil samples were prepared for digestion and analysis. Soil samples were spread on trays and dried in an oven at 105 °C for six hours. A respirator was worn during weighing, digestion, and dilution. Laboratory gowns, latex gloves, and safety glasses were also used during digestion. 0.5000 grams of finely pulverized sample (90% passing through a 75-micron mesh) were weighed and poured into a 250-ml beaker. Moistened with a small amount of distilled water, 4 ml of concentrated nitric acid will be added, then heated on the hotplate until nitrous fumes (brown smoke) completely evolve. About 8 ml. Concentrated nitric acid was added, and the sample was heated. Next, 8 ml of concentrated hydrochloric acid was added and evaporated until incipient dryness (syrupy). The sample was secured so it would not dry out. Leaching of the digested sample was done by adding 25 ml of concentrated hydrochloric acid, then heating until the volume reduced to approximately 15 ml. The beaker's wall was rinsed with distilled water and heated to dissolve the salts. It was then removed from the hotplate and cooled. The digested solution was transferred to a 100-ml volumetric flask by using a filtering funnel and diluted to the mark with 10% hydrochloric acid. A stopper was used with the flask and shaken thoroughly. It was left to stand for an hour to settle the residue or filter the solution if necessary. Concentrations and identification of the heavy metals were determined using an atomic absorption spectrophotometer from the University of Science and Technology of the Southern Philippines Analytical Chemistry Laboratory.

Data Analysis

A one-way analysis of variance (one-way ANOVA) was used to determine the statistical significance of the differences in the mean of the physicochemical parameter values and heavy metal concentrations from the three sampling stations. The Kruskal-Wallis H Test was the nonparametric alternative to the one-way ANOVA after assumptions were not met. It was used to determine if there are statistically significant differences between the groups of physicochemical parameter values and the heavy metal concentrations among the three sampling stations.

Results and discussions

Profile of Sampling Site

The site location and light intensity of the three (3) stations in Gibong River is shown in Table 1. S1A (La Caridad) is located at N 8°32'01.786" E 125°54'31.134" with an LI of 430 LUX or the sample taken with moderate light lighting. Samples from S1B (La Caridad) and S1C (La Caridad) located at N 8°31'59.00" E 125°54'31.134" and N 8°32'0.979" E 125°54'28.751" respectively were taken with an LI of 809 LUX (moderate to adequate light equivalent to overcast daylight) and 1555 LUX (adequate light equivalent to full daylight). Samples from S2A (Poblacion) and S2B (Poblacion) located at N 8°36'20.899" E 125°54'28.310" and N 8°36'20.899" E 125°54'28.310" were carried with an LI that is moderate to adequate light, equivalent to overcast daylight (S2A LI=675 LUX; S2B LI=682 LUX). Meanwhile, S2C (Poblacion) (Location: N 8°36'21.000" E 125°54'26") sample was taken with an LI of 1699 or adequate light equivalent to full daylight. S3C (New Maug) (LA: N 8°36'21.000" E 125°54'26") was also carried out during full daylight LI (LI= 1080 LUX) while S3A and S3B (New Maug) located at an LE of N 8°36'20.899" E 125°54'28.310" and N 8°31'18.000" E 125°54'27.000" were taken with LI that is moderate light, equivalent to traditional office light (LI= 410 LUX) and overcast daylight (LI= 643 LUX).

Table 1. Location and Light Intensity.

Station	Substation	Location	Light Intensity (LI)
S1 (La Caridad)	S1A	N 8°32'01.786" E 125°54'31.134"	430 LUX
	S1B	N 8°31'59.00" E 125°54'31.134"	809 LUX
	S1C	N 8°32'0.979" E 125°54'28.751"	1555 LUX
S2 (Poblacion)	S2A	N 8°36'20.899" E 125°54'28.310"	675 LUX
	S2B	N 8°36'20.899" E 125°54'28.310"	682 LUX
	S2C	N 8°36'21.000" E 125°54'26"	1699 LUX
S3 (New Maug)	S3A	N 8°36'20.899" E 125°54'28.310"	410 LUX
	S3B	N 8°31'18.000" E 125°54'27.000"	643 LUX
	S3C	N 8°36'21.000" E 125°54'26"	1080 LUX

Light intensities ranging from 180 to 900 LUX are essential for photosynthesis, plant growth, and development in various vegetation types.

These intensities affect the interaction between photosynthetic microorganisms and trace or heavy metals, directly affecting vital cellular functions and metal toxicokinetics. Alternatively, they change the soil medium's characteristics, such as UV radiation altering the structure and reactivity of dissolved organic matter in natural water. As light intensity increases, cellular metal concentrations may rise among plants and animals (Bareja, 2022; Cheloni & Slaveykova, 2018).

Soil Quality of Gibong Riverbanks in Terms of Physicochemical Parameters

The soil is a mixture of organic and inorganic materials including disintegrated rocks and humus. Soil undergoes diverse environmental pressures and may vary extensively in terms of texture, proportions, and contents of different forms of organic and mineral compositions (Byju's The Learning App, 2020). Table 2 shows soil physicochemical characteristics of Gibong River in three (3) stations.

pH

The soil pH level among the three sampling sites implies that the riverbank soils are still at their optimum pH level based on the agricultural soil standards from the Department of Environment and Natural Resources.

Table 2. Soil Physicochemical Parameter Values from La Caridad, Poblacion and New Maug.

Physicochemical Parameters	La Caridad Mean (SD)	Poblacion Mean (SD)	New Maug Mean (SD)
pH	8.75 (2.52)	10.41 (0.11)	7.63 (0.91)
Conductivity (µS/cm)	634.67 (330.48)	437.67 (176.00)	277.50 (214.06)
salinity (ppt)	0.33 (0.19)	0.23 (0.10)	0.16 (0.09)
TDS (mg/L)	443.67 (240.86)	242.00 (137.88)	221.83 (152.62)
Temperature (˚C)	27.90 (4.78)	28.17 (0.64)	29.60 (3.94)
Moisture (%)	30.60 (4.45)	22.09 (14.96)	36.37 (1.25)
Organic matter (%)	9.75 (1.18)	8.37 (0.67)	8.16 (1.10)
Texture	Grainy Clay Loam	Grainy Clay Loam	Grainy Clay Loam
Soil Type	Clay Loam	Clay Loam	Clay Loam

In general, agricultural soil must reach the correct balance of pH between 5.5 and 7.5, depending on the types of crops or vegetables grown. On the other hand, a high (alkaline) soil pH usually decreases the concentrations of heavy metals. The solubility of heavy metal compounds, especially in the form of oxides, hydroxides, carbonates, or mineral forms, depends on the pH value (Krol, Mizerna, & Bozym 2020).

Table 3 shows the results of the statistical analysis in determining the significant difference among the pH levels of soil samples taken from the three locations in Gibong Riverbanks.

Table 3. Kruskal Wallis Test for Soil pH Values.

Sampling Sites	N	Mean Rank	Chi-Square	df	Asymp. Sig.
La Caridad	3	4.67	3.85	2	.15
Poblacion	3	7.33			
New Maug	3	3.00			

With a P-value of 0.15 which is lower than α=0.05, the soil pH median values of samples from La Caridad, Poblacion and New Maug have no significant differences. In effect, this means that the soil samples from the three different sources have equivalent pH level.

Soil Electrical Conductivity

Electrical conductivity is also a known important factor that can affect electrical fields, enhancing plant growth (if within a desirable range) as well as increasing the bioaccumulation of heavy metals in plants (within normal to higher ranges) that varies across plant species (Yuan, L., Guo, P., Guo, S., *et al.*, 2020). The optimal electrical conductivity value for plant growth is usually between 0.8 and 1.8 dS/m and should not exceed 2.5 dS/m. Table 4 shows the statistical analysis data used to determine the significant differences among the soil electrical conductivity levels of samples taken from the three locations of the Gibong Riverbank.

Table 4. One-way Analysis of Variance for Soil Electrical Conductivity Values.

Sampling Sites	N	Mean	StDev	95% CI	F-Value	P-Value
La Caridad	3	634.67	330.48	(-186.29, 1455.62)	1.55	0.29
Poblacion	3	437.67	176.00	(0.46, 874.88)		
New Maug	3	277.50	214.06	(-254.24, 809.24)		

Legend: Pooled StDev= 265.53

With a P-value of 0.29 which is higher than α=0.05, the soil electrical conductivity level of samples from La Caridad, Poblacion and New Maug have no significant differences. In effect, this means that the soil samples from the three different sources have equivalent soil electrical conductivity level.

Soil Salinity

Soil salinity is the concentration of dissolved ions in soil pore water. As soil salinity increases, the potential of the soil pore water decreases, thus obliging plants to overcome an increasingly high energy gap for soil water uptake (Visconti & Paz, 2016). The study result suggests that the soil samples were of good level of salinity and may support optimum crop production. A high concentration of solute salts in soil causes more than 4 dS/m electrical conductivity. The soil samples from the three locations were determined to be non-saline (0-2 dS/m). Non-saline soil is desirable for normal crop growth, while salinity in soil increases mobility of heavy metals (Acosta *et al.*, 2011). Table 5 shows the non-parametric analysis data to determine the significant differences in the medians of soil salinity levels from the three locations of Gibong Riverbank.

Table 5. Kruskal Wallis Test for Soil Salinity Values.

Sampling Sites	N	Mean Rank	Chi-Square	df	Asymp. Sig.
La Caridad	3	6.67	2.78	2	.25
Poblacion	3	5.33			
New Maug	3	3.00			

With a p-value of 0.25, which is higher than α=0.05, the soil salinity median values of samples from La Caridad, Poblacion, and New Maug have no significant differences. In effect, this means that the soil samples from the three sources have equivalent salinity level.

Total Dissolved Solids

While the results are relatively low for further heavy metal investigation, soil TDS may still indirectly affect heavy metal activities in the soil. The total dissolved solids reflect the sum of particulate materials dissolved in soil and measure salinity. The effect of high or low TDS can be similar to that of the electric conductivity and salinity parameters. Table 6 shows the statistical analysis data used to determine the significant differences among the total dissolved solids values of samples taken from three locations along the Gibong River.

Table 6. One-way Analysis of Variance for Total Dissolved Solids Values.

Sampling Sites	N	Mean	StDev	95% CI	F-Value	P-Value
La Caridad	3	443.67	240.86	(-154.66, 1041.99)	1.35	0.33
Poblacion	3	242.00	137.88	(-100.52, 584.52)		
New Maug	3	221.83	152.62	(-157.30, 600.96)		

Legend: Pooled StDev= 190.70

With a P-value of 0.33 which is higher than α=0.05, the total dissolved oxygen levels of the soil samples from La Caridad, Poblacion, and New Maug have no significant differences. In effect, this means that the soil samples from the three different sources have equivalent or the same total dissolved solids values.

Temperature

The temperature range detected in the sites are within desirable values for agricultural lands. High temperature ranges (>30 °C) would already affect soil-to-plant transfer of heavy metals such as Cd and Zn, although it also decreases their bioavailability at the same time (Cornu *et al.*, 2015). Table 7 shows the statistical analysis to determine the significant differences in the temperature levels of soils taken from the three locations of Gibong Riverbank.

Table 7. One-way Analysis of Variance for Soil Temperature Values.

Sampling Sites	N	Mean	StDev	95% CI	F-Value	P-Value
La Caridad	3	27.90	4.78	16.04, 39.76)	0.19	0.83
Poblacion	3	28.17	0.64	(26.57, 29.76)		
New Maug	3	29.60	3.94	(19.81, 39.39)		

Legend: Pooled StDev= 3.21

With a P-value of 0.83 which is higher than α=0.05, the soil temperature of samples from La Caridad, Poblacion and New Maug have no significant differences. In effect, this means that the soil samples from the three different sources have equivalent temperature level.

Soil Moisture

Aside from the fact that the sampling site is a riverbank, it is also observed to be submerged in water during rainy days – the reason for its high moisture content. While majority of plants such as trees, shrubs and flowers require moisture levels between 21% - 40% and vegetables between 41% to 80%, heavy metals' lability are also reduced with higher soil moisture, which could be due to increased pH, precipitation of the metals with sulfides, and higher concentration of amorphous Fe oxides, especially under submerged condition (Zheng & Zhang, 2011). Table 8 shows the statistical analysis data to determine the significant differences among the soil moisture values of samples taken from the three locations of Gibong River.

Table 8. One-way Analysis of Variance for Soil Moisture Values.

Sampling Sites	N	Mean	StDev	95% CI	F-Value	P-Value
La Caridad	3	30.60	4.45	(19.54, 41.66)	1.89	0.23
Poblacion	3	22.09	14.96	(-15.07, 59.26)		
New Maug	3	36.37	1.25	(33.26, 39.47)		

Legend: Pooled StDev= 10.00

With a P-value of 0.23 which is higher than α=0.05, the soil moisture values of samples from La Caridad, Poblacion, and New Maug have no significant differences. In effect, this means that the soil samples from the three different sources have equivalent soil moisture values.

Organic Matter Content

Soil organic matter content has a variety of components. Organic matter could include heavy metals which could impact not only the mineralization of the soil organic matter, but also the fact that it may contribute to the accumulation and distribution of the trace metals. On the other note, the 3 sampling sites possessed the same soil texture which is grainy clay.

Although the molecular mechanism is still unclear, clay minerals in soil was observed to improve environmental quality of soil and alleviate the hazards to heavy metals to plants because of its immobilization effect, the pH and water conditions in the soil (Xu *et al.*, 2017). Table 9 shows the statistical analysis data to determine the significant differences among the organic matter values of samples taken from the three locations of Gibong Riverbank.

Table 9. One-way Analysis of Variance for Organic Matter Values.

Sampling Sites	N	Mean	StDev	95% CI	F-Value	P-Value
La Caridad	3	9.75	1.18	(6.81, 12.68)	2.18	0.19
Poblacion	3	8.37	0.67	(6.71, 10.03)		
New Maug	3	8.16	1.10	(5.43, 10.90)		

Legend: Pooled StDev= 1.15

With a p-value of 0.19 which is higher than α=0.05, the soil organic matter vaues of samples from La Caridad, Poblacion and New Maug have no significant differences. In effect, this means that the soil samples from the three different sources have equivalent values.

Soil Quality of Gibong Riverbank in terms of Heavy Metal Concentrations

Table 10. Average Heavy Metal Concentration in Riverbank Soil Samples from La Caridad, Poblacion and New Maug.

Heavy Metal	Standard Value (ppm)	La Caridad (ppm) Mean (SD)	Poblacion (ppm) Mean (SD)	New Maug (ppm) Mean (SD)
copper, ppm	3100	99.70 (2.67)	125.77 (6.24)	127.44 (22.82)
chromium, ppm	380	1769.22 (277.29)	2172.56 (128.26)	1824.22 (344.96)
lead, ppm	400	34.94 (7.56)	56.03 (4.31)	57.07 (14.07)
cobalt, ppm	50	47.22 (3.05)	57.14 (3.24)	48.43 (6.93)
manganese, ppm	2000	1182.89 (128.55)	1243.56 (53.88)	1128.63 (160.99)
nickel, ppm	1000	95.24 (7.23)	96.85 (11.39)	73.43 (22.27)
cadmium, ppm	17	3.97 (0.75)	5.88 (0.64)	4.42 (0.59)

Copper

Copper, in animal bodies at lower concentrations, acts as a co-factor for various enzymes of redox cycling; however, at higher concentration disrupts the human metabolism leading to anemia, liver and kidney damage, stomach and intestinal irritation. Table 11 shows the statistical analysis data to determine any significant differences among the copper concentrations of the soil samples taken from the three locations of Gibong Riverbanks.

Table 11. Kruskal Wallis Test for copper Concentrations.

Sampling Sites	N	Mean Rank	Chi-Square	df	Asymp. Sig.
La Caridad	9	6.22	13.19	2	0.001
Poblacion	9	18.78			
New Maug	9	17.00			

With a P-value of 0.001 which is lower than α=0.05, the copper median concentration values of samples from La Caridad, Poblacion and New Maug have significant differences. In effect, this means that the concentration values of heavy metal from the three stations have different medians or are coming from different distributions. All the copper concentration values from the three locations, however, are noted to be lower than the standard/permissible value (3100ppm) for agricultural soil among the three locations.

Chromium

Chromium is a hard, silvery metal with a blue tinge which has a lot of industrial uses such as production of stainless steel to beauty products; however, the World Health Orgnization recognize Cr (VI) as a human carcinogen, particularly when taken into the body of humans through food and water sources. Table 12 shows the non-parametric statistical analysis data to determine any significant differences among the chromium concentrations in soil samples taken from the three locations of Gibong Riverbank.

Table 12. Kruskal Wallis Test for chromium Concentrations.

Sampling Sites	N	Mean Rank	Chi-Square	df	Asymp. Sig.
La Caridad	9	10.00	10.26	2	0.006
Poblacion	9	20.89			
New Maug	9	11.11			

With a P-value of 0.01 which is lower than α=0.05, the chromium median concentration values of samples from La Caridad, Poblacion and New Maug have significant differences. In effect, this means that the concentration values of heavy metal from the three stations have different medians or are coming from different distributions. All the chromium concentration values from the three locations and are noted to be higher than the standard/permissible value (380ppm) for agricultural soil among the three locations namely La Caridad (1769.22ppm), Poblacion (2172.56ppm), and New Maug (1824.22ppm). This result indicates alarming contamination of chromium in the riverbank soils.

Lead

Lead is widely used for car batteries, cable sheathing, pipes, and many other industrial products. While it has no known biological role, its accumulation in the body is known to cause serious health problems with its toxic and carcinogenic effects. Table 13 shows the statistical analysis data to determine any significant differences among the lead concentrations in soil samples taken from the three locations of Gibong Riverbank.

Table 13. One-way Analysis of Variance for lead Concentrations.

Sampling Sites	N	Mean	StDev	95% CI	F-Value	P-Value
La Caridad	9	34.94	7.56	(29.13, 40.75)	15.38	0.00
Poblacion	9	56.03	4.31	(52.72, 59.34)		
New Maug	9	57.07	14.07	(46.25, 67.88)		

Legend: Pooled StDev= 13.86

With a p-value of 0.00 which is lower than α=0.05, there is a significant difference in the lead concentrations in the soil samples from La Caridad, Poblacion, and New Maug. Furthermore, all the lead concentration values from the three locations are noted to be lower than the heavy metal standard/permissible value (400ppm) for agricultural soil among the three locations.

Cobalt

Cobalt, a magnetic, lustrous, silvery-blue metal is a technologically important metal used in batteries, electric and hybrid-electric vehicles, energy storage units, metalworking, mining, and construction industries. Just like many other heavy metals, it is essential for survival and growth of microbes, as well as nutritional needs of plants, animals, and human beings. On the other hand, toxicity of cobalt has been linked to serious ailments in human beings which include hematological, immunological, cardiovascular, gastrointestinal, and even psychiatric signs and symptoms. Table 14 shows the non-parametric statistical analysis data to determine any significant differences among the cobalt concentrations in soil samples taken from the three locations of Gibong Riverbank.

Table 14. Kruskal Wallis Test for cobalt Concentrations.

Sampling Sites	N	Mean Rank	Chi-Square	df	Asymp. Sig.
La Caridad	9	8.11	16.43	2	0.00
Poblacion	9	22.56			
New Maug	9	11.33			

With a P-value of 0.00 which is lower than α=0.05, the cobalt median concentration values of samples from La Caridad, Poblacion and New Maug have significant differences. In effect, this means that the concentration values of heavy metal from the three stations have different medians or are coming from different distributions. All the cobalt concentration values from the three locations, however, are noted to be at a borderline of the standard/permissible value (50ppm) for agricultural soil among the three locations namely La Caridad (47.22ppm), Poblacion (57.14ppm), and New Maug (48.43ppm). Furthermore, this result importantly indicates significantly notable contamination of cobalt in the riverbank soils of Poblacion.

Manganese

Manganese is commonly used in welding, battery cathodes, electronics to micronutrient components in fertilizers and animal feed. Adequate amount of manganese intake is recommended to humans but exposures to high levels is toxic and dangerous. Table 15 shows the non-parametric analysis data to determine the significant differences in the medians of manganese concentrations in water taken from the three locations of Gibong Riverbanks.

Table 15. Kruskal Wallis Test for manganese Concentrations.

Sampling Sites	N	Mean Rank	Chi-Square	df	Asymp. Sig.
La Caridad	9	14.00	1.87	2	0.39
Poblacion	9	16.56			
New Maug	9	11.44			

With a P-value of 0.39 which is higher than α=0.05, the manganese concentration median values of soil samples from La Caridad, Poblacion and New Maug have no significant differences. In effect, this means that the soil samples from the three different sources have equivalent or the same median for manganese concentration values. It is also notable that all the resulting concentration values are below the standard/permissible value of manganese (2000ppm) for agricultural soil among the three locations namely La Caridad (1182.89ppm), Poblacion (1243.56ppm) and New Maug (1128.63ppm).

Nickel

Nickel is a silvery metal and is a common material for rechargeable batteries, portable computers, power tools, electric vehicles and many more. On the other hand, studies reported that exposure to nickel dust or ingestion in high amount leads to increased pulmonary and nasal cancer. Table 16 shows the non-parametric analysis data to determine the significant differences in the medians of nickel concentrations in soil taken from the three locations of Gibong Riverbanks.

Table 16. Kruskal Wallis Test for nickel Concentrations.

Sampling Sites	N	Mean Rank	Chi-Square	df	Asymp. Sig.
La Caridad	9	16.78	10.65	2	0.01
Poblacion	9	18.22			
New Maug	9	7.00			

With a P-value of 0.01 which is lower than α=0.05, the nickel concentration median values of soil samples from La Caridad, Poblacion and New Maug have significant differences. In effect, this means that the soil samples from the three different sources have different nickel concentration value medians or are coming from different distributions. It is also notable that all the resulting concentration values are below the standard/permissible value of nickel (1000ppm) for agricultural soil among the three locations namely La Caridad (95.24ppm), Poblacion (96.85ppm) and New Maug (73.43ppm).

Cadmium

Cadmium, a silvery metal with a bluish tinge to its surface is widely used in manufacturing batteries, welding works, inorganic pesticides, and fertilizers. It has no known beneficial function in the human body but great concentration is usually in the kidneys and the liver of human beings. Furthermore, cadmium is a cumulative toxin. Long-term exposure to cadmium may lead to renal tubular dysfunction in humans, and there is sufficient evidence that exposure causes lung cancer. Table 17 shows the statistical analysis data to determine any significant differences among the cadmium concentrations of soil samples taken from the three locations of Gibong riverbanks.

Table 17. One-way Analysis of Variance for cadmium Concentrations.

Sampling Sites	N	Mean	StDev	95% CI	F-Value	P-Value
La Caridad	9	3.97	0.75	(3.39, 4.54)	20.41	0.00
Poblacion	9	5.88	0.64	(5.39, 6.38)		
New Maug	9	4.42	0.59	(3.96, 4.87)		

Legend: Pooled StDev= 1.05

With a p-value of 0.00 which is lower than α=0.05, there is a significant difference in the cadmium concentrations in the soil samples from La Caridad, Poblacion, and New Maug. Furthermore, all the cadmium concentration values from the three locations are noted to be lower than the heavy metal standard/permissible value (17ppm) for agricultural soil among the three locations namely La Caridad (3.97ppm), Poblacion (5.88ppm), and New Maug (4.42ppm).

Conclusion and recommendations

The riverbank soils in the Gibong riverbank are generally suitable for agricultural lands due to their location, light intensity, and physicochemical characteristics. However, certain parameters, such as electrical conductivity, pH, and salinity, may contribute to heavy metal accumulation and distribution. The study found alarming concentration levels of chromium and cobalt in all three locations, with cobalt concentrations on the borderline of reaching the standard or permissible value. The rest of the heavy metals studied did not present alarming values.

A more dangerous form of chromium is chromium (VI), recognized as a human carcinogen by the US-EPA and WHO. Its toxicity includes respiratory, skin, cardiovascular, and genetic aberrations. Natural and anthropogenic activities, such as mining, metalworking, and second-generation fertilizers, could have contributed to the elevated Cr content in the riverbank soils. Cobalt toxicity can cause hematological, immunological, cardiovascular, endocrinological, gastrointestinal, dermatological, ophthalmological, and neurological problems. Possible sources of cobalt include animal feed supplements from nearby poultry and livestock farms and fertilizers. Cobalt enters and accumulates in ecosystems through wind-blown dust and rainwater run-off.

The research findings have led to recommendations for various stakeholders, including townspeople, consumers, farmers, and fishermen, the Department of Health, the Department of Environment and Natural Resources, local government units, and future researchers. The study aims to protect the Gibong River by minimizing heavy metal contamination and ensuring the safety of plant and animal food. It also aims to inform local consumers about the quality of riverbank soil and the safety of goods consumed, raised, and grown in the identified areas. The Department of Health should use the results to develop health protection programs for people and local consumers of food harvested from the river and riverbank. The Department of Environment and Natural Resources should implement policies and programs for the preservation, protection, assessment, and rehabilitation of the Gibong Riverbank.

The Local Government Unit should use the results to inform affected entities and implement protection programs to prevent pollution or contamination of the River.

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