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RESEARCH PAPER

Heavy metal concentration and contamination assessment in the water of Gibong River in Prosperidad, Agusan Del Sur, Philippines

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Abstract

The study investigated the physicochemical characteristics, temperature, electrical conductivity, turbidity, salinity, dissolved oxygen, and heavy metal concentrations in Gibong River waters in Prosperidad, Agusan del Sur. While pH levels were optimal for agriculture and fishing across all locations, temperature and electrical conductivity showed significant differences. Poblacion had the highest temperature, and La Caridad had the highest electrical conductivity. Turbidity, salinity, dissolved oxygen, and dissolved solids showed no significant differences among locations. Heavy metal concentrations, including cadmium and cobalt, were generally low. Copper and chromium concentrations were equivalent among stations, with chromium levels approaching or slightly exceeding permissible values. Lead concentrations were significantly higher in New Maug but below the permissible limit. Manganese concentrations were highest in La Caridad but below the permissible limit, while nickel concentrations showed no significant differences. The study's findings contribute valuable data on physicochemical parameters and heavy metal contamination in Gibong River, informing environmental protection initiatives and policies in Agusan del Sur, Philippines. The results serve as a baseline for ongoing monitoring and management strategies to safeguard water quality in this important tributary of the Agusan River.

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Introduction

There are numerous downsides of industrial and technology revolution in the 21st century. Entailing the said revolutions is the utilization of various organic and inorganic resources in massive amounts and in processes that end up with harmful materials as waste or by-products (Road National Research Council, 2012). In modern manufacturing, industrial and even agricultural industries, the utilization of organic and inorganic chemicals are very popular. Proven to make processes and products efficient and effective, heavy metals are widely used nowadays. An in-demand heavy metal, cadmium, for instance is processed all over the world and utilized in manufacturing of semiconductors and electronics (Persistence Market Research, 2020). Other heavy metals such as cobalt, chromium, copper, magnesium, iron, manganese, nickel and zinc are widely used for many different purposes (Chemicool, 2020). Many heavy metals are also noted to be essential requirements for physiological and biochemical functions in organisms; and their absence could result to deficiency diseases or syndromes (Engwa *et al.*, 2019).

Heavy metal elements and compounds in materials are emitted or released back to the environment as it is or sometimes in its simplest elemental form. The more of these elements are used in manufacturing materials, the more are also released back to the environment. The return of the elements to the environment poses a problem when they accumulate in an undesirable amount and in unintended places. Contributing to the release of harmful and toxic heavy metals includes factories, mining companies, and industrial facilities. People significantly contribute to heavy metal contamination in the environment through automobile emissions, use of insecticides, utilization and disposal of heavy metal-based materials for everyday activities.

Accumulation of heavy metals in terrestrial and aquatic ecosystems and habitats is a threat not only to economic activities and health of humans, but also to the lives of many organisms in the ecosystem (Masindi & Muedi, 2018). Aquatic and terrestrial organisms can seriously be endangered by heavy metal pollution. In humans, exposure to heavy metals may lead to toxicity causing various systemic disorders and even cancer and death (World Health Organization, 2011). Animals have been reported to have suffered from fatal illnesses such as anemia and other circulatory illnesses, respiratory and nervous system diseases after being exposed to large amount of heavy metals (Shen *et al.*, 2019).

To minimize, if not eliminate the disastrous effects of heavy metal pollution; mitigating and preventive measures are being done worldwide. Many programs and research developments by government and non-government agencies have been noted to have contributed significantly to solve this global concern (United Nations Industrial Development Organization, 2018).

The province of Agusan del Sur is known to have 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 many 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, household run-offs, transported animal and human excretions and domestic waste are known to be major contributory of heavy metal and synthetic compound wastes in the neighboring provinces of Agusan del Sur and Agusan del Norte (Velasco *et al.*, 2016). Gibong River, a tributary of the Agusan River that passes through the provinces of Agusan Del Sur and Agusan del Norte is previously noted to have been contaminated with some heavy metals. Traces of heavy metals such as mercury, lead and cadmium were detected in upstream of 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 Gibong river is quite limited, especially that previous researches only analyzed water contamination of selected heavy metals and contamination in tilapia species found in the river. Heavy metal contamination in Gibong River could originate in big and small mining, 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 the river imposes a great threat, not only to the aquatic and terrestrial plants and animals in the area, but to the human residents. Heavy metals can accumulate in aquatic and terrestrial plants, including food crops that are consumed by humans and grass that are consumed by land animals daily. The metals can also accumulate in many food sources such as aquatic and terrestrial animals, including fish, poultry and livestock etc. through direct exposure or through consumption of contaminated vegetations. There are no studies conducted yet to ascertain the level of heavy metal contamination in Gibong River. Thus, this study aimed to establish preliminary data on the presence and contamination of heavy metals in Gibong River-one of the longest tributaries of Agusan River in Agusan del Sur, Philippines extending within the municipality of Prosperidad.

Materials and methods

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

Research locale

The study assessed the water physicochemical characteristics, and heavy metal concentration in the water samples extracted from the three sampling stations in the Gibong River (Fig. 1). Gibong River is a source of irrigation for some 6,000 hectares of rice fields in three municipalities in Agusan Del Sur. Within the sampling municipality site, the river extends approximately 33 kilometers from the north to the south end of the municipality of Prosperidad. Prosperidad is a first-class municipality and capital of the province of Agusan del Sur, Philippines. It is politically subdivided into 32 barangays. According to the 2015 census, it has a population of 82,631 people and according to the Philippine Statistics Authority, the municipality has a land area of 505.15 square kilometers (195.04 sq mi), constituting 5.06% of the 9,989.52 Km² (3,856.98 sq mi) total area of Agusan del Sur. It has a tropical rainforest climate

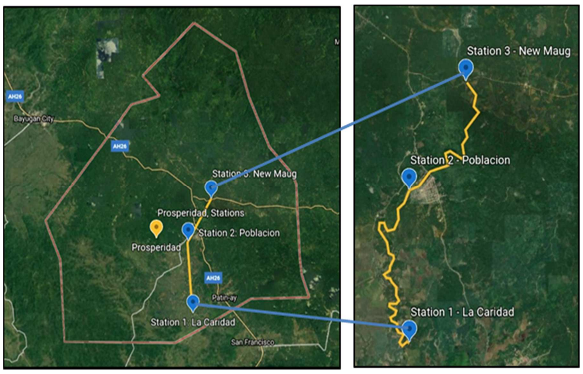

Fig. 1. Prosperidad sites map

Sampling scheme

Water sampling was done three consecutive times with two-week interval. All three sampling stations were Barangays of the Municipality of Prosperidad where Gibong River passes through. A permit and authorization from the Municipal Environment and Natural Resources Office (MENRO) was secured before the sampling procedure.

Single grab samples of water per station were quickly taken using dippers at the middle spot of the river within a 6-hour timeframe. The dipper was attached to a rope to reach the middle part of the river and collect surface water samples at the depth of 20 cm from the surface of the water. The water samples were assessed immediately for physicochemical characteristics and stored in plastic containers. It was then stored in an ice bucket ready for transport.

Station profile

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

Physicochemical parameters

The physicochemical parameters such as dissolved oxygen, water temperature and water salinity were tested onsite using a ‘Professional Digital DO Meter with handheld water quality tester and temperature measurement’ from the University of Science and Technology of Southern Philippines Chemistry Laboratory. Sample plastic containers were washed with distilled water prior to sampling and the Pro DO sensor was calibrated prior to usage using the DO% in water saturated air 1-point calibration method.

The parameters were measured immediately after filling the plastic containers with the water samples by inserting the probe into the water sample container and moving the probe in the water to release any air bubbles and provide fresh sample to the sensor cap. Continuous stirring and allowing the temperature to stabilize, the reading in mg/L was recorded. Water pH, conductivity and total dissolved solids (TDS) were also tested onsite using Portable pH/EC/TDS/Temperature Meter in the same manner. Turbidity and chemical oxygen demand were measured at the Instrumentation and Analysis laboratory of the University of Science and Technology of Southern Philippines in Cagayan de Oro City within 24 hours following the university’s protocols.

Heavy metal concentrations

Within 24 hours from sampling, the samples were taken to the Instrumentation and Analysis laboratory of the University of Science and Technology of Southern Philippines in Cagayan de Oro City for analysis using the university’s protocols. To determine the concentrations of heavy metals in the collected samples, the water samples were prepared and weighed in Erlenmeyer flasks with three replicates for each. Under a fume hood, the samples were digested with aqua regia (HNO_3 67%: HCl 37% = 3:1). The standards were then prepared and the total metal content of the samples in replicates were determined by Flame Atomic Absorption Spectrometry (FAAS).

Data analysis

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, as well as the heavy metal concentrations among the three sampling stations.

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 discussion

Profile of sampling sites

The site location and light intensity of the three (3) stations in Gibong River is shown in Table 1 below. Station 1 (S1, La Caridad) located at N 8°31'59.00" E 125°54'31.134" was taken with a Light Intensity of 809 LUX (moderate to adequate light equivalent to overcast daylight). Station 2 (Poblacion) located at N 8°36'20.899" E 125°54'28.310" revealed an LI that is moderate to adequate light, equivalent to overcast daylight (LI=682 LUX). Station 3 (New Maug) (N 8°31'18.000" E 125°54'27.000" were taken with LI that is moderate light, equivalent to overcast daylight (LI= 643 LUX).

Table 1. Characteristics of research setting

Station	Location	Light Intensity (LI)
S1 (La Caridad)	N 8°31'59.00" E 125°54'31.134"	809 LUX
S2 (Poblacion)	N 8°36'20.899" E 125°54'28.310"	682 LUX
S3 (New Maug)	N 8°31'18.000" E 125°54'27.000"	643 LUX

Subject to varied physiological limits of plants in the area, the light intensities recorded (180 to 900 LUX) are desirable to meet most of vegetations’ optimum requirements for photosynthesis, plant growth and development (Bareja, 2022). Furthermore, different light intensities and spectral composition affects the interaction between photosynthetic microorganisms and trace or heavy metals directly by affecting vital cellular functions and metal toxicokinetics and toxicodynamics or indirectly, by changing the soil medium characteristics. UV radiation, for example, alters the structure and reactivity of dissolved organic matter in natural water, which in most cases, decreases the water's metal binding capacity and enhances metal bioavailability (Cheloni and Slaveykova, 2018). It can be expected that the increasing light intensity in the sites may cause an increase in the cellular metal concentrations among plants and animals.

Water quality of Gibong River in terms of physicochemical parameters

Results and analyses from the determination of the values of the water physicochemical parameters in the three sampling stations are tabulated and discussed below (Table 2).

Table 2. Water physicochemical parameter values from La Caridad, Poblacion and New Maug

Physicochemical Parameters	La Caridad Mean (SD)	Poblacion Mean (SD)	New Maug Mean (SD)
pH	8.01 (2.03)	7.08 (0.66)	7. 04 (0.47)
Temperature (°C)	27.67 (0.21)	28.45 (0.09)	27.13 (0.42)
Conductivity (µS/cm)	351.67 (23.18)	273.67 (15.14)	201.63 (1.58)
Turbidity (NTU)	5.85 (5.68)	3.14 (3.04)	2.09 (0.98)
Salinity (ppt)	0.30 (0.17)	0.18 (0.14)	*
DO (mg/L)	6.96 (2.59)	6.78 (3.09)	7.59 (1.87)
COD (mg/L)	22.45 (15.92)	17.03 (2.79)	48.81 (74.65)
TDS (mg/L)	338.33 (270.02)	227.60 (149.31)	116.40 (16.12)

Table 3. One-way analysis of variance for pH values

Sampling sites	N	Mean	StDev	95% CI	F-value	*p*-value
La Caridad	3	8.01	2.03	(2.96, 13.06)	.57	0.59
Poblacion	3	7.08	0.66	(5.44, 8.72)		
New Maug	3	7.03	0.47	(5.86, 8.22)		

Table 4. Kruskal Wallis test for temperature values

Sampling sites	N	Mean rank	Chi-Square	df	Asymp. Sig.
La Caridad	3	4.50	6.31	2	.04
Poblacion	3	8.00			
New Maug	3	2.50			

Table 5. One-way analysis of variance for electrical conductivity values

Sampling sites	N	Mean	StDev	95% CI	F-value	*p*-value
La Caridad	3	351.67	23.18	(294.08, 409.25)	65.88	.00
Poblacion	3	273.67	15.14	(236.05, 311.29)		
New Maug	3	201.63	1.58			

Pooled StDev= 66.45

pH

Table 3 shows the statistical analysis data to determine the significant differences among the pH levels of water taken from the three locations of Gibong River. With a P-value of 0.59 which is higher than α=0.05, the water pH of samples from La Caridad, Poblacion and New Maug have no significant differences. In effect, this means that the water samples from the three different sources have equivalent pH level.

Temperature

Table 4 shows the non-parametric analysis data to determine the significant differences in the medians of temperature levels of water taken from the three locations of Gibong River. With a P-value of 0.04 which is lower than α=0.05, the water temperature median values of samples from La Caridad, Poblacion and New Maug have significant differences. It further shows that the water samples from Poblacion (28.45°C) have the highest temperature, followed by the samples from La Caridad (27.67°C) and the samples from New Maug (27.13°C) with the lowest temperature.

Conductivity

Table 5 shows the statistical analysis data to determine the significant differences among the Water Electrical Conductivity levels of samples taken from the three locations of Gibong River. With a P-value of 0.00 which is lower than α=0.05, there is a significant difference in the water electrical conductivity level of the samples from La Caridad, Poblacion and New Maug.

Table 6. One-way analysis of variance for water turbidity values

Sampling sites	N	Mean	StDev	95% CI	F-value	*p*-value
La Caridad	3	5.85	5.68	(-8.26, 19.96)	.80	.49
Poblacion	3	3.14	3.04	(-4.40, 10.69)		
New Maug	3	2.09	.98	(-.35, 4.53)		

Pooled StDev= 3.67

Table 7. Kruskal Wallis test for water salinity values

Sampling sites	N	Mean rank	Chi-Square	df	Asymp. Sig.
La Caridad	3	7.33	4.633	2	.10
Poblacion	3	4.67			
New Maug	3	3.00			

Table 8. One-way Analysis of variance for dissolved oxygen values

Sampling sites	N	Mean	StDev	95% CI	F-value	*p*-value
La Caridad	3	6.96	2.59	(.54, 13.38)	. 08	.92
Poblacion	3	6.78	3.09	(-.89, 14.45)		
New Maug	3	7.59	1.87	(2.95, 12.23)		

Pooled StDev= 2.25

Table 9. Kruskal Wallis test for chemical oxygen demand values

Sampling sites	N	Mean rank	Chi-Square	df	Asymp. Sig.
La Caridad	3	5.33	. 09	2	.96
Poblacion	3	5.00			
New Maug	3	4.67			

Table 10. Kruskal Wallis test for total dissolved solids values

Sampling sites	N	Mean rank	Chi-Square	df	Asymp. Sig.
La Caridad	3	7.33	5.96	2	.051
Poblacion	3	5.67			
New Maug	3	2.00			

Turbidity

Table 6 shows the statistical analysis data to determine the significant differences among the Water Turbidity levels of samples taken from the three locations of Gibong River. With a P-value of 0.493 which is higher than α=0.05, the water turbidity levels of samples from La Caridad, Poblacion and New Maug have no significant differences. In effect, this means that the water samples from the three different sources have equivalent Turbidity level.

Water salinity

Table 7 shows the non-parametric analysis data to determine the significant differences in the medians of salinity levels of water taken from the three locations of Gibong River. With a P-value of 0.10 which is higher than α=0.05, the water Salinity median values of samples from La Caridad, Poblacion and New Maug have no significant differences. In effect, this means that the water samples from the three different sources have equivalent Salinity level.

Dissolved oxygen

Table 8 shows the statistical analysis data to determine the significant differences among the dissolved oxygen values of samples taken from the three locations of Gibong River. With a P-value of 0.92 which is higher than α=0.05, the dissolved oxygen levels of the water samples from La Caridad, Poblacion and New Maug have no significant differences. In effect, this means that the water samples from the three different sources have equivalent or the same dissolved oxygen levels.

Chemical oxygen demand

Table 9 shows the non-parametric analysis data to determine the significant differences in the medians of chemical oxygen demand levels of water taken from the three locations of Gibong River. With a P-value of 0.96 which is higher than α=0.05, the chemical oxygen demand median values of samples from La Caridad, Poblacion and New Maug have no significant differences. In effect, this means that the water samples from the three different sources have equivalent chemical oxygen demand levels.

Total dissolved solids

Table 10 shows the non-parametric analysis data to determine the significant differences in the medians of total dissolved oxygen levels of water taken from the three locations of Gibong River. With a P-value of 0.051 which is higher than α=0.05, the total dissolved solids median values of samples from La Caridad, Poblacion and New Maug have no significant differences. In effect, this means that the water samples from the three different sources have equivalent total dissolved solids levels.

Table 11. Heavy metal concentrations in Gibong River water 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)
Cadmium, ppm	0.01	*n.d.	*n.d.	*n.d.
Cobalt, ppm	0.05	*n.d.	*n.d.	*n.d.
Copper, ppm	0.05	0.02 (0.01)	0.01 (0.01)	0.02 (0.01)
Chromium, ppm	0.05	0.06 (0.02)	0.05 (0.01)	0.05 (0.01)
Lead, ppm	0.05	0.00 (0.00)	0.01 (0.01)	0.03 (0.02)
Manganese, ppm	0.20	0.05 (0.03)	0.05 (0.10)	0.01 (0.01)
Nickel, ppm	0.20	0.03 (0.03)	0.01 (0.01)	0.02 (0.01)

* not detected

Table 12. One-way analysis of variance for copper concentrations

Sampling sites	N	Mean	StDev	95% CI	F-value	*p*-value
La Caridad	9	.02	. 01	(.01, .03)	.49	.62
Poblacion	9	. 01	. 01	(.01, .02)		
New Maug	9	. 02	. 01	(.01, .03)		

Pooled StDev= . 01

Table 13. One-way analysis of variance for chromium concentrations

Sampling sites	N	Mean	StDev	95% CI	F-value	*p*-value
La Caridad	9	.06	. 02	(.04, .08)	1.83	.18
Poblacion	9	.05	. 01	(.04, .05)		
New Maug	9	.05	. 01	(.05, .06)		

Water quality of Gibong River in terms of heavy metal concentrations

Results and analyses from the determination of heavy metal concentrations in terms of copper, chromium, lead, manganese, and nickel in water samples from three locations are tabulated and discussed below (Table 11).

Cadmium

In all the water samples taken from the three locations in this study, there were very low concentrations of cadmium that they could not be detected by the method used. This indicates that the river water is devoid of the worrisome concentration of cadmium.

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 cadmium, in all the water samples taken from the three locations in this study, there were very low concentrations of cobalt that they could not be detected by the method used. This indicates that the river water is devoid of the worrisome concentration of cobalt.

Copper

Table 12 shows the statistical analysis data to determine any significant differences among the copper concentrations of water samples taken from the three locations of Gibong River. With a P-value of 0.62 which is higher than α=0.05, the copper contents of the water samples from La Caridad, Poblacion and New Maug have no significant differences. In effect, this means that the water samples from the three different sources have equivalent copper levels. It is also notable that all the resulting concentration values are below the standard/permissible value of copper (0.075 ppm) for agricultural water among the three locations.

Chromium

Table 13 shows the statistical analysis data to determine any significant differences among the chromium concentrations of water samples taken from the three locations of Gibong River. With a P-value of 0.18 which is higher than α=0.05, the chromium contents of the water samples from La Caridad, Poblacion and New Maug have no significant differences. In effect, this means that the water samples from the three different sources have equivalent chromium levels. The three locations present an indication that the level of chromium are in the borderline of reaching the permissible value.

Table 14. Kruskal Wallis test for lead concentrations

Sampling Sites	N	Mean Rank	Chi-Square	df	Asymp. Sig.
La Caridad	9	9.39	6.35	2	.04
Poblacion	9	14.22			
New Maug	9	18.39			

Table 15. Kruskal Wallis test for manganese concentrations

Sampling sites	N	Mean rank	Chi-Square	df	Asymp. Sig.
La Caridad	9	19.11	7. 02	2	.03
Poblacion	9	13.67			
New Maug	9	9.22			

Table 16. Kruskal Wallis test for nickel concentrations

Sampling sites	N	Mean rank	Chi-Square	df	Asymp. Sig.
La Caridad	9	16.28	2.05	2	.36
Poblacion	9	11.06			
New Maug	9	14.67			

Lead

Table 14 shows the non-parametric analysis data to determine the significant differences in the medians of lead concentrations in water taken from the three locations of Gibong River. With a P-value of 0.04 which is lower than α=0.05, the lead concentration median 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 lead concentration values from the three locations, however, are noted to be lower than the standard/permissible value (0.05ppm) for agricultural water among the three locations.

Manganese

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 River. With a P-value of 0.03 which is lower than α=0.05, the manganese concentration median values of samples from La Caridad, Poblacion and New Maug have significant differences. In effect, this means that the water samples from the three stations have different medians or are coming from different distributions. All concentration values were noted to be below the standard/permissible value of manganese in agricultural waters.

Nickel

Table 16 shows the non-parametric analysis data to determine the significant differences in the medians of nickel concentrations in water taken from the three locations of Gibong River. With a P-value of 0.36 which is higher than α=0.05, the nickel concentration median values of water samples from La Caridad, Poblacion and New Maug have no significant differences. In effect, this means that the water samples from the three different sources have equivalent or the same median for nickel concentration values. It is also notable that all the resulting concentration values are below the standard/permissible value of nickel (0.20 ppm) for agricultural water among the three locations.

Conclusion

The location, light intensity and physicochemical characteristics of the river stations are generally within favorable ranges for agricultural/ irrigation water. While some of the actual parameter values do not always promote heavy metal contamination and distribution in the water such as chemical oxygen demand, electrical conductivity, dissolved oxygen, pH, water salinity and turbidity, the other parameters such as high temperature, total dissolved solids, and high organic matter content, may contribute to heavy metal accumulation and distribution in one way or another.

With respect to the heavy metals studied and the result of the heavy metal concentration analysis, the Gibong river waters under study do not present alarming values of the heavy metals identified; However, the three locations present an indication that the level of chromium are in the borderline of reaching the permissible value.

Chromium (VI) is recognized as a human carcinogen by the US-EPA and WHO. Its toxicity includes respiratory, skin, cardiovascular, and even genetic and chromosomal aberrations. Natural and anthropogenic activities are possible sources of chromium environmental contamination. Mining, metal works, use of second-generation fertilizers evident in the locality could have contributed to the elevated Cr content in the River.

The townspeople residing near Gibong River should use the result of the study to help the government in ensuring that the river will not be polluted and contaminated by heavy metals, and the plant and animal food harvested from the river and riverbank ecosystems are safe. Also, the result of study should be used to update the local consumers as to the quality of agricultural land and the safety of specific goods they consume, raised, and grown from the identified areas of Gibong river. The data obtained should also be utilized to orient the farmers and fishermen about the status of the river. The farmers and fishermen around the area must understand the environmental situations according to the result of the study for them to be able to develop preventive and safety measures in the preservation, protection, and rehabilitation of the River water.

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