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Transport Analysis of Copper in Boac River Marinduque, Philippines

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Abstract: In 1996, over 1.6 million cubic meters of mine tailings were released along Boac River, Marinduque, Philippines declaring it biologically dead. Numerous studies found traces of heavy metals along this river, and bioaccumulation became a problem. Several heavy metals contaminating the river were reported to be ingestible by humans; one of which is Copper (Cu). With that, this study investigated Cu dispersion in the downstream area of Boac River. This was first done by coordinating with the "Development of Health Index: Vulnerability to Extreme Environmental Events for Marinduque island." (D-HIVE) project in collecting the water quality data, rainfall data, and digital elevation models (DEMs). Using the Hydrologic Engineering Center's River Analysis System (HEC-RAS) 6.2, the analyses were conducted by inputting the collected data. The flood hazard maps showed minimal spread in high-elevation areas and distinct spread in low-lying areas. The highest flood velocity was in the starting and middle points of the watershed, indicating these areas have the highest potential to lift Cu content and transport it into the downstream area and floodplain. The spatial variability maps showed that pH increases while Cu content decreases as water flows toward the downstream area. Overall, this study successfully determined the dispersion of Cu along Boac River.

Keywords: Copper dispersion, river, geographic information system, modelling

1. Introduction

Heavy metals are known to cause adverse effects on both human health and environmental health [1]. Some examples of these heavy metals include Lead (Pb), Zinc (Zn), Copper (Cu), Cadmium (Cd), Chromium (Cr), Arsenic (As), and Nickel (Ni). These heavy metals can occur naturally; however, the problem arrives when these heavy metals occur in high concentrations, and these high concentrations are typically caused by anthropogenic activities such as mining, manufacturing, and other industrial processes [2].

The Philippines has experienced many industrial pollution accidents due to mining. One of the country's worst mining accidents is the mining disaster of 1996 where 1.6 million cubic meters of mine tailings were released along Boac River, leaving this river biologically dead. Moreover, numerous studies prove that the plants, soil, air, and water in the country are contaminated with heavy metals [3], [4]. These indicate the presence of heavy metals in agricultural and aquatic products such as rice and fish [5]. In an article by Dizon [6], the findings of Mogpog municipal health officer Dr. Edsel Muhi, an epidemiologist, on the effect of the 1996 Marinduque mining disaster on Mogpog, Boac, and Sta. Cruz was reported. The study showed that even decades after the mining incident, residents of these towns showed As and Pb contents in their blood, with residents in Sta. Cruz having the highest content. Dr. Edsel Muhi also found several heavy metals contaminating Boac River that can be ingested by people; one of which is Copper (Cu). This shows that Boac River may have high Cu content due to dispersion from the nearby Maguilaguila open mining pit. In

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fact, in a previous study it was found that due to the mine-tailings spill the highest concentration of Cu in the marine sediments was 3,080 ppm in 1998, and 15,400 ppm in 2019 [7].

Copper (Cu) is a micronutrient and heavy metal contaminant that plays a vital role in plant and soil or wetland systems. It is mainly associated with organic matter and clay minerals in soils and wetlands [8]. The bioavailability and toxicity of Cu in plant and soil depends on its chemical speciation. Soil pH is used to control Cu availability, and an increased soil pH reduces Cu availability. Cu deprivation results to reduced growth rate and seed setting. It also causes reduced photosynthetic ability and pollen fertility which leads to reduced yield performance. On the other hand, excess Cu can be toxic as it results in underlying cellular damage which confines microbiological functions in both the upper layer of soil and the root system of green cover plants. Therefore, it can be said that a moderate amount of Cu is essential in aquatic environments, but it can also become detrimental in high concentrations [9].

Heavy metals can cause problems to both human health and environmental health by contaminating the water supply and other bodies of water. With the mining incident in Marinduque, this paper aimed to address possible Cu contamination in the Maguilaguila open mining pit and its dispersion throughout the Boac River in the event of flooding. Low pH reading was also measured in the pit ranging from 3.6 to 4.5. This is considered to be of high acidity that is harmful to human and environment health. It was reported that Cu has an indirect relationship with pH [8].

The coverage of this paper was limited to the Boac River located in Region IV-B, Philippines as the study area. This study mainly focused on the Cu and pH content of the the said river and determine its dispersion going to the downstream area.

2. Methodology

Due to rapid urbanization and industrialization, anthropogenic activities have significantly increased the concentration of heavy metals released into the environment, polluting soils and water bodies [10]. The dispersion of these heavy metals can occur through inundation and sediment transport, stipulating that the contamination can further reach the ends of water systems. The related literature and related studies indicated that Cu is one of the metals frequently studied for heavy metal dispersion [11]- [15].

Philippines is typhoon-prone, using flood hazard maps may prove to be extremely beneficial to the country [16], [17] when managing floods as it can demonstrate floodwater behavior. In addition, since flood water movement can be predicted using flood hazard maps, it indicates that heavy metals concentration in the flood water can also be assessed on how it would be dispersed during a flood event. This led the researchers to conduct this study wherein the dispersion of Cu and pH content of Boac River was modelled using flood hazard mapping.

2.1 Conceptual Framework

3. The conceptual framework of this study is presented in

Fig. **1**. The data collected were the Digital Elevation Model (DEM) of Marinduque, historical rainfall data, and water quality data of the water samples. Sampling was conducted last February 2022, water samples were taken at two (2) sampling points in the Maguilaguila open mining pit, and seven (7) points along the Boac River. The DEM and rainfall data were the main components input on HEC-RAS 6.2 to conduct flood hazard analysis on Boac River. Then, water quality analysis was conducted by using the geometry data in the flood hazard analysis as the base layer and by assigning the precise values to this layer by using the water quality data. This is to determine the content and dispersion of Cu and pH levels in the river. The results of this analysis were then compared to the total Cu values and the required range of pH levels of the revised WQG DAO 2016-08, respectively. This is to determine if the Cu content and pH levels exceeded the standard values.

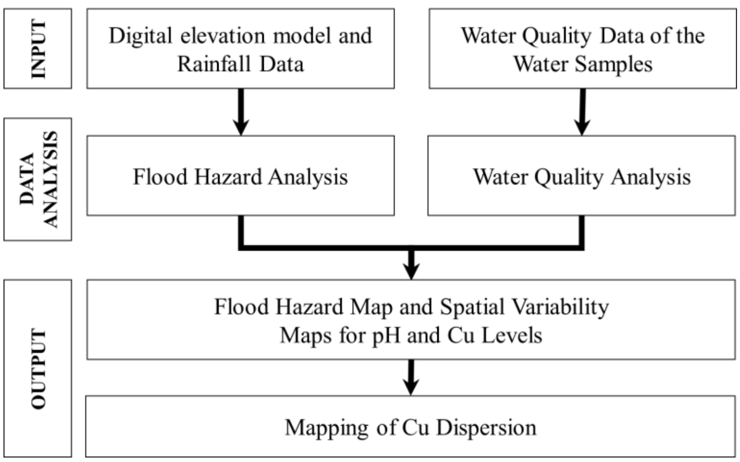


Fig. 1 - Conceptual framework

3.1 Research Design

This research was designed as a quantitative study with the aim of determining the Cu and pH dispersion of Maguilaguila open mining pit into Boac River. A quantitative study, as defined by Cohen [18], utilizes empirical methods and statements that describe real situations through numerical terms. Empirical evaluation is also applied in this kind of study; to assess all the factors affecting the topic in interest through observation.

As for the quantitative research method, this study used scientific modeling to conduct flood hazard analysis and to map the dispersion of Cu and pH in the river. Scientific modeling is a type of research method that represents or describes a selected aspect of the world through visual images [19]. This study utilized GIS tools in HEC-RAS 6.2 to perform flood hazard analysis and map Cu and pH dispersion. Moreover, this method can help viewers easily understand the concept and the results discussed in the study.

3.2 Data Gathering Procedures

This study underwent three (3) phases as presented in Fig. 2. These phases are the processes needed in order to accomplish the objectives of this paper.

The first phase was the collection of secondary data which are the water quality data, rainfall data, and DEM of the study area. Due to the nature of this study being conducted fully online because of the restrictions implemented by the Inter-Agency Task Force for Management of Infectious Diseases due to the COVID-19 pandemic, this phase was accomplished in collaboration with D-HIVE, a community-based research and development project. The DEM of the study area was also available through this project.

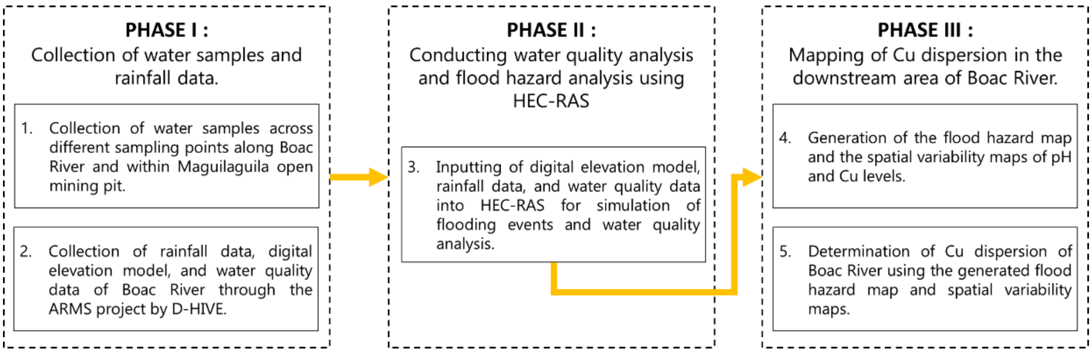


Fig. 2 - Methodological framework

D-HIVE conducted water sampling in the study area last February 2022 when most flooding occurred. The water samples were said to have been collected all across Marinduque, but mostly from the rivers Boac and Mogpog, using plastic bottles which followed the operational protocol developed by USEPA No. SESDPROC-201-R4. However, based on this paper's study area, the only samples considered were two (2) that were from the Maguilaguila open mining pit, and seven (7) from the Boac River. The assessment of these water samples was also done by D-HIVE. They used an Olympus Vanta X-ray Fluorescence or XRF scanner to measure in situ Cu concentrations, pH levels, and other water quality parameters. The XRF scanners were portable to address the remoteness of the sampling areas. The rainfall data of the study area was also previously collected by D-HIVE.

A study about manganese concentration was conducted in the same river and produced significant relationship with flooding [20]. The study supports the idea that copper could also undergone the same accumulation in the river. The researchers were able to obtain the Cu concentrations and pH levels of the water samples that were used in the conduct of the study.

The second and last phase of this study involved the use of HEC-RAS 6.2 to accomplish the main objective of this paper which is to model the dispersion of Cu in the study area. First, the flood hazard analysis was conducted by adding a terrain in the software's RAS Mapper using the DEM of Marinduque.

Next, the precise values of the gathered water quality data, specifically Cu content and pH values, were inputted into the geometry data created in the flood hazard analysis to perform a water quality analysis. This was done to generate spatial variability maps for Cu content and pH values of Boac River which assessed the dispersion of these water quality data along the river. The geometry data generated were then overlayed on top of the base layers to assign the Cu values to specific points in the area. Color coding of the geometry data was then conducted to distinguish values visually along the region. The legend for the Cu spatial variability map was auto-generated based on the Cu values inputted into the geometry data. The same process was done for creating the pH levels spatial variability map. Even though this study focuses only on Cu dispersion, the pH values were investigated in order to have a comprehensive understanding of how Cu is transported along the flow of the river.

3.3 Data Gathering Instruments

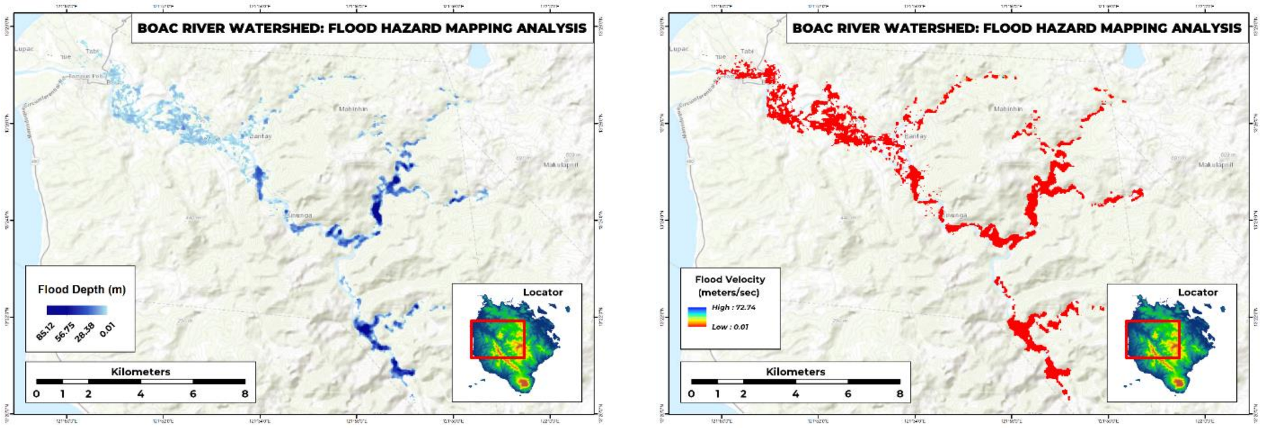
An XRF is an elemental analysis device with an X-ray source used to irradicate a specimen causing it to emit or fluoresce its X-ray characteristics 21. It can analyze all elements except for hydrogen, helium, and lithium. A portable XRF can determine the concentration of heavy metal in water through indoor and field studies [15].

HEC-RAS is a software capable of one and two-dimensional hydraulic calculations for natural and constructed channels [22]. It contains different river analysis components such as steady flow water surface profile computations, one- and two-dimensional unsteady flow simulation, sediment transport, and water quality analysis. HEC-RAS 6.2 was used to model the flood hazard map and simulate the Cu dispersion in Boac River.

4. Results and Discussion

One of the objectives of this study was to simulate a flood event and generate a Flood Hazard Map for Boac River. These Flood Hazard Maps are expressed in terms of flood depth as shown in Fig. 4(a) and flood velocity as shown in Fig. 4(b). This was accomplished using the software HEC-RAS 6.2.

Fig. 3 presents the flood hazard maps generated through conducting flood hazard analysis. Based on these maps, there are four (4) starting points of water inflow in the watershed area of Boac River and the highest elevation point of water inflow was 52.73 meters above sea level.



(a) (b)

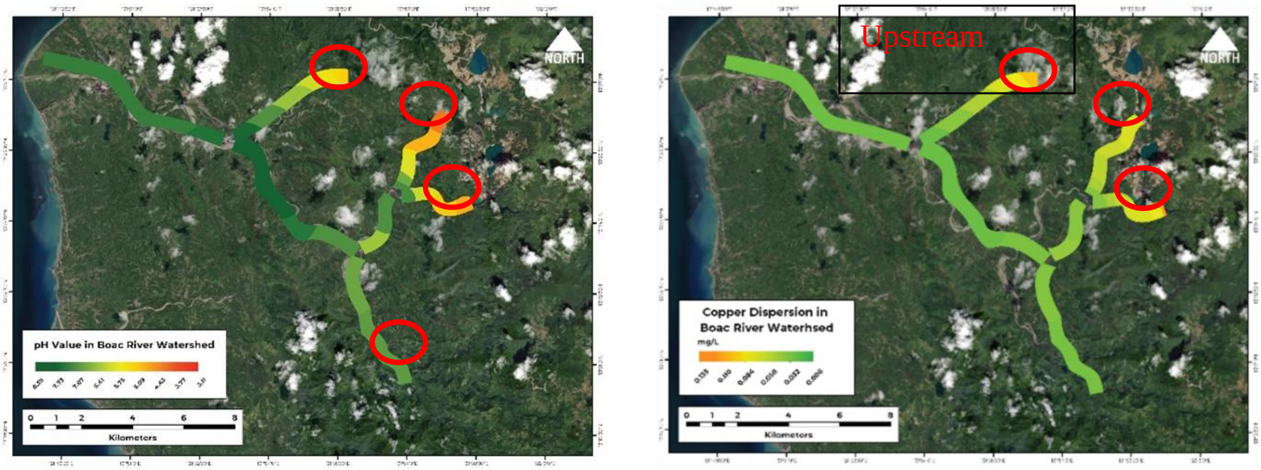
Fig. 3 - Flood hazard analysis of Boac River watershed showing different simulations; (a) flood depth; (b) flood velocity

Fig. 3(a) demonstrates the simulated flood depth relative to sea level. The darker blue regions represent areas with higher flood depth while lighter blue regions represent areas with lower flood depth. From this figure, it can be observed that most of the darker blue regions are located at the upstream area of Boac River. Thus, in the higher elevation, a higher flood depth is observed.

As for Fig. 3(b), the velocity of the simulation flood event is shown. This figure categorizes the intensity of velocity through colors: blue for areas with high velocities, green to yellow for areas with medium velocities, and red for areas with low velocities. It can be observed that most regions of the study area have low velocities in the event of a flood. However, the velocity of water was at its highest in the starting and middle points of the watershed, which means that it is in these high velocity areas that water has the highest potential to lift Cu content from the sediment and transport it down into the downstream area and to the floodplain. The highest velocity of flood, which was detected at one of the starting points on the northern part of the map, was 72.74 meters per second, indicating that water is moving abruptly at these points, while the lowest velocity was 0.01 meters per second. It is noted that the simulation results show most of the study area were observed to have low velocities and only very few areas have high velocities.

The flood hazard maps also gave information on the spread of water. There is minimal spread in areas with high elevations, and distinct spread of water in the low-lying areas. Since low flood velocities were observed in low-lying areas, the spread of water would not have any detrimental impact on communities near this region when flooding occurs.

As demonstrated by the spatial variability maps, pH increases while Cu content decreases as water flows towards the downstream area and the alluvial plain. This can be specifically seen in Fig. 4(a), where the pH was observed to be acidic with a value of 3.11 in the northeastern starting point of water flow whereas in the middle points of the watershed, a basic pH of 8.39 was identified. Meanwhile, the Cu content was observed to be decreasing. In Fig. 4(b), highest value of Cu was observed in the eastern starting point of the water flow with a value of 0.0135 mg/L, while the lowest Cu value observed was 0.006 mg/L, identified in the middle points and low-lying areas of the watershed. With that, the correlation between pH levels and Cu content is observed to be indirectly proportional. This may be due to Cu being chemically basic in nature and the fact that low pH levels can also encourage solubility of heavy metals as the metal cations are released with the increased level of hydrogen ions.



(a) (b)

Fig. 4 - Spatial variability maps for water parameters of Boac River, Marinduque; (a) pH levels; (b) Cu dispersion

In the Cu spatial variability map, higher Cu levels were observed in the northern part at the three starting points of water inflow. This could be attributed to its proximity to the mining pits such as the Maguilaguila dam, San Antonio Pit, Tapian Pit, and Makulapnit dams which are in the northern part of the Boac watershed. As for the pH levels spatial variability maps, lower pH levels were observed at the starting points of water inflow. As the water flowed downstream, the pH levels got higher. This may be due to the fact that Cu is considered a base metal, and with its presence gradually dissipating as water moves downstream, the pH level gets higher or less acidic.

The values for the Cu levels were within the WQG as it does not exceed the limit of 0.20 mg/L for Class C water body as stated in the DAO 2021-19. The detected range of pH levels in the three starting points of the water inflow was acidic and was identified to not be within the stated range of 6.5 to 9.0 in WQG for Class C in the DAO 2016-08. These comparisons can be seen in Table 1.

Table 1 - Comparison of results to WQG Of DAO 2016-08 and DAO 2021-19

	Transport Analysis of Copper in Boac River, Marinduque, Philippines	**DAO 2016-08**	**DAO 2021-19**
Cu Concentration	0.006 mg/L to 0.0135 mg/L	-	0.20 mg/L
pH levels	3.11 to 8.39	6.5 to 9.0	-

The Cu levels are well within the range of the water quality guidelines, but the low levels of Cu could affect crop production as Cu is an essential micronutrient for plants. The normal Cu concentrations needed in plants range from 5 to 20 ppm and this plays roles in the process of photosynthesis and respiration. Due to the role of Cu in plants, its deficiency results in reduced yield or plant growth. In a study investigating Cu deficiency in plants, it was found that plants grew on a nutrient solution with sufficient Cu content, increasing their plant maturation by 200% to 1200%, as opposed to plants showing signs of Cu deficiency where their growth was restricted [24]. Cu deficiency may also reduce the fertility of plants, which in turn affects seed production since Cu is associated with both male and female reproductive organs of plants [25].

The trends of Cu concentrations and pH levels observed in this paper are supported by the trend reported in a study by David & Plumlee [23]. The pH levels are lower or more acidic the closer it is to the mining site, and more alkaline the further it is. The same trend is observed with the dissolved Cu concentration except for Bol River, wherein the concentration decreases the further it is from the mine. They observed in the downstream of Boac River within 6 km of the south of Tapian outflow that the parameters rapidly approach baseline conditions of 0.01 mg/L Cu and a pH level of around 7. They also reported that Mogpog River has significantly higher values compared to Boac River. They attributed the reduction of Cu levels in the Boac watershed to its self-mitigating geology wherein a great percentage of the watershed is composed of carbonate-rich bedrock. They identify that the primary route of Cu removal that is dissolved in surface water is through its incorporation in bed load.

Furthermore, it would also be very important to conduct risk assessment in the area. In the study of [26], they were able to identify the risk level in different zones in their project sites considering flooding as the main hazard, this would be very important to be done in an area like Boac whose main problem is elevated metal concentration in water as it could help plan mitigations in the area by focusing first on zones that are on the highest risk because of this contamination. Another research focusing on the geo-accumulation of manganese in the rivers of Boac and Mogpog [20] found that there is a moderate positive correlation between Mn content and flood depth which suggests that Mn contamination in the floodplain is promoted by extensive flooding. It was said that Mn-bearing sediments and silts were likely transported from the abandoned mine pits to the downstream areas of the rivers whenever flooding occurs which could also be performed using RAS [27]. This further supports the results of this study that Cu is dispersed following the flow of water, from higher elevations with higher flood depths to the downstream area and floodplains where lower elevations are observed. The study also mentioned that, in the rivers of Boac and Mogpog, heavy metals are carried by surface waters. Therefore, frequent flooding in these areas will lead to more concentration of heavy metals entering soils and contaminating floodplains and nearby areas; it may even exceed the permissible limits of WQG. With the effect of climate change, the river could experience a higher frequency of flood [28], [29] which could induce increased accumulation of metal downstream as long as the pit continues to exist there.

5. Conclusion

The pith and marrow of the whole study is that the flood hazard map effectively displayed the depth and velocity of Boac River, Marinduque, Philippines. In addition, it was also able to assess the Cu and pH dispersion in the downstream area of the Boac River and floodplain decades after the 1996 mining incident. This was done by simulating a flood hazard map and generating spatial variability maps of pH and Cu dispersion on the study area.

The flood hazard map effectively displayed the depth and velocity of Boac River, as well as the flow of water from the starting points toward the downstream area. The correlation between the spatial variability maps showed how Cu is dispersed within the study area. As observed from these maps, pH increases from 3.11 to 8.35 and Cu content decreases from 0.135 mg/L to an almost zero value of 0.006 mg/L as water flows towards the downstream area and the floodplain, showing the influence of pH to Cu content. This led to the conclusion that Cu was dispersed from the starting points of water inflow to the downstream area of Boac River.

Considering the detected range of pH levels, the water inflow in the starting points were observed to have lower pH than most areas within the watershed and its values were not within the water quality guidelines (WQG) for Class C water bodies of DAO 2016-08. This may impact the nutrient availability in this region which in turn affects the growth of plants along the area.

The Cu levels of the watershed are within the WQG for Class C water bodies of DAO 2021-19. These values show that the amount of Cu present within the river is not toxic and will not threaten the health of the public and the surrounding environment. However, low levels of Cu may affect crop yield performance, crop growth, and photosynthetic ability of plants along the floodplain region.

Overall, this study successfully determined the dispersion of Cu along Boac River through generating flood hazard maps and spatial variability maps. Through the spatial variability maps, the correlation between Cu and pH levels was observed to be indirectly proportional, which may be attributed to the fact that Cu is basic in nature. These maps also showed that the pH levels in the starting points of the study area were more acidic than the rest of the region, and this affects plant growth in this area. As for the Cu levels, it was observed to be low throughout the study area which may result to issues with Cu deficiency along the floodplain region.

6. Recommendations

To further study how Cu is transported throughout Boac River, the researchers recommend widening the boundaries of the study area by including the upstream area of the river. This will allow future researchers to map the critical areas where Cu levels are most concentrated along the river. Other affected rivers in the province of Marinduque can also be explored and studied for their Cu levels. The values can then be compared to the findings of this study. Rainfall runoff modelling should also be conducted in the area to identify how often the abandoned open mine pit discharge contaminated water to boac river [

The water parameters this study focused on were pH levels and Cu content only. It is recommended to assess the relationships among other water parameters that affect sediment transport such as electronic conductivity, total dissolved solids, and temperature, to have a better understanding of how Cu is dispersed along the river. Moreover, the result of this study shows that Cu is also dispersed along the floodplain, so it is best to look into the dispersion of Cu in soils to help determine its possible impact on the health of the public and environment. In a previous study, it was found that the marine sediments had Cu concentrations of up to 3,080 ppm in 1998 to 15,400 ppm in 2019 [7]. Thus, further studies on the heavy metal concentration in the sediment should be explored.

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