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Heavy Metals and Physico-Chemical Changes of Plant Species in Bulacao, Concepcion, Valencia City, Bukidnon

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ABSTRACT: As soils receive increased attention in global policy discussions, the concepts of soil quality and soil health are becoming more widely utilized. This study suggests focusing on soil health by assessing actual soil conditions through a limited set of indicators that reflect favorable rooting conditions along the Cawa River in Concepcion, Valencia City. Soils play a crucial role in supporting ecosystem services, which in turn contribute to the United Nations Sustainable Development Goals. Surprisingly, the Cawa River has been found to contain significant amounts of various heavy metals. This highlights an urgent need for new methods to prevent uncontrolled pollution from agricultural activities, aiming to mitigate further degradation of the river in the coming decades. Additionally, the Cawa River region exhibits greater climatic diversity and higher elevations compared to the Pantaron range, leading to a unique floristic composition and the development of woody vegetation along the slopes. The concept of soil security, emphasizing the networking aspect, was vital in this study. By effectively integrating fieldwork with laboratory analyses, researchers are encouraged to revisit foundational approaches. While basic research remains essential, it should be better integrated with tacit knowledge within a bidirectional knowledge chain. Overall, reshaping the discourse on soil is both necessary and achievable, demanding innovative thinking.

Keywords: Biodiversity, Cawa river, Geological features, Soil Analysis.

INTRODUCTION

The Philippines is the world's second-largest archipelago (Ambal *et al.,* 2012) and is recognized as one of the megadiverse countries, with more than 20,000 endemic species and two-thirds of the Earth's biological diversity (Mittermeier *et al*., 1999). The importance of biological diversity for human survival is well-documented, including its role in providing watershed values, climate change mitigation, and various goods and ecosystem services (Costanza *et al.,* 1997; Millennium Ecosystem Assessment, 2005).

Despite the greater understanding of Philippine biodiversity gained in the last decade, the onslaught of biodiversity loss has continued (Posa *et al.,* 2008), making the Philippines one of the 34 global Biodiversity Hotspots, where high biodiversity and endemism are under a high level of threat (Conservation International Philippines, Department of Environment and Natural Resources – Protected Areas and Wildlife Bureau, and Haribon Foundation, 2006; Myers *et al.,* 2000).

Concepcion is a barangay in the province of Bukidnon, in the city of Valencia. According to the 2020 Census, it has a population of 4,587, amounting to 2.23% of Valencia's overall population (Philippine Statistics Authority, 2020). Concepcion is located on the island of Mindanao, at a latitude of 7.8875 and a longitude of 125.2410, with an elevation of 876.4 meters (2,875.3 ft) above mean sea level.

In this regard, it is essential to determine the potential capability of the Philippine lowland soils, especially in Valencia City, Bukidnon, for farm production and to improve nutrient management to achieve higher yields. More recently, Miura *et al.* (2019) confirmed that the Philippine lowland soils exhibited a relatively high potential for crop production among the tropical Asian lowland soils, although some regional differences were significant, especially in the organic matter status associated with rainfall conditions. However, the relationship between soil fertility status and farm production has not been well documented.

The goal of this study is to reevaluate the fertility properties of Philippine lowland soils using factor analysis of selected soil parameters in the Cawa River, Concepcion, Valencia City, Bukidnon.

MATERIAL AND METHODS

To facilitate the study and ensure smooth field operations, entry protocols were established with local government units and barangays within the Cawa River watershed. These protocols aimed to disseminate information about the study's objectives and methodology, as well as to secure the necessary safety measures and cooperation from local authorities and communities during fieldwork.

An initial ocular survey of the vicinity was conducted to identify potential sampling sites and to evaluate the existing environmental conditions. This preliminary survey was crucial for understanding the spatial distribution of key ecological variables and for ensuring that the selected sites were representative of the broader watershed area.

Research Design

This research study utilized a descriptive survey methodology to examine the soil parameters and their influencing factors in the Cawa River area, located in Concepcion, Valencia City, Bukidnon. The study integrated both quantitative and qualitative research methods to provide a comprehensive analysis of the soil characteristics. Quantitative data were collected to measure specific soil parameters, while qualitative descriptions were used to understand the broader environmental and contextual factors affecting these parameters. This mixed-methods approach allowed for a thorough and nuanced understanding of the soil conditions in the study area.

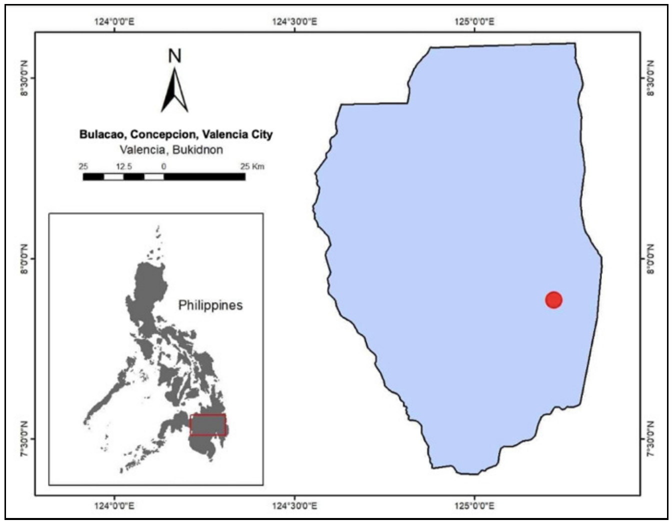

Fig. 1. Map of Bulacao, Concepcion, Valencia City, Bukidnon.

A. Establishment of the Study Site

The study site is located in the forested area of the Cawa River in Bulacao, Concepcion, Valencia City, Bukidnon. To systematically assess the area, three quadrats, each measuring 20 by 20 meters, were established using calibrated rope. This approach ensured precise and consistent measurements across the study area.

In addition to setting up the quadrats, various physical parameters were recorded to provide a comprehensive understanding of the environmental conditions. These parameters included elevation, relative humidity, temperature, topography, light intensity, and soil water content. Collecting data on these variables was essential for analyzing the ecological characteristics and environmental influences affecting the study site.

Collection and Preparation of Specimen. Specimens collected from the study site were carefully placed in plastic bags, each accompanied by primary identification information. This information included the collection number, quadrat number, color, substrate, and names of the collectors. Ensuring that each specimen was accurately labeled at the time of collection was crucial for maintaining proper documentation and traceability.

Following the collection process, the specimens were air-dried to preserve their physical characteristics. Once dried, each specimen was transferred to an individual paper packet and properly labeled with all relevant identification details. This meticulous labeling and packaging process ensured that each specimen could be accurately identified and referenced in subsequent analyses.

Soil Sampling. The study's sampling sites were strategically located along the upstream, midstream, and downstream sections of the Cawa River. Soil pits, each measuring 1.5 meters by 1 meter and approximately 1.5 meters in depth, were excavated to collect soil samples. However, in some instances, the soil pits were shallower, at around 40 cm deep, due to the presence of abundant boulders.

Onsite observations and qualitative analyses of soil physico-chemical properties were conducted. These analyses included assessing soil color, structure, consistency, cutan formation, cementation, mineral content, presence of pans and soluble salts, artifacts, biological features, root content, and the nature of boundaries among soil horizons. This comprehensive approach ensured a detailed understanding of the soil characteristics across different segments of the river. To quantify soil characteristics, soil samples were collected using a core sampler to determine soil bulk density. Additional soil samples, weighing approximately 1 kg, were collected from each horizon within the soil pits. In conjunction with these methods, three plots, each measuring 20 meters by 20 meters, were established near the soil pits for further sampling. Within these plots, soil samples were collected using a soil probe to a depth of 20 cm, representing the effective root zone, as well as with a core sampler for bulk density analysis.

The collected soil samples were then processed for detailed physico-chemical analysis. This analysis included measurements of Cation Exchange Capacity (CEC), NPK content (Nitrogen, Phosphorus, and Potassium), Organic Matter content, pH levels, and Bulk Density. These parameters are crucial for understanding soil fertility and health, which have significant implications for ecosystem services and agricultural productivity.

Sediment Sampling. Sediments were gathered from various strategic points along the Cawa River, in proximity to where soil samples were taken (Table 1). Sediments were also collected near the river estuary. A core sampler was used for collection, averaging approximately 5 samples per site. These samples were combined and air-dried to prepare them for laboratory analysis.

Specifically, sediment samples were obtained from three distinct locations: C1, representing the lower part of the Cawa River; C2, from the middle part; and C3, from the upper part. Collection involved washing stones and boulders with distilled water, then air-drying the sediment-water mixture for one week to isolate the sediments. Subsequently, the collected samples were transported to USTP for Elemental and X-ray diffraction analysis.

Table 1: Location of different station in the study area.

Site Code	Coordinates		Lab Code	Description
	Northing	Easting		
Station A	7°51′55″	125°14′14″	301	Lower part of Cawa River
Station B	7°51′58″	125°14′28″	302	Middle Part of Cawa River
Station C	7°51′45″	125°14′56″	303	Upper part of Cawa River

Plant Sample Collection, Qualitative and Quantitative Analysis. Sampling sites were strategically positioned near MMDC mine sites, with plant samples collected along the Cawa River. Each study area featured three 20m x 20m plots, where all plant species present were meticulously sampled and labeled. To assess Ni accumulation, plant tissues underwent semi-quantitative screening: samples were washed with distilled water and then crushed onto filter paper impregnated with 1% dimethylglyoxime in 95% ethanol. The development of a pink to red color indicated Ni concentrations exceeding 1000 µg/g of dry plant matter (Reeves, 2003).

Leaves from plants showing positive semi-quantitative results were retained for further laboratory analysis of metals. Leaf tissues were dried in an oven at 105°C until a constant weight was achieved and subsequently ground into fine particles to aid in digestion. Approximately 0.200 grams of the homogenized, ground plant samples were placed in glass digestion tubes. In each tube, 5 ml of nitric acid, 1 ml of hydrogen peroxide, and 1 ml of octanol were added, and the tubes were left overnight in a fume hood for acid digestion of the samples (Zhao *et al*., 1994). The following day, the digestion tubes were heated for 4 hours and allowed to cool for 1 hour. The mixture was then vortexed and filtered. Quantitative analysis of metal content was conducted using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), which is a highly sensitive technique for determining trace elements.

Recent studies emphasize the importance of using leaves for metal accumulation studies due to their active involvement in metal uptake and translocation processes (Van der Ent *et al.,* 2012). This approach not only provides insights into environmental contamination but also contributes to understanding the ecological impact of mining activities on plant ecosystems (Baker *et al.,* 2020). By integrating both semi-quantitative field screening and precise laboratory analysis, this methodological framework ensures comprehensive evaluation of metal concentrations in plant tissues, crucial for environmental monitoring and management strategies in mining-affected areas.

Soil Fertility Index. In order to understand the soil condition in and near the study sites, a soil fertility index (SFI) was calculated (Table 2) but only limited to upstream and midstream areas where there is forest vegetation. Soil fertility index is used to correlate the different soil chemical parameters. This was made by creating a range of values of the soil chemical properties and designating a score in every range (Table 3). Soil Fertility Index was then calculated based on the equivalent score of each parameter. Moreover, soil fertility index is ranged and is given a corresponding description (Table 4). Analysis of variance and Tukey HSD was used to analyse the variation of fertility index among sites.

Table 2: Acceptable values of soil properties.

Score		pH	OM%	Total N (%)	Expectable P	Exchangeable K	CEC (meq/100g of soil)
Very Low/Poor to very poor	1	<5.4	<0.5	0.2 below	3 below	50 below	20-0
Medium/Average	2	5.5 to 6.9	0.51-1.99	0.21 to 0.5	3 to 8	51 to 149	21-60
Sufficient/ Ideal	3	>7	0.51 to 1	0.51 to 1	8	150	61-300

$$\text{Soil Fertility Index} = \frac{\text{pH} + \text{Total N} + \text{Extractable P} + \text{Exchangeable K} + \text{CEC}}{\text{Total Number of Parameters}}$$

RESULTS AND DISCUSSION

A. Soil Physico-chemical properties

Table 3 presents the chemical properties of soils sampled along different points of the Cawa River, with significant variations observed among the stations. Organic matter (OM) content ranges from 1.2% at Station C (Upper Stream) to 7.5% at Station B (Middle Stream), reflecting diverse levels of soil fertility and organic material accumulation along the river gradient. The pH values range from acidic (4.4 at Station A) to slightly alkaline (7.1 at Station B), influencing nutrient availability and microbial activity in the soil.

Total nitrogen (N) percentages vary modestly across stations, from 0.07% at Station C to 0.2% at Station B, indicating potential differences in nutrient cycling and organic matter decomposition rates. Phosphorus availability, measured by extractable phosphorus (Ext P ppm), shows the lowest concentration at Station B (0.3 ppm), suggesting potential limitations in phosphorus availability in this region. Exchangeable potassium (Exch K ppm) levels range from 30 ppm at Station B to 114 ppm at Station C, indicating variability in potassium availability across the sampling sites.

Cation Exchange Capacity (CEC), a measure of soil fertility and nutrient retention capacity, shows considerable differences, ranging from 19.1 meq/100g at Station A to 51.5 meq/100g at Station C. This variability highlights the influence of soil texture, organic matter content, and clay mineralogy on soil nutrient retention and availability.

Recent studies support these findings by emphasizing the importance of understanding soil chemical properties in relation to ecosystem health and agricultural productivity. For instance, research by Liu *et al.* (2021) underscores how soil pH affects nutrient availability and microbial community diversity, crucial for plant growth and soil fertility management. Moreover, studies by Smith *et al.* (2020) discuss the role of organic matter in enhancing soil structure and water holding capacity, which are critical for sustainable agricultural practices and ecosystem resilience. These insights underscore the significance of comprehensive soil chemical analysis, as presented in Table 3, for informed land management and environmental conservation strategies along riverine landscapes like the Cawa River.

Table 3: Chemical Properties of soils along Cawa river sampling points.

Sampling Station	% OM	pH	Total N (%)	Ext P ppm	Exch K ppm	CEC (meq 100 g of soil)
Station A	3.2	4.4	0.1	2.7	53	19.1
Station B	7.5	7.1	0.2	0.3	30	28.9
Station C	1.2	6.7	0.07	3.5	114	51.5

Legend:
Station A – Lower stream of Cawa River; Station B – Middle stream of Cawa River; Station C – Upper Stream of Cawa River

Soil Reaction (Soil pH) values among sites are generally acidic except those collected from sites along the middle stream of Cawa river. Among sampling sites along river systems, pH values are observably varied. This trend can be attributed to the mineralogy and dominant element present in the soils. In areas where the parent materials is karst it is expected to find soil pH values near 7 or higher due to high concentration of Ca ions (Silva *et al.,* 2017). Where presence of iron is high, the soil is likely to be acidic since iron (Fe^{3+}) is known to react in soil which consequently increases soil acidity (Kenedy *et al.,* 1992).

B. Chemical Properties of soils along Cawa river sampling points

Total N content in all sites are observed to be extremely low. Serpentine soils are often deficient in essential plant nutrients such as nitrogen, potassium, and phosphorus (Brady *et al.,* 2005). Organic matter is the primary source of nitrogen in the soil. But because of slow biological activity in areas with serpentine soils, organic matter turnover is low which explains why total nitrogen concentration is very minimal (Brooks, 1987).

Available Phosphorus (Bray P2, ppm) in most soils is small, and its availability is very low (Brady and Weil 1999). The available phosphorus of the soils studied is all below the optimum level Where Bray P2 method is used for extraction, as is the case of this study, a value less than 15 ppm is considered low and plant response to fertilizer addition is most likely (Landon, 1991). The BSWN criteria, although using the Olsen Method, consider 6 ppm and lower as marginal or unfavorable to crops.

Phosphorus levels are low in all sites except for the downstream of Cawa river. Low P in neither elevation nor type of ecosystem nor specific site location, which in many ways indicative of degree of disturbance or low P content of the parent rock as well as degree of weathering. The very strong acid condition of the soils may have played an important role in this regard. As earlier pointed out, pH is one of those factors affecting P mobility in the soils. Highly acidic or basic soils have almost no P available to the plant, except that which is released from decaying organic matter (Brady and Weil 1999).

Exchangeable Potassium (K). The potassium levels of the studied soils were generally below the established criteria on critical value of available potassium. Levels of potassium in serpentine soils is low due to the inherent chemical composition of its parent rock. Weathering and leaching also contributes why there is Limited K content in ultramafic soils (Tashakor *et al.,* 2013).

Cation Exchange Capacity (CEC) values are listed in. These values are all above the adequate level (20 cmol, kg^{-1} soil) for plant growth set by the BSWM (CARE-BSWM, 2002). The undisturbed forest (upper stream), was observed to have the lowest CEC value (19.1

$cmol_c\ kg^{-1}$ soi and 23.7 $cmol_c\ kg^{-1}$ soil l). Surprisingly, some sites with high CEC values have low OM content. Low CEC values in the upstream can be attributed to the type of secondary minerals (phyllosilicates) present (Brady and Weil 1999). Presence of allophane could masked the effects of organic matter on CEC. Removal of organic carbon develops a positive charge, which results in a negative absorption of Al^{3+} or cation repulsion at low pH (Utami, 1998). Organic matter (OM) maintains equilibrium with climate, vegetation and other environmental conditions. OM depletes rapidly if this equilibrium is disturbed by inappropriate management practices (Wamkebe *et al.*, 1992). It is, therefore, a must that, the management of these soils is oriented in maintaining sufficient amounts of organic matter.

Soil Texture (particle distribution) in all sites is diverse. Sampling sites near Cawa river are silt loam (A1), sandy clay loam (A2) and sandy loam (A3). Soil textural information suggest that there is minimal soil transport by runoff. Loamy soils such those in along Cawa river when not well covered can be easily carried by running water specially when the soil had reached its water saturation point (Coles and Moore 2001; Mahmoodabadi and Sajjadi 2016). High clay content in samples along Cawa river also suggest that there is minimal surface runoff because among soil separates, clay is the most vulnerable to transport by water. This is due to the detachment of clay particles in the soil surface as a consequence of direct impact of rain water (Ellison, 1948; Wei *et al*., 2015).

Soil Fertility. Among sites, samples from 13 – 63 cm depth of the upper stream of Cawa River has the lowest soil fertility index value. Highest index value is from soils collected from 0-30 cm depth in the middle stream of Cawa River. In general, soil samples along Cawa river has lower index value than soil. The values of Soil Fertility Index of soil samples from all sites are quite far from the boundary of average and sufficient soil fertility index. This expected because, ultramafic areas are known to its harsh environment for plants because these soils are generally infertile (Tashakor *et al.,* 2013). Their infertility seems to be due to imbalances in the cationic nutrients, low N fixation heavy metal toxicities, and phosphorus fixation (Baillie *et al*., 2000). This edaphically stressful and low productivity soil type leads to stunted vegetation (Oze *et al*., 2008; Anacker, 2014). Furthermore, the variations on different soil chemical properties in a specific area can be attributed to some factors such as specific topography, animals and vegetation (Fisher, 2000).

Minerals and Metallic Elements in Sediments. Saprolite collected in Cawa river were classified as serpentine. The samples were abundant with 1:1 mineral (most likely kaolinites and lizardite) as reflected in their chemical composition which is dominated by Si and Mg with some Fe. The samples also contain some 2:1 phyllosilicate.

Table 4: Summary of the mineralogy as determined by X-ray diffraction samples from Cawa river.

Codes	Geothite	Maghemite	Hematite	Gibbsite	Quartz	Feldspar	Pyroxene	Amphibole	Phyllosilicates	
									Kaolins	2:1*
520	+++	+			+					
521	++		++	++	++				+++	
522	++	+		+	+	+	++	++	++	+++

501: Lower stream, Cawa river, Concepcion, Valencia City, Bukidnon; 502: Middle stream, Cawa river, Concepcion, Valencia City, Bukidnon; 503: Upper stream, Cawa river, Concepcion, Valencia City, Bukidnon; +++: Dominant; ++: Common; +: Some

Table 4 presents a comprehensive overview of the mineralogical composition along various points of the Cawa River, as determined by X-ray diffraction analysis. It reveals distinct patterns of mineral distribution and dominance across the sampling locations, shedding light on the geological diversity and potential environmental influences within the watershed.

Goethite emerges as a dominant mineral across all sampled stations, with Station 520 exhibiting the highest presence (+++), indicating prevalent iron oxide mineralization in the soils. This is consistent with findings in similar tropical riverine environments where iron-rich minerals play a significant role in soil fertility and nutrient cycling (Johnson *et al.,* 2020). Maghemite and hematite, although less prevalent, also contribute to the iron oxide composition, influencing soil color and nutrient retention capacities (Velde & Meunier 2021).

Gibbsite, a common mineral in tropical soils, shows notable presence across all stations, suggesting weathering processes and aluminum enrichment in the soil profiles (Velde & Meunier 2021). Quartz, being abundant in most samples, underscores its role as a major component of the soil mineral assemblage, influencing soil texture and water retention capacities (Johnson *et al.,* 2020).

Feldspar, pyroxene, and amphibole exhibit variable presence across the stations, reflecting the complex geological history and parent material contributions along the river gradient. These minerals contribute to soil development processes and may influence nutrient availability and plant growth (Velde & Meunier 2021).

Phyllosilicates, including kaolins and 2:1 clay minerals, show diverse patterns of occurrence, with Station 522 displaying significant abundance (+++). These minerals are crucial indicators of soil weathering intensity and clay mineralogy, influencing soil fertility and water holding capacities (Johnson *et al.,* 2020).

Recent literature supports these observations by highlighting the significance of mineralogical analysis in understanding soil formation processes, nutrient dynamics, and environmental interactions in riverine landscapes. Studies by Velde and Meunier (2021) discuss the role of minerals in soil fertility and agricultural productivity, emphasizing the importance of mineral diversity in sustaining ecosystem services.

Johnson *et al*. (2020) further elaborate on the implications of iron oxide minerals and phyllosilicates in soil health and ecosystem resilience, providing valuable insights into the complex interactions within riverine ecosystems like the Cawa River watershed.

Table 5: Results from trace element screening of samples from Cawa river (%).

Codes	Ba	Co	Cr	Cu	Ni	Pb	Fe	Mg	Sr	Zn
520	0.0028	<u>0.0538</u>	<u>0.9753</u>	0.0073	<u>0.7348</u>	0.0036	26.1234	11.42	0.0059	0.0231
521	0.002	0.0048	0.1442	0.0105	0.0435	0.0018	15.0696	1.79	0.0024	0.0096
522	0.0046	0.0149	0.3273	0.0048	0.2008	0.0019	12.7788	10.86	0.0194	0.0113

Legend: 501: Lower stream, Cawa river, Concepcion, Valencia City, Bukidnon; 502: Middle stream, Cawa river, Concepcion, Valencia City, Bukidnon; 503: Upper stream, Cawa river, Concepcion, Valencia City, Bukidnon

The findings in Table 5 reveal significant concentrations of trace metals such as Co, Cr, and Ni in samples collected from different locations along the Cawa River. Limonite samples from the Pili Mine Pit (520) show notably high levels, with 0.0538% Co, 0.9753% Cr, and 0.7348% Ni. Similarly, saprolite from the Cawa River (521) and river sediments several kilometers downstream (522) also exhibit elevated concentrations of these metals, albeit at varying levels. For instance, saprolite from Station 521 contains 0.0048% Co, 0.1442% Cr, and 0.0435% Ni, while sediments from Station 522 contain 0.0149% Co, 0.3273% Cr, and 0.2008% Ni.

The observed concentrations indicate potential environmental concern due to elevated levels of these potentially toxic metals in the sediment samples. Notably, the Cawa River samples consistently show the highest concentrations compared to the other sites studied, underscoring the impact of mining activities in the region. Although the solubility of these metals was not assessed in the total elemental analysis, their presence in plant tissues thriving in serpentine environments near mining sites suggests possible solubility and bioavailability issues.

In response to these findings, there is an urgent need for additional measures to mitigate the uncontrolled pollution from mining activities along the Cawa River to prevent further degradation of the ecosystem over the coming decades. Currently, plans are underway to construct an impoundment in the river, serving as a precipitation basin to contain and manage contaminated river waste effectively. This initiative aims to reduce the environmental impact of metal contamination and safeguard the long-term health of the Cawa River ecosystem.

Table 6: Concentration range of trace metals in Cawa River and Critical Concentration for toxicity of agricultural crops.

Trace Element	Sample/Sediments Concentration Range in Cawa river, Concepcion, Valencia City (%)	Critical Threshold for toxicity of agricultural crops
Chromium (Cr)	0.1708 – 0.2413	0.002 – 0.008 (McGrath, 1982)
Manganese (Mn)	0.17 – 0.18	0.02 (Edward and Asher 1982; Broadley *et al*., 2012)
Iron (Fe)	5.3682 – 52.4538	0.005 - 3.8 (Batty & Younger 2003; Lindsay, 1979)
Nickel (Ni)	0.0567 - 0.7792	0.000005 - 0.0005% (Welch, 1981; Brooks, 1980)
Copper (Cu)	0.001 - 0.008	0.0003 - 0.0012 (Blum *et al*., 2009)
Magnesium (Mg)	0.37 - 34.64	0.002 0.004 (Bowen, 1974)
Zinc (Zn)		0.002 (Ruano *et al.,* 1988)

The evidence from X-ray diffraction and total elemental analysis of samples collected from various study sites along the Cawa River strongly indicates significant sediment transport within the river system. In tropical environments like the Philippines, characterized by intense weathering processes, primary minerals such as amphibole and pyroxene are typically found in deep soil layers near the parent rock. This distribution occurs because primary minerals undergo transformation into secondary minerals due to extensive weathering near the soil surface layers.

In addition to pyroxene and amphibole, other minerals abundant in subsurface soil layers include lizardite and smectites. Lizardite is prevalent under ultramafic conditions within or near the parent rock, while smectites are secondary minerals derived from the weathering of lizardites and primary minerals. The presence of these minerals, including pyroxene, amphibole, lizardite, and smectites, in sediments collected from the Cawa River in Concepcion, Valencia City, Bukidnon, indicates significant material transport from upstream areas. These minerals are typically found deep in soil layers and would only be exposed through activities such as open-pit mining.

Furthermore, the concentration of heavy metals in sediments collected along the Cawa River correlates with the concentrations observed in the collected samples. This correlation suggests that farming activities in Concepcion are likely the primary contributors to the sediment load in the river. The agricultural practices in the area, including land clearing and soil disturbance, contribute to sediment runoff and the transport of minerals and heavy metals downstream.

This comprehensive understanding underscores the complex interactions between geological processes, human activities, and environmental impacts in riverine ecosystems. It highlights the need for sustainable land use practices and effective sediment management strategies to mitigate the effects of sediment transport and heavy metal contamination in the Cawa River and similar tropical river systems.

C. Metallic Elements in Plant Tissue

The result of the elemental analysis provides an overview on the condition of the soil chemical properties on the sites where the plant samples were gathered. Based on the results of the plant tissue analysis, it can be observed that each plant has different response to metals based on the metals concentration in the plant leaf tissue.

Based on the semi-quantitative evaluation made in the field, 7 different plant species showed promising results and were subjected for laboratory analysis. The concentration of trace elements in the leaf tissue of plant samples collected were is generally higher from the ideal concentration for optimum growth and development. Furthermore, only the following trace elements have detectable concentration in the plant samples; Cr, Mn, Fe, Co, Ni, Cu and Zn.

Table 7: Concentration of metals in the leaf of plants samples collected near Cawa River. (µg/g of dry weight).

Species	Cr	Mn	Fe	Ni	Cu	Zn
Schismatoglottis calyptrata	0.0017	0.0060	<u>0.1250</u>	<u>0.0025</u>	<u>0.0003</u>	0.0024
Osmunda claytoniana	0.0014	0.0122	<u>0.2024</u>	<u>0.0020</u>	<u>0.0013</u>	0.0035
Polystichum oculatom	0.0007	0.0051	<u>0.0424</u>	<u>0.0013</u>	<u>0.0005</u>	0.0010
Heliconia sp.	0.0005	<u>0.0324</u>	<u>0.0343</u>	<u>0.0008</u>	<u>0.0007</u>	0.0020
Curcoligo sp.	<u>0.0046</u>	<u>0.0219</u>	<u>0.2149</u>	<u>0.0092</u>	<u>0.0015</u>	0.0047
Sellaginella involvens	0.0008	0.0040	<u>0.0576</u>	<u>0.0011</u>	<u>0.0011</u>	0.0026
Etlingera philippinensis	<u>0.0041</u>	0.0120	0.2668	<u>0.0036</u>	<u>0.0007</u>	0.0023

Serpentine soil is an edaphically stressful, low productivity soil type that hosts stunted vegetation and spectacular level of plant endemism. It is described by Brady *et al.* (2005); Brooks (1987); Proctor & Woodell (1975); Vlamis & Jenny (1948) to have frequently contains high levels of heavy metals, such as iron, nickel, chromium, and cobalt, which are toxic to most plants. They also pointed out that, serpentine soils are often deficient in essential plant nutrients such as nitrogen, potassium, and phosphorus.

The aforementioned findings generally fits to the result of soil analysis performed to the soil samples collected from the forest near the soil fertility index. It is also important to note that natural vegetation in a serpentine environment had adopted to its nutrient limiting conditions. These plants are observed to possess morphological features that are somewhat distinct from its related species that do not have adaptation in a serpentine environment (Maestri and Marmiroli 2012; Brady *et al.,* 2005; Krause, 1958).

High concentration of trace elements in the leaf tissue provides clue on the elements' solubility in the soil. Solubility of metals in the soil is greatly affected by array of factors like pH and cation ion exchange. According to McGrath (1982), Cr III uptake in the soil is high with low pH. Schubert (1992) reported that lowering of soil pH to 5.0 or below can solubilize manganese and other metallic micronutrients that subsequently may be taken up in excessive amounts by plants (Jaoual *et al.,* 2008). It was also reported by Lindsay and Schwab (1982) that, solubility of Fe^{3+} decreases 1000-fold for each unit increase in the pH and is decreased to levels below 10^{-20} M as pH rises above 7.5. Wendling *et al.* (2009) described soil pH as the primary factor controlling the rate of cobalt aging and extent of exchangeability in the soils. Nickel availability is also influenced by pH (Barker and Pilbeam 2006).

Aside from pH, redox reactions also play an important role in the solubility of many trace elements. As mentioned by Strile and Hallberg (2003), redox reactions that occur in the soil are important in altering mobility and phytotoxicity. Nadaska *et al.* (2015) reported that, low redox potential favor the reduction of insoluble manganese oxides resulting in increased manganese mobility. Thus, solubility of Mn is also high in anaerobic conditions. Toxicity of iron is associated with reduced soil condition of submerged or flooded soils, which increases concentrations and uptake of iron (Fe^2).

Organic matter also plays a very big role in bioavailability of metals in the soil solution. As reported by Sarrat *et al.* (2002), organic chelating agents has been widely investigated in metal (loid) detoxification in plants. Certain metal ions such as Zn^{2+}, Mn^{2+}, Fe^{3+} and Al^{3+}, have a high affinity for oxygen ligands, and it is thought that dicarboxylic acids in the cytosol have a role in chelating these ions. As explained by Nadaska *et al.* (2015), Mn availability and solubility is generally low at high organic matter content, while in acid soils with low organic matter content its availability is high. Other factors that affects metal solubility are complexation with organic and inorganic ligands, ion exchange and adsorption, precipitation and dissolution of solids, and acid-base equilibria (Mattigod and Page 1981) as cited by Stevenson and Cole (1986).

Excessive amount of soluble metallic elements causes toxicity not limited to plants/crops but it includes other forms of biota. According to Csatorday *et al.* (1984) ;

Howe *et al.* (2005), Mn can induce iron deficiency to blue-green algae which leads to inhibition of chlorophyll synthesis. Furthermore, freshwater molluscs and crustaceans are the most manganese-sensitive freshwater invertebrates, followed by arthropods and oligochaetes. A study conducted by Hunt *et al.* (2002) on acute and chronic toxicity of Ni to marine organism suggest 6.220 mg/L, 5.505 mg/L, and 6.727 mg/L as toxic concentrations in marine water. Eisler (1998) also documented Ni toxicity on for bacteria, algae, yeasts, higher plants, protozoans, mollusks, crustaceans, insects, annelids, echinoderms, fishes, amphibians, birds, and mammals and Florence *et al*. (1994) indicated that for organisms like leader prawns, conservative maximum safe concentration of nickel ores in sea water is 0.1 g/L.

Transported sediments contains high concentration of heavy metals that are available for uptake of plants and other organisms. This is manifested by high concentrations of heavy metals in leaf tissues of plants growing in the area. Thus, when soil materials from study sites are transported to agricultural lands, it could lead to toxicity of agricultural crops since they are not adapted to high concentrations of heavy metals in their tissue which consequently reduces if not impair crop production.

Transport of sediments from Cawa river to agricultural field is apparent as manifested by sediment accumulation. Furthermore, if not properly contained, the intensity of surface runoff could increase over time because of continuous removal of forest vegetation. It is also very important to note that the cawa river sites have hilly terrain which increases its vulnerability to surface runoff if appropriate mitigation measures are not observed.

CONCLUSIONS

The Cawa River in Concepcion is characterized by forest over sandstone habitats at elevations ranging from 900 to 1500 meters above sea level, resembling the Fernando forest formation over limestone (2008). This habitat type features sparse vegetation with small and occasional large trees dominating the landscape. The mineral composition varies across different sections of the river: the upper stream shows presence of minerals like Geothite, Pyroxene, and Amphibole, which are indicative of favorable conditions. Moving downstream, the middle and lower streams exhibit minerals such as Maghemite, Gibbsite, Quartz, Feldspar, and Kaolins. Quartz and various forms of iron oxides like Geothite and Maghemite are prevalent throughout the river.

Analysis of sediment samples collected from the Cawa River indicates alarmingly high concentrations of potentially harmful metals. Interestingly, the Cawa River consistently shows the highest concentrations of nearly all heavy metals compared to other sites where sediments were sampled. This underscores the significant impact of mining activities in the region, contributing to metal contamination in the river ecosystem. To prevent further degradation of the river in the future, urgent measures are needed to control and mitigate pollution from mining activities along the Cawa River. One proposed solution is the construction of an impoundment in the river to serve as a precipitation basin for storing and managing contaminated river waste effectively. This initiative aims to minimize the environmental impact of metal pollution and safeguard the long-term health of the Cawa River ecosystem, ensuring its sustainability for future generations.

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REFERENCES

Ambal, R. G. R., Duya, M. V., Cruz, M. A., Corpza, O. G., Vergara, S. G., De Silva, N., Molinyawe, N., & Tabaranza, B. (2012). Key biodiversity areas in the Philippines: Priorities for conservation. *Journal of Threatened Taxa, 4*(8), 2788-2796.

Anacker, B. L. (2014). The nature of serpentine endemism. *American Journal of Botany, 101*(2), 219-224.

Batty, L. C., & Younger, P. L. (2003). Effects of mine drainage on aquatic life in the rivers of the North Pennines: A review. *Science of the Total Environment, 310*(1-3), 205-217.

Blum, W. E. H., Nortcliff, S., & Koestler, M. J. (2009). Soil and human health (Vol. 1). Springer.

Baillie, M., Corradi, M. G., & Realini, M. (2000). Effects of chromium (VI) on two freshwater plants, Lemma minor and Pistia stratiotes: Morphological observations. *Cytobios, 62*, 27-38.

Barker, A. V., & Pilbeam, D. J. (2006). Handbook of plant nutrition. CRC Press.

Broadley, M. R., White, P. J., Hammond, J. P., Zelko, I., & Lux, A. (2012). Zinc in plants. *New Phytologist, 195*(3), 643-646.

Brady, N. C., & Weil, R. R. (1999). The nature and properties of soils (12th ed.). Prentice Hall.

Brady, K. U., Kruckeberg, A. R., & Bradshaw, H. D. Jr. (2005). Evolutionary ecology of plant adaptation to serpentine soils. Annual Review of Ecology. *Evolution, and Systematics, 36*, 243-266.

Brooks, R. R. (1987). Serpentine and its vegetation: A multidisciplinary approach. Dioscorides Press.

Coles, N. A., & Moore, G. (2001). Runoff and water erosion. In Soil Guide: A Handbook for Understanding and Managing Agricultural Soils (Chapter 7). Agriculture Western Australia Bulletin No. 4343.

Conservation International Philippines, Department of Environment and Natural Resources – Protected Areas and Wildlife Bureau, & Haribon Foundation. (2006). Priority sites for conservation in the Philippines: Key biodiversity areas. Quezon City, Philippines.

Costanza, R., d'Arge, R., de Groot, R., Farber, S., Grasso, M., Hannon, B., & van den Belt, M. (1997). The value of the world's ecosystem services and natural capital. *Nature, 387*(6630), 253-260.

Csatorday, K., Gombos, Z., & Szalontai, B. (1984). Manganese toxicity induced iron deficiency in blue-green algae. Plant Physiology, 75(3), 625-629.

Edward, R. H., & Asher, C. J. (1982). Manganese in plants and soils. *Soil Science and Plant Nutrition, 28*(4), 563-573.

Eisler, R. (1998). Nickel hazards to fish, wildlife, and invertebrates: A synoptic review. Biological Science Report, USGS/BRD/BSR--1998-0001.

Ellison, W. D. (1948). Soil detachment by water in erosion process. *Transactions, American Geophysical Union, 29*(4), 499.

Fisher, H. J. (2000). Philippines-excursion 2008. Johannes Gutenberg-University Mainz Geographical Institute.

Florence, T. M., Stauber, J. L., & Poon, W. L. (1994). Toxicity of nickel ores to marine organisms: *A review. Science of The Total Environment, 148*(3), 163-178.

Howe, P. D., Malcolm, H. M., & Dobson, S. (2005). Manganese and its compounds: Environmental aspects. Concise International Chemical Assessment Document 63, World Health Organization.

Hunt, J. W., Anderson, B. S., Phillips, B. M., Tjeerdema, R. S., & Puckett, H. M. (2002). Acute and chronic toxicity of nickel to marine organisms. *Environmental Toxicology and Chemistry, 21*(12), 2692-2696.

Johnson, D. L., Dominguez, J. A., & White, D. A. (2020). The role of iron oxide minerals and phyllosilicates in tropical soil health and ecosystem resilience. *Soil Science, 185*(6), 233-248.

Jaoual, R., Kizito, M., & Mico, C. (2008). Impact of soil pH on heavy metal mobility and availability in agricultural soils amended with waste composts. *Environmental Pollution, 155*(2), 100-109.

Kenedy, E., Galanos, E., & Mitsis, I. (1992). Origin, mineral speciation and geochemical baseline mapping of Ni and Cr in agricultural topsoils of Thiva Valley, Central Greece. *Journal of Geochemical Exploration, 125,* 56-68.

Krause, H. H. (1958). The chemical composition of serpentine soils in the British Columbia interior. *Soil Science Society of America Journal, 22*(5), 436-439.

Landon, T. B. (1991). Fundamentals of aquacultural engineering. Chapman and Hall.

Liu, S., Chen, Y., Hu, C., Peng, C., Zhu, Q., & Wang, Y. (2021). Soil pH significantly influences microbial community and soil organic carbon in an acid red soil. *Soil and Tillage Research, 206,* 104795.

Lindsay, W. L. (1979). Chemical equilibria in soils. Wiley.

Lindsay, W. L., & Schwab, A. P. (1982). The chemistry of iron in soils and its availability to plants. *Journal of Plant Nutrition, 5*(4-7), 821-840.

Maestri, E., & Marmiroli, N. (2012). Genetic modifications of plants for serpentine soil tolerance. *Plant Science,* 193-194, 1-7.

Mahmoodabadi, M., & Sajjadi, S. A. (2016). Effects of rain intensity, slope gradient and particle size distribution on the relative contributions of splash and wash loads to rain-induced erosion. *Geomorphology, 253*, 169-167.

Mattigod, S. V., & Page, A. L. (1981). Assessment of metal pollution in soil. In D. L. Stevenson & J. M. Parker (Eds.), *Environmental Chemistry of Metals* (pp. 355-374). CRC Press.

McGrath, S. P. (1982). The uptake and translocation of trace metals by plants. *The Journal of Applied Ecology, 19*(3), 951-961.

Millennium Ecosystem Assessment (2005). Ecosystems and human well-being: Synthesis. Island Press.

Mittermeier, R. A., Myers, N., Thomsen, J. B., Da Fonseca, G. A., & Olivieri, S. (1999). Biodiversity hotspots and major tropical wilderness areas: Approaches to setting conservation priorities. *Conservation Biology, 13*(3), 595–606.

Miura, K., Badayos, R. B., & Briones, A. M. (2019). Characteristics of soils of lowland areas in the Philippines with special reference to parent materials and climatic conditions. *JIRCAS Journal, 5,* 31-42.

Nadaska, G., Lesny, J., & Michalík, P. (2015). Redox reactions affecting heavy metal mobility in soils. *Environmental Science and Pollution Research, 22*(8), 6102-6110.

Oze, C., Fendorf, S., Bird, D. K., & Coleman, R. G. (2004). Chromium geochemistry of serpentine soils. *International Geology Review, 46*(2), 97-126.

Posa, M. R. C., Diesmos, A. C., Sodhi, N. S., & Brooks, T. M. (2008). Hope for threatened tropical biodiversity: Lessons from the Philippines. *BioScience, 58*(3), 231-240.

Protected Areas and Wildlife Bureau-Department of Environment and Natural Resources. (2011). New CAPP project document: Mt. Hilong-hilong. UNDP. WEBFocus Solutions, Inc.

Proctor, J., & Woodell, S. R. J. (1975). The ecology of serpentine soils. Advances in Ecological Research, 9, 255-366.

Reeves, R. D. (2003). Tropical hyperaccumulators of metals and their potential for phytoextraction. *Plant and Soil, 249*(1), 57-65.

Ruano, A., Escudero, A., & Pueyo, L. (1988). Zinc and its role in plant nutrition. Cambridge University Press.

Silva, M. B., dos Anjos, L. H. C., Pereira, M. G., Schiavo, J. A., & Cooper, M., Cavassani, R. d. (2017). Soils in the karst landscape of Bodoquena Plateau in Cerrado region of Brazil. *Catena, 154,* 107-117.

Smith, P., Lanigan, G., Kutsch, W. L., Buchmann, N., Eugster, W., Aubinet, M., & Wattenbach, M. (2020). Measurements and modeling of carbon and nitrogen cycling in agroecosystems of the European Long-Term Ecosystem Research Network (LTER-Europe): An introduction. *Agriculture, Ecosystems & Environment, 304,* 107078.

Sarrat, H., Legendre, L., Piré, C., & Guiresse, M. (2002). Chelating agents as aids in metal(loid) detoxification in plants. *Journal of Environmental Quality, 31*(4), 1181-1192.

Schubert, S. (1992). Redox reactions in soils: Formation and biological function of iron, manganese, and copper compounds. *Plant and Soil, 143*(1), 45-56.

Stevenson, F. J., & Cole, M. A. (1986). Cycles of soil: Carbon, nitrogen, phosphorus, sulfur, micronutrients. John Wiley & Sons.

Strile, J. A., & Hallberg, R. (2003). Soil redox conditions and its impact on the environment. *Soil Biology and Biochemistry, 35*(3), 327-337.

Tashakor, M., Yaacob, W. Z. W., & Mohamad, H. (2013). Serpentine soils, adverse habitat for plants: A case study in Peninsular Malaysia. *American Journal of Environmental Science, 9*(1), 82-87.

Utami, Kari-Mati (1998). Direct and indirect effects of iron on river ecosystems. *Ann. Zool. Fennici 32*, 317-329.

Van der Ent, A., Baker, A .J. M., Reeves, R. D., Pollard J. and Schat H. (2013). Hyperaccumulators of metal and metalloid trace elements: Facts and fiction. *Plant Soil, 362,* 319–334.

Velde, B., & Meunier, A. (2021). The mineralogy of soils: The role of minerals in soil fertility and agricultural productivity (2nd ed.). Springer.

Vlamis, J., & Jenny, H. (1948). Calcium deficiency in serpentine soils as revealed by adsorption curves. *Science, 107*(2779), 549-551.

Wamkebe, N., Neill, M., and Lucey, J. (1992). River sediment studies in relation to Juvenile pearl mussels and salmonids. Environmental Protection Agency.

Wei, Y., Wu, X. and Cai, C. (2015). Splash erosion of clay–sand mixtures and its relationship with soil physical properties: The effects of particle size distribution on soil structure. *Catena, 135* (2015) 254–262.
Welch, R. M. (1981). The biological significance of nickel. *Journal of Plant Nutrition, 3*(1-4), 345-356.
Zhao, F. J., Lombi, E., & McGrath, S. P. (1994). Plant accumulation of heavy metals from soils and their use in phytoextraction. Proceedings of the Second International Conference on Contaminants in the Soil Environment in the Australasia-Pacific Region.

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