

Assessment of Heavy Metal Accumulation in Agricultural Crops in a Nickel Mining Site in Agusan Del Norte

Jobelle Jayoma Capilitan^{1,2*} and Ian Dominic Flormata Tabañag^{1,3}

¹*School of Engineering, University of San Carlos, Talamban, Cebu City, 6000, Philippines*

²*Caraga State University, Butuan City, Philippine*

³*Philippine Council for Industry, Energy, and Emerging Technology Research and Development, Department of Science and Technology (DOST-PCIEERD), Bicutan, Taguig City, 1631, Philippines*

ABSTRACT

Ni laterite exploration by surface mining is destructive to the local biological landscape. A sustainable approach is mine restoration using vegetation. Nonetheless, substantial concentrations of heavy metals are present in areas impacted by anthropogenic activities, such as mining. Crops may absorb heavy metals from the soil, which can have adverse effects on the land, water, and human health. This study assesses the accumulation of heavy metals (Cr, Cu, Ni, Mn, and Zn) in the soil and the consumable parts of crops (roots, leaves, and fruits) at the nickel laterite mining site in Tubay, Agusan del Norte, along with the potential health risks associated with human intake. The concentration of heavy metals in the soil and crops significantly exceeds the maximum permissible limit (MPL) set by the FAO and WHO. The concentration of heavy metals in the edible sections is ranked as follows: Mn > Ni > Zn > Cr > Cu. The Target Hazard Quotient (THQ) assessed non-carcinogenic risks, indicating that Cr, Cu, Mn, and Ni exceeded 1. The THQ number signifies significant health risks associated with prolonged consumption of the plant's edible parts.

Keywords: Health risk, heavy metal accumulation, nickel mine, target hazard quotient, XRF

INTRODUCTION

Agriculture is essential to the nation's food security. In an agrarian country like the Philippines, agriculture constitutes the foundation of its economy. For many years, agriculture-related activities have been a primary source of income and employment (Philippine Statistics Authority, 2024).

Mining has also significantly contributed to nation-building, economic stability, and

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E-mail addresses:

jjcapilitan@carsu.edu.ph (Jobelle Jayoma Capilitan)

ian.tabanag@pcieerd.dost.gov.ph (Ian Dominic Flormata Tabañag)

* Corresponding author

technological advancements in the Philippines. In 2022, the Philippines led the global nickel (Ni) source market, accounting for an estimated 11%–12% of global output (GlobalData, 2022; Moon, 2024), ranking second among the world's nickel-producing countries (Moon, 2024). As of June 2024, the country has 36 operational metallic mines, primarily concentrated on nickel, with 24 mining companies located in the Caraga region (Mines and Geosciences Bureau, 2024). The Caraga region is recognized as the primary nickel producer, accounting for 46.57% of the overall metallic mineral production value. Nonetheless, the continuous effort to achieve economic stability, involving agriculture and mining operations as pivotal sectors in the region's development, presents threats to agricultural quality and the environment.

Mining operations, particularly the extraction of nickel (Ni) from laterite ores using open-pit methods, exacerbate the accumulation of heavy metals, leading to significant ecological and human health concerns (Setia et al., 2023) due to mine waste, including tailings, dams, and overburden waste rock sites (Apodaca et al., 2018; Gavhane et al., 2021). Mining activities are crucial in the release of numerous heavy metals into the environment, substantially contributing to contamination by copper, iron, manganese, and zinc (Haghighizadeh et al., 2024; Hu et al., 2024). Hence, in the absence of organic decomposition, they accumulate in the soil, endangering plants, human health, and the environment (Sadak, 2023).

Heavy metal contamination of soil can harm humans through direct ingestion or contact with contaminated soil and the food chain (Wuana & Okieimen, 2011). The conditions of the soil and land pollution are significant concerns regarding the safety of the food supply. The challenge of ensuring that food is safe to consume is essential worldwide. Compared to the routes of inhalation or skin contact exposure, food consumption is acknowledged as the principal means by which humans are exposed to various environmental toxins; this accounts for over 90 percent of the total intake (Akinyele & Shokunbi, 2015). It is fundamentally dependent on the condition of the soil, and the detrimental effects that contaminants such as heavy metals have had on crop quality have put human health at risk. The accumulation of heavy metals in crops is an increasing concern, as elevated levels of toxic elements can jeopardize plant health and present significant risks to human consumption. According to their potential nutritional functions, the World Health Organization (WHO) divided trace elements into three categories: potentially toxic heavy metals, elements of probable physiological importance, such as manganese (Mn) and nickel (Ni), and essential elements, like chromium (Cr), copper (Cu), and zinc (Zn) (Muñoz-Olivas & Cámara, 2007). However, as carcinogenic substances, excessive and continuous ingestion and exposure to these heavy metals may damage DNA, proteins, and lipids by creating free radicals (Gupta et al., 2022; Sadak, 2023).

Numerous studies have demonstrated that the accumulation of heavy metals is a risk to human health (Fodoué et al., 2022; Ghaneei-Bafghi et al., 2024; Haghighizadeh et al.,

2024; Hu et al., 2024; Setia et al., 2023). Concerns emerge when crop cultivation for mine rehabilitation is executed without prior evaluation of heavy metal pollution. The ramifications of heavy metal contamination in agriculture are substantial, underscoring the necessity for soil and crop compatibility evaluations, an essential component of post-mining operations.

This study evaluates the accumulation of chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), and zinc (Zn) on selected crops that were grown in the rehabilitated area at the nickel mining site in Tubay, Agusan del Norte. It compares the results to the recommended amounts for each element set by the World Health Organization (WHO) and the Food and Agriculture Organization (FAO).

An X-ray fluorescence (XRF) spectroscopy investigation of the soil is carried out to ascertain the level of heavy metals in the soil and the crops. According to a study by Peralta et al. (2020), in-situ soil studies using XRF spectroscopy have been proven to be an effective tool for detecting the amount of metal contamination. This technology can concurrently determine the overall concentration of several different elements at a relatively low running cost and with a minimal sample requirement (McComb et al., 2014). The technology known as X-ray fluorescence, which is more usually abbreviated as XRF, is both quick and non-destructive. These benefits are compared to ICP-OES and ICP-MS, which provide extensive preparation for solid samples. Comparative research demonstrates that XRF is an excellent method for analyzing contaminated soils and crops because it does not degrade samples during analysis (Kim et al., 2022; McComb et al., 2014).

This study also investigates the potential adverse health effects that may be caused by heavy metals in the edible parts of crops if ingested by adults, using the bioconcentration factor (BCF) and the Target Hazard Quotient (THQ). The health risk assessment (HRA) method, such as the THQ, has been utilized in the investigations concerning the intake of vegetables exposed to toxic metals in the area (Gupta et al., 2022; Kharazi et al., 2021; Li et al., 2018). This information, which has never been

investigated, is crucial to assessing and determining post-mining considerations and mine rehabilitation alternatives. This research is limited to the nickel mining site in Tubay, Agusan del Norte, focusing on the crops grown in the rehabilitated area.

MATERIALS AND METHODS

Study Area

The nickel mining site is located within the municipal boundaries of Tubay, Jabonga, and Santiago in Agusan del Norte of Region XIII (Caraga), Philippines (Figure 1). It lies 9°10'30" north and 125°29'30" east at an elevation ranging from 310 to 325 meters above sea level. The mining site is inside a 4,995-hectare region bordered by water features, including the Kaliniwan River to the east, Lake Mainit to the north, and Butuan Bay to the

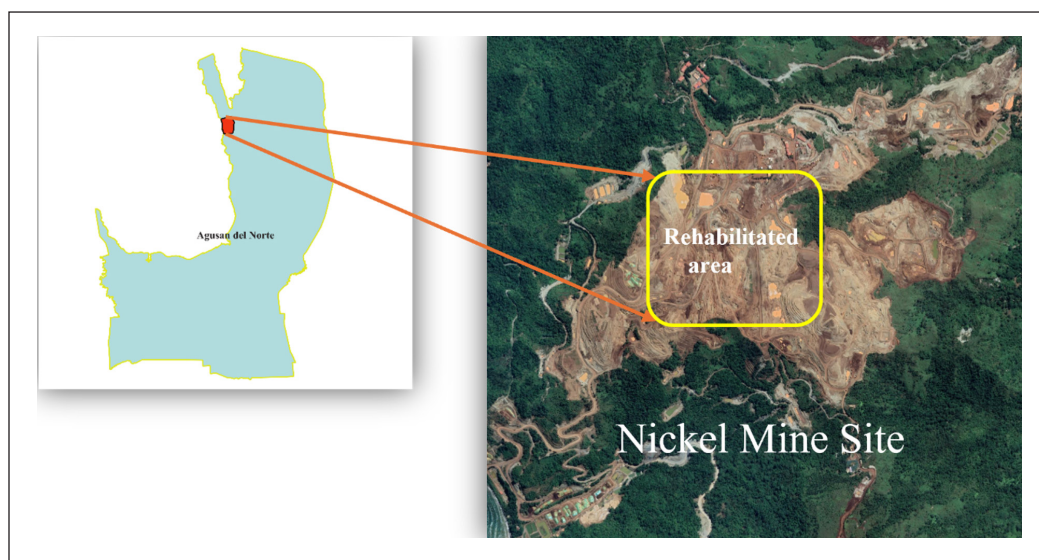


Figure 1. Study area

west. The site is characterized by a tropical climate, receiving an annual rainfall of 3,978.43 mm based on precipitation data from 2004 to 2024 (Climate Engine, 2024).

The surface mining and associated activities have caused significant land degradation at the site. As of 2021, the mine site has undergone post-mining operations, where approximately 20% of the mined-out area has been partially rehabilitated through cropping or growing agricultural plants for food consumption.

Sampling and Analysis

The nickel mine site has partially restored the excavated sections by cultivating crops intended for human consumption. Preliminary evaluation and suitability analysis, however, were not performed. This study collects plant samples at their harvesting stage at rehabilitated locations, including eggplant, lady's finger, Malabar spinach, taro, and tomato, and the edible portion of the plant (root, leaf, fruit) was saved for individual analysis. Subsequently, the samples were cleaned and rinsed with distilled water to eliminate contaminants. Plant specimens are chopped, air-dried for 16 hours, oven-dried at 80 degrees Celsius for one hour, and ground into powder. Representative samples for each crop weighing approximately 20 grams were enclosed in airtight plastic bags to avert moisture ingress and contamination prior to XRF analysis. Figure 2 shows the sample preparation and analysis.

Epson 1 EDXRF was utilized to determine chromium, copper, manganese, nickel, and zinc levels in the soil and the crop samples. Standard operating procedures and calibration protocols were meticulously followed during the laboratory XRF analysis. Approximately

0.5 g of the powdered samples (soil and crops) were placed in a 3.6 µm transparent Mylar film and inserted into a 30-mm container cup. This technique examines loose powdered substances, offering the X-ray analyzer a level surface and elevating the sample above the beam. Finely ground samples demonstrate increased homogeneity and reduced void spaces, improving analytical precision.

To determine if the levels of the heavy metals are within limits, the maximum allowable limits for Cr, Cu, Mn, Ni, and Zn in soil and vegetables are listed in Table 1 (Food and Agriculture Organization, 2004; World Health Organization, 1996).

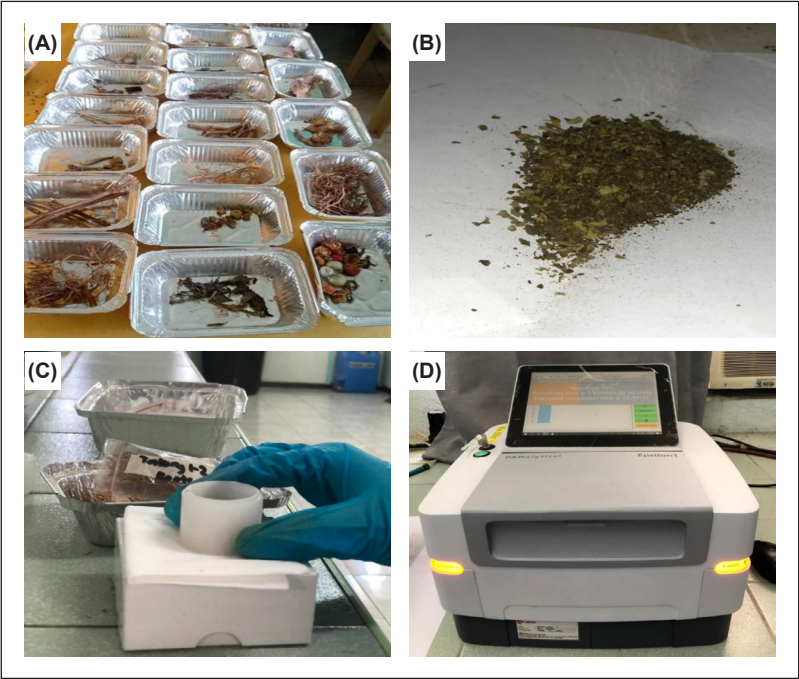


Figure 2. Sampling preparation and analysis: (A) Plant samples separated by parts while edible portions are subjected to analysis; (B) Plant samples in decreased particle size; (C) Samples placed in the 30-mm container cup for analysis; (D) Epson 1 EDXRF for X-ray Fluorescence spectroscopy analysis

Table 1
Maximum Permissible Limit (MPL) of heavy metal concentrations in soil and vegetables according to WHO/FAO

Heavy metal	Maximum permissible level in soil in mg/kg	Maximum permissible level in vegetables in mg/kg
Chromium (Cr)	110	1.3
Copper (Cu)	100	10
Manganese	2000	500
Nickel (Ni)	50	10
Zinc (Zn)	200	99.4

Statistical Analysis

The relationship between heavy metals is determined using Pearson's correlation analysis, while a simple linear regression approach assessed the relationships between heavy metals in the soil and crops.

Bioconcentration Factor (BCF)

According to Li et al. (2012), the accumulation factor predicts the possible transfer of contaminants, such as heavy metals, from the soil to the portion of crops humans consume. If the BCF is less than 1, the plant can only ingest metals and cannot accumulate them. In any other case, if BCF is less than 1, the plant will store metals in the soil (Kharazi et al., 2021; Sulaiman & Hamzah, 2018). Based on Equation 1, BCF is given by:

$$BCF = \frac{\text{metal concentration in the edible part of the crop (dw)}}{\text{metal concentration in root – soil (dw)}} \quad [1]$$

Health Risk Assessment

The potential health risk of heavy metals in crops was assessed using the target hazard quotient (THQ), using the estimated daily intake (EDI) and oral reference dose (RfD) (Khan et al., 2013; Kharazi et al., 2021; USEPA, 1989). The maximum tolerable daily intake is shown in Table 2. The THQ describes the non-carcinogenic health risk associated with the hazardous element. Non-carcinogenic health consequences are unlikely if THQ is <1. If the THQ is >1, health issues may occur. Non-carcinogenic health consequences are not statistically likely, with a THQ greater than 1 (Antoine et al., 2017). THQ is calculated as illustrated in the studies of (Antoine et al., 2017; Khan et al., 2013; Kharazi et al., 2021) presented in Equation 2, while EDI is calculated using Equation 3 for ingested substrate:

$$THQ = \frac{EDI}{RfD} \quad [2]$$

$$EDI = \frac{E_{FR} \times Ed \times IR \times C}{BWa \times ATn} \times 10^{-3} \quad [3]$$

Where EFR is the exposure frequency to heavy metal (350 days/year), Ed is the exposure duration (40 years for non-carcinogenic effects), IR is the crop ingestion rate (65 g/day), C is the concentration in a wet weight of the trace element in the crop, BWa as the body weight reference for an adult of 70 kg, and the exposure time considering 365 days in 40 years, for ATn (Antoine et al., 2017; Hassan et al., 2022). Ma Reference dose (RfD) values for ingested elements are listed in Table 3.

Table 2
Maximum tolerable daily intake

Heavy Metal	MTDI (mg/day)
Chromium (Cr)	0.035–0.2
Copper (Cu)	2.5–3
Manganese (Mn)	2–5
Nickel (Ni)	0.1–0.3
Zinc (Zn)	60–65

Source: Gebeyehu & Bayissa, 2020

Table 3
Reference dose (RfD) values

Heavy Metal	RfD _{ing} (mg/kg/day)
Chromium (Cr)	3.00×10^{-3}
Copper (Cu)	3.00×10^{-4}
Manganese (Mn)	$1.4.00 \times 10^{-1}$
Nickel (Ni)	2.00×10^{-2}
Zinc (Zn)	3.00×10^{-1}

Source: Zheng et al., 2015

RESULTS AND DISCUSSIONS

Heavy Metal Level in the Soil

Table 4 presents the amounts of heavy metals in the soil, as determined by X-ray fluorescence (XRF) spectroscopy, specifically for chromium, copper, manganese, nickel, and zinc. The values were contrasted with the Maximum Permissible Limit (MPL) set by the World Health Organization (WHO) and the Food and Agriculture Organization (FAO). The data reveal that all soil samples have levels exceeding the permissible limits.

WHO/FAO stipulates that the maximum allowable limit for chromium (Cr) in soil is 110 mg/kg. The data presented in Table 4 indicate that the chromium concentration in the soil significantly exceeds the threshold across all samples, varying from 4,460 mg/kg to 10,276.67 mg/kg, which is 40–93 times higher than the safe limits.

The elevated concentration of copper indicates a marginal exceedance of the permissible threshold of 100 mg/kg established by WHO/FAO for all soil samples. Copper values in the soil samples range from 111.03 to 165.73 mg/kg, 1.1 to 1.6 times above the permissible limit. Although the Cu content is slightly lower than that of other heavy metals under study, it is still a cause of concern due to the possible crop accumulation and long-term degradation. The manganese content in the soil also presents a slight exceedance of the MPL, which is 1.2 to 2.3 times greater than the WHO/FAO limit of 2,000 mg/kg. Mn in the soil ranges from 2390 mg/kg to 4516.67 mg/kg.

Table 4
Heavy metal levels in the soil in comparison to the Maximum Permissible Limit (MPL)

Soil samples	Cr	Cu	Mn	Ni	Zn
S _{Eggplant}	10,276.67	165.73	4,330.00	8,623.33	404.23
S _{Lady's Finger}	4,460.00	111.03	2,390.00	3,666.67	597.40
S _{Malabar spinach}	7,160.00	143.57	4,516.67	5,356.67	450.00
S _{Taro}	9,313.33	143.70	4,413.33	9,483.33	438.30
S _{Tomato}	7,110.00	159.30	3,570.00	4,943.33	337.77
MPL	110.00	100.00	2,000.00	50.00	200.00

Nickel concentrations in soil samples markedly exceed the maximum allowable limit of 50 mg/kg, categorizing it as a serious pollutant. XRF data reveal that nickel concentrations are raised by a factor of 73 to 189, ranging from 3,666.67 to 9,483.33 mg/kg. Zinc concentrations surpassed the maximum permissible limit by 1.7 to 3 times, with values between 337.77 mg/kg and 597.40 mg/kg.

Cr and Ni levels are critically high, while Cu, Mn, and Zn, although exceeding the limits, are significantly less hazardous than Cr and Ni. A strong positive correlation is observed between Cr and Ni (0.90), Cr and Mn (0.90), Cr and Cu (0.78), and Cu and Mn (0.76), as illustrated in Figure 3. Conversely, Zn exhibits negative correlations with Mn (-0.54), Cr (-0.52), and Cu (-0.49). The negative results signify that an increase in Zn concentration correlates with a drop in the levels of these metals.

The regression analysis establishes that there is a significant positive correlation between Cr and Ni ($r = .90, p < 0.05$), Cr and Mn ($r = .90, p < 0.05$), Cr and Cu ($r = .78, p < 0.05$), and Cu and Mn ($r = .76, p < 0.05$). This information suggests they share the same geochemical behavior or identical contamination sources. On the contrary, there is a weak negative correlation for Mn and Zn ($r = .54, p < 0.05$) and Cr and Zn ($r = .52, p < 0.05$), suggesting that higher Zn levels correspond to lower Mn and Cr levels, respectively, due to competitive interactions or distinct source of contamination. While Cu and Zn ($r = 0.49, p > 0.05$), Ni and Zn ($r = .22, p < 0.05$) exhibit non-significant correlations, indicating that Cu and Ni are not predictors of Zn in the soil.

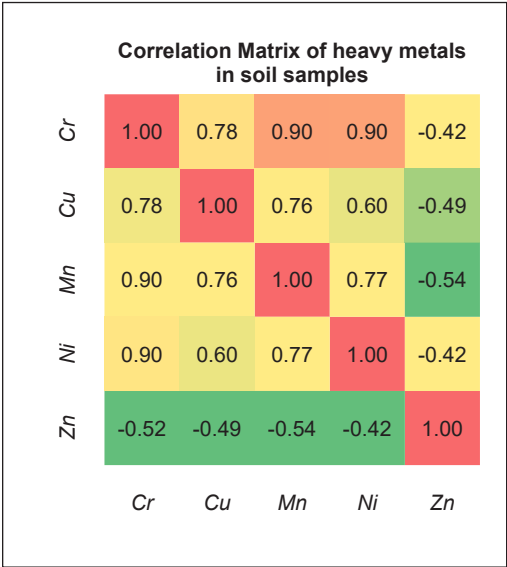


Figure 3. Correlation matrix of heavy metals in soil samples

Heavy Metal Levels in the Crops

Concentrations of heavy metals in the edible portions of selected crops, as ascertained by X-ray fluorescence (XRF) spectroscopy, such as the Cr, Cu, Mn, Ni, and Zn, are listed in Table 5. The Maximum Permissible Limit (MPL) was established by the World Health Organization (WHO), and the Food and Agriculture Organization (FAO) served as a reference point for comparison. The readings indicate that the concentration of heavy metals present in the edible portions of the crop has significantly surpassed the maximum allowed limit.

Table 5

Heavy metal levels in the crops in comparison to the Maximum Permissible Limit (MPL)

Crop Samples	Cr	Cu	Mn	Ni	Zn
Eggplant	133.67	44.73	285.27	168.67	84.97
Lady's finger	58.73	20.73	159.43	62.07	101.03
Malabar spinach	183.57	-	785.77	408.23	143.8
Taro	90.73	45.1	118.47	114.33	152.43
Tomato	90.27	45.63	161.87	86.67	108.77
MAL	1.3	10	500	10	99.4

Chromium (Cr) has exceeded the limit by about 45 to 141 times the MPL of 1.3 mg/kg. The Cr content in crops ranges from 58.73 to 183.57 mg/kg, where eggplant dominates the Cr accumulation in its edible portions. Chromium (VI) compounds have severe and potentially deadly effects on the respiratory, cardiovascular, gastrointestinal, hepatic, renal, and neurological systems when ingested in significant quantities for an extended period (Tchounwou et al., 2012; UK Health Security Agency, 2022). According to research by the U.S. Department of Health and Human Services (2012), individuals who unintentionally or purposefully ingested high doses of chromium (VI) compounds experienced severe effects on their respiratory systems, cardiovascular systems, gastrointestinal systems, hematological systems, hepatic systems, renal systems, and neurological systems, which either resulted in death or required medical treatment.

A slight exceedance of the permissible limit of copper is noted in the edible components of the sample crops. Approximately, Cu content is 2 to 4.5 times exceeding the threshold established by the WHO/FAO, with values ranging from 20.73 mg/kg to 45.63 mg/kg. There was no detected Cu in Malabar spinach. The consumable portion of the eggplant possesses the highest Cu content. This matches a Bangladeshi study that found no copper in Malabar spinach (Fahad et al., 2015). At higher concentrations, copper is stored in the liver, brain, and kidneys (Royer & Sharman, 2023). Copper poisoning is a leading contributor to the development of Wilson's disease. Oxidative stress, DNA damage, and reduced cell development are all caused by an excess of copper (Oe et al., 2016).

The permissible limit of manganese (Mn) in the crops by WHO/FAO indicates that the Mn level of Malabar spinach of 785.77 mg/kg is above the 500 mg/kg limit by 1.5 times. All other crops examined have exhibited reduced Mn values. Excessive manganese consumption leads to motor dysfunction and reduced neurotransmitter levels, as manganese primarily impacts the central nervous system, similar to Parkinson's disease (Flora, 2014; Keen et al., 2012).

Ni level in the edible portions for all sample crops highly exceeded the MPL by 6 to 40 times the permissible limit of 10 mg/kg. The highest Ni content is at 408.23 mg/kg for Malabar spinach. Acute exposure to nickel compounds can result in nausea, vomiting,

diarrhea, dizziness, cough, and shortness of breath, while a lethal overdose of nickel compounds can occur (Das et al., 2019; Genchi et al., 2020; Public Health England, 2009). Nickel exposure ranges from acute skin contact to occupational inhalation (Chen et al., 2017). Ni is found in both natural sources and anthropogenic activities and is present in many applications due to its unique physicochemical properties (Genchi et al., 2020).

Zinc level in crops is limited to 99.4 mg/kg by the WHO/FAO. All Zn content in the crops surpassed the limit except eggplant (84.97 mg/kg). Taro has the highest Zn content, at 152.43 mg/kg, approximately 1.5 times the MPL. Apparent signs of Zn toxicity are nausea, vomiting, epigastric discomfort, lethargy, and weariness. (Nazir et al., 2015; Sandstead, 2015; Wallig & Keenan, 2013), acute poisoning caused by zinc can cause abdominal pain, nausea, and disorientation. The zinc amount used to induce vomiting ranged from 225 to 400 mg.

Cr and Ni levels in the crops pose severe health risks, with high exceedance of the limit, while Cu and Zn exceeded the MPL moderately. Malabar spinach has the highest amounts of Cr, Mn, and Ni. This is because leafy vegetables absorb more heavy metals than roots and fruit vegetables (Mishra & Kumari, 2021; Sultana et al., 2022). This helps explain why fruit vegetables such as eggplant, lady’s finger, and tomato have reduced Cr, Mn, and Ni contents. Studies suggest that root crops like taro are high in Cr and Ni (Mishra & Kumari, 2021; Sultana et al., 2022).

Figure 4 depicts the average concentration of heavy metals (Cr, Cu, Mn, Ni, and Zn) in the consumable portions of the crops and their variability in the samples. Manganese exhibits the highest concentration, accompanied by considerable diversity among crops. Furthermore, Ni has a high concentration with considerable variability, suggesting distinct accumulating patterns across all crops. Cr, Ni, and Zn values present moderate

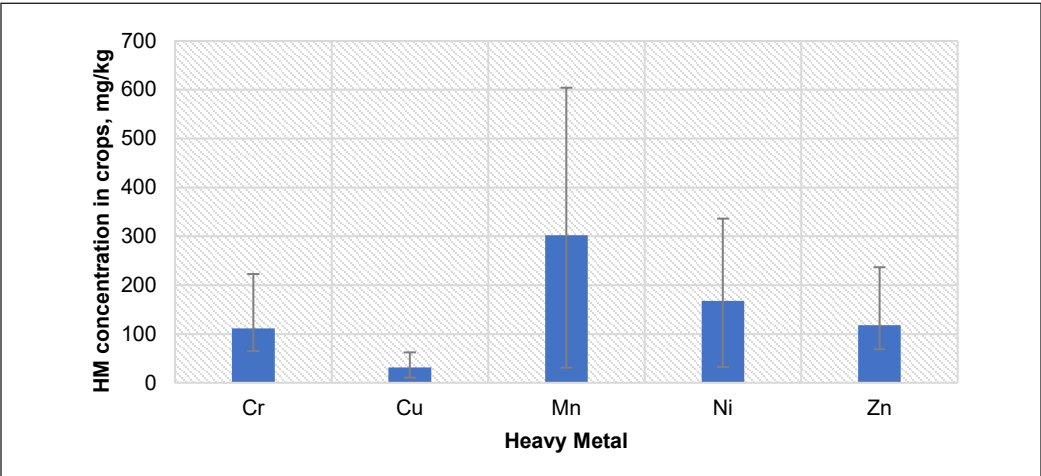


Figure 4. Heavy metal concentrations in the edible portion of the crops

concentration and variability, while Cu has the lowest concentration with noticeable variations within the crop. The heavy metal in edible portions of the crops follows the order Mn>Ni>Zn>Cr>Cu.

Bioconcentration Factor

Figure 5 shows the bioavailable metal fraction or the Bioconcentration Factor (BCF) for the edible portions under study. The BCF refers to the total quantity of metal the crop takes from the soil. It is the principal pathway for potentially hazardous metals to enter the food chain, concerning food safety (Akinyele & Shokunbi, 2015; Gebeyehu & Bayissa, 2020). Eggplants have the lowest BCF for Cu concentration at 0.004, which means less copper accumulates in their edible portion. The calculated BCF in eggplant is highest for Mn at 0.028, followed by Ni (0.016), Cr (0.013), and Zn (0.008). Mn (0.06) and Zn (0.023) BCF values of the lady’s finger are relatively higher among the elements present in its edible portions, which suggests that Mn and Zn are absorbed more in the lady’s finger compared to Cu (0.005), Cr (0.013), and Ni (0.014). Notably, Mn, Ni, and Cr BCF levels in Malabar spinach are highest at 0.110, 0.057, and 0.026. Zn (0.020) is also notably high in Malabar spinach. This shows that Malabar spinach absorbs more heavy metals than other assessed crops in this study. The BCF values for taro are lowest for Cu (0.005), followed by Cr (0.010), Ni (0.012), Mn (0.013), and Zn (0.016). In tomatoes, Cu also has the lowest BCF (0.006), with the highest at Ni (0.023). Calculated values for Cr, Ni, and Zn are 0.013, 0.0.12, and 0.015, respectively. For all crops, Cu BCF is the lowest.

These findings indicate that at BCF< 1, the bioavailability of the Cr, Cu, Mn, Ni, and Zn in the edible portions of the crop samples under study is minimal. Plants do not store the metals in their tissues but only absorb them.

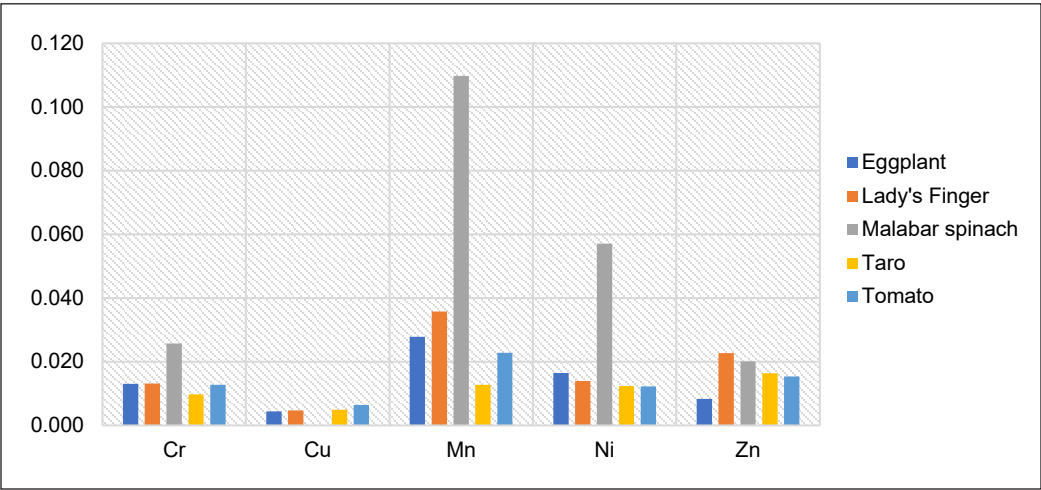


Figure 5. Bioconcentration Factor (BCF)

Health Risk Assessment

Table 6 shows the estimated daily intake (EDI) calculation, considering the adult population exposed for 40 years, assuming a daily intake of 65 g of the crops under study. Based on the result, Cr values are a little over the MTDI values, while Cu, Mn, Ni, and Zn values for all crops are below the suggested maximum tolerable intake values in the study presented by Gebeyehu and Bayissa (2020). However, when crops are consumed altogether in a day, Ni and Cr exhibit a total EDI of 0.75 mg/day and 0.5 mg/day, respectively, exceeding the MTDI for Ni and Cr. The combined EDI in the crops is still below the maximum limit for Mn, Cu, and Zn.

In Table 7, THQ calculation revealed that most crops have THQ>1, which means there is a high potential for damaging health effects if consumed over an extended period. Copper THQ values for all crops are significantly larger than the other metals under investigation and are most concerning. The highest THQ value was found for tomatoes (135.44) and taro (133.44). When consumed excessively, copper toxicity may lead to oxidative stress, DNA damage, and cell development suppression (Oe et al., 2016).

THQ values for Cr, Mn, and Ni are also significantly above 1 and are alarming due to their substantial health effects. The human respiratory, cardiovascular, gastrointestinal, hepatic, renal, and neurological systems can all be adversely affected by chromium (Cr-VI),

Table 6
Estimate Daily Intake (EDI) values in comparison to Maximum Tolerable Daily Intake (MTDI) in mg/day

Crop samples	Estimate Daily Intake (EDI) mg/day				
	Cr	Cu	Mn	Ni	Zn
Eggplant	0.12	0.04	0.25	0.15	0.08
Lady's finger	0.05	0.02	0.14	0.06	0.09
Malabar spinach	0.16	0.00	0.70	0.36	0.13
Taro	0.08	0.04	0.11	0.10	0.14
Tomato	0.08	0.04	0.14	0.08	0.10
Total EDI for all crops	0.50	0.14	1.35	0.75	0.53
MTDI (mg/day)	0.035–0.2	2.5–3	2.0–5.0	0.1–0.3	60–65

Table 7
Target Hazard Quotient (THQ) of individual metals

Crop samples	Cr	Cu	Mn	Ni	Zn
Eggplant	39.67	132.77	1.81	7.51	0.25
Lady's finger	17.43	61.54	1.01	2.76	0.30
Malabar spinach	54.48	-	5.00	18.17	0.43
Taro	26.93	133.86	0.75	5.09	0.45
Tomato	26.79	135.44	1.03	3.86	0.32

with some of these reactions having the potential to be fatal (Tchounwou et al., 2012; UK Health Security Agency, 2022) while nickel toxicity can cause nausea, vomiting, diarrhea, dizziness, cough, and shortness of breath, and may lead to death (Das et al., 2019; Genchi et al., 2020; Public Health England, 2009). Values for Zn, however, are less than 1.

A Hazard Quotient is a dimensionless figure representing the likelihood of an individual experiencing adverse health impacts. The elevated THQ values for Cu, Cr, Ni, and Mn in the crop samples indicate a possible long-term health hazard associated with their consumption. The data suggest that regular intake of these crops may pose a considerable health risk, particularly to the community and local consumers who are exposed to them.

CONCLUSION

The X-ray fluorescence (XRF) spectroscopy analysis determines heavy metals in the soil and crops. The heavy metal accumulation (Cr, Cu, Mn, Ni, Zn) in the soil is high and beyond the maximum allowable limit by the World Health Organization (WHO). These accumulations are translated to the crops, and the edible portions are analyzed to determine the levels of heavy metals. Cr, Cu, Mn, Ni, and Zn display values that exceed the maximum permissible values by the WHO. Cr and Ni levels in the crops pose severe health risks, with high exceedance of the limit, while Cu and Zn exceeded the permissible limit moderately. Manganese is most significant in the edible portions of the sample crops, following the order $Mn > Ni > Zn > Cr > Cu$. Malabar spinach, a leafy vegetable, has the most Cr, Mn, and Ni since leafy vegetables absorb more heavy metals than roots and fruits. The BCF for all crops is below 1, signifying that crops do not amass significant concentrations of heavy metals in their consumable parts. The Health Risk Assessment (HRA) using Target Hazard reveals elevated levels of Cu, Cr, Ni, and Mn. This suggests that consuming substantial quantities of crops daily may have long-term health risks. This study reveals that the assessed crops (eggplant, lady's finger, Malabar spinach, taro, and tomato) pose a health hazard and are unsuitable for growing in the mined-out nickel mine site. Consequently, the intentional rehabilitation of the mine for agricultural purposes may not be an optimal solution for the present condition of the mining site. Additional research may be required to advance crop production using soil enhancers that are appropriate for agricultural practices.

Despite being profitable, growing edible crops can have many adverse effects. Mining companies should have a thorough evaluation, feasibility study, and soil assessment to ensure that crops are suitable and safe for consumption. Creating a database of crops suited for rehabilitation would be beneficial, and creating maps that match those crops' suitability will provide more specific information regarding the management of mine revegetation and planning. Phytomining and renewable energy (solar and wind) sourcing will be good alternatives, as this will help minimize health risks in the food chain. However, data on this is not yet available on the site. Further studies and site validation are needed.

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