

ANALYSIS OF CHEMICAL FRACTIONS AND EVALUATION OF COPPER (Cu) CONTAMINATED LEVELS IN SOIL SAMPLES OBTAINED FROM A Pb/Zn MINING SITE LOCATED IN HICH VILLAGE, THAI NGUYEN PROVINCE

Vuong Trung Xuan*, Phan Thanh Phuong, Pham Thi Thu Ha

TNU - University of Sciences

ARTICLE INFO	ABSTRACT
Received: 08/5/2024	Currently, the contamination of heavy metals within ore mining regions is pronounced both domestically in Vietnam and globally. The primary objective of this study is to elucidate the chemical speciation of copper (Cu) and conduct an assessment of the magnitude and probability of contamination of Cu in soil samples procured from the Pb/Zn mining, at the Hich village, Dong Hy district, Thai Nguyen province, in order to furnish critical data pertinent to the environmental stewardship of soil resources within this geographical domain. The determination of Cu's chemical fractions in soil specimens was conducted following Tessier's extraction procedure, utilizing the ICP-MS technique. Results revealed that the mean Cu concentrations across the five tailing samples ranged from 15.524 to 35.192 mg kg ⁻¹ , while in the seven agricultural samples, concentrations ranged between 15.359 to 21.198 mg kg ⁻¹ . Predominantly, Cu was identified within the soil fractions in the order of residues (F5) > carbonate (F2) > Fe/Mn oxides (F3) > exchangeable fraction (F1) > organic carbon (F4). Compliant with Vietnamese standards, Cu concentrations in agricultural soil samples remained below permissible limits. Based on the Igeo index, the majority of soil samples exhibited mildly contaminated levels. Furthermore, according to the Risk Assessment Code (RAC), 11 out of the 12 analyzed soil samples were classified as having a medium risk level.
Revised: 31/5/2024	
Published: 31/5/2024	
KEYWORDS	
Heavy metal pollution	
Chemical speciation	
Soil pollution	
Contaminated evaluation	
Heavy metal content	

PHÂN TÍCH DẠNG HOÁ HỌC VÀ ĐÁNH GIÁ MỨC ĐỘ Ô NHIỄM CỦA ĐỒNG (Cu) TRONG MẪU ĐẤT Ở KHU VỰC MỎ Pb/Zn LÀNG HÍCH, TỈNH THÁI NGUYÊN

Vương Trường Xuân*, Phan Thanh Phương, Phạm Thị Thu Hà

Trường Đại học Khoa học - ĐH Thái Nguyên

THÔNG TIN BÀI BÁO	TÓM TẮT
Ngày nhận bài: 08/5/2024	Hiện nay, sự ô nhiễm của kim loại nặng trong các khu vực khai thác quặng đang trở nên rất nghiêm trọng tại Việt Nam và trên toàn cầu. Mục đích của nghiên cứu này là phân tích dạng hóa học của đồng (Cu) và đánh giá mức độ, nguy cơ ô nhiễm của nguyên tố này trong mẫu đất ở khu vực mỏ Pb/Zn Làng Hích, huyện Đông Hy, tỉnh Thái Nguyên, để góp phần có được những thông tin cần thiết trong quản lý môi trường đất ở khu vực này. Hàm lượng Cu trong các dạng hóa học trong các mẫu đất được phân tích theo phương pháp chiết Tessier, sử dụng kỹ thuật ICP-MS. Kết quả cho thấy nồng độ trung bình của Cu trên năm mẫu cát từ 15,524 đến 35,192 mg kg ⁻¹ , trong khi đó ở bảy mẫu nông nghiệp, nồng độ dao động từ 15,359 đến 21,198 mg kg ⁻¹ . Chủ yếu, Cu được xác định trong các phân tử đất theo thứ tự: cặn (F5) > cacbonat (F2) > oxit Fe/Mn (F3) > phân tử trao đổi (F1) > cacbon hữu cơ (F4). Tuân thủ các tiêu chuẩn Việt Nam, nồng độ Cu trong các mẫu đất nông nghiệp vẫn ở dưới ngưỡng cho phép. Dựa trên chỉ số Igeo, hầu hết các mẫu đất cho thấy mức độ ô nhiễm nhẹ. Hơn nữa, theo Mã đánh giá rủi ro (RAC), 11 trong số 12 mẫu đất được phân tích được xác định là có mức độ rủi ro trung bình.
Ngày hoàn thiện: 31/5/2024	
Ngày đăng: 31/5/2024	
TỪ KHÓA	
Ô nhiễm kim loại nặng	
Dạng hóa học	
Ô nhiễm đất	
Đánh giá ô nhiễm	
Hàm lượng kim loại nặng	

DOI: <https://doi.org/10.34238/tnu-jst.10317>

* Corresponding author. Email: xuanvt@tnu.edu.vn

1. Introduction

Naturally occurring heavy metals have been present in the environment since ancient times, but human activities like mining have significantly escalated their environmental contamination levels [1]. Copper (Cu) contamination in soil poses significant environmental challenges globally. Anthropogenic activities, including mining, industrial processes, and agricultural practices, contribute to its accumulation in soil, leading to adverse impacts on ecosystems and human health [2].

Copper (Cu) is an essential trace element that plays pivotal roles in various physiological processes crucial for human health. It serves as a cofactor for numerous enzymes involved in fundamental biochemical reactions, including antioxidant defence mechanisms, neurotransmitter synthesis, connective tissue formation, and iron metabolism regulation [3]. Furthermore, copper is integral to the function of key enzymes such as cytochrome oxidase and superoxide dismutase, which are vital for cellular respiration and free radical scavenging, respectively [4]. However, while copper is essential in small amounts, excessive intake can lead to toxicity, manifesting as gastrointestinal disturbances, liver damage, and neurological disorders [5].

In evaluating the presence of heavy metal pollution, particularly copper, in soil, it is customary to measure the total copper concentration. However, for a comprehensive assessment of copper levels and contamination potential, it is imperative to analyze its chemical fractions within the soil matrix [6]. Numerous sequential extraction techniques are employed to delineate the chemical fractions of metals in soil, with the Tessier sequential extraction method being prominently utilized for this purpose in various studies [7]–[9]. Based on this process, five main fractions of metals in the soil will be extracted: exchangeable form (F1), carbonate fraction (F2), fraction bound to Fe/Mn hydroxide-oxide (F3), fraction bound to Fe/Mn hydroxide (F3), with organic matter (F4) and residual residue (F5) [10]. Metals in the F1 fraction bind to colloidal particles in sediments (clay, hydrates of iron oxides, manganese oxides, and humic acids) by weak adsorption forces. Metals in sediments in this form are very mobile and can be easily released back into the water environment when there is a change in the ionic strength of water [10]. Metals that exist in the form of carbonate salt precipitate (F2) are very sensitive to changes in solution pH. When the pH of the soil solution decreases, metals in this form will be released in a flexible free form [10]. Metals in the F3 fraction are adsorbed on the surface of Fe-Mn oxygen hydroxide and are unstable under reducing conditions because the oxidation state of iron and manganese will be changed under this condition, so the metals in Soil will be released into the water phase [10]. In the F4 fraction, metals in organically bound fraction will be unstable under oxidizing conditions. These compounds will then decompose and the metals will be released into the water phase [10]. In residual fraction (F5), naturally occurring mineral salts can retain metal traces within their stable structural matrix. Therefore, metal ions in this fraction will not be dissolved under natural conditions [10]. Various methodologies exist for assessing the extent and risk associated with heavy metal contamination in soil, with the Igeo index and RAC (Risk Assessment Code) emerging as widely adopted approaches for evaluating heavy metal contamination in soil [11].

Previous research has highlighted the elevated concentrations of heavy metals, including lead (Pb), zinc (Zn), and cadmium (Cd), in the soil of the Pb/Zn mining region located in Hich village [12], [13]. However, limited attention has been given to studying the chemical speciation of copper (Cu) and evaluating its contamination level and associated risks in agricultural and waste soils in this area. Consequently, this investigation aims to (1) analyze the chemical fractions of copper in both tailing and agricultural soils within the Pb/Zn mining region of Hich village, Dong Hy district, Thai Nguyen province, employing the Tessier sequential extraction method and ICP-MS (Inductively Coupled Plasma Mass Spectrometry) technique. Furthermore, this study endeavours to assess the extent and risk of copper contamination in the soil within this research area utilizing the Igeo index and RAC (Risk Assessment Code).

2. Materials and Methods

2.1. Soil samples

In November 2023, a total of 12 surface soil specimens (0-30 cm depth) were collected from the Pb/Zn mining vicinity in Hich village (21°43.401'N; 105°51.276'E), situated in Dong Hy district, Thai Nguyen province. These samples comprised 5 from tailing areas and 7 from farmland adjacent to the disposal site. Upon arrival at the laboratory, the samples underwent pretreatment, involving natural air drying, followed by crushing and sieving through a 2 mm mesh sieve, before being securely stored in airtight plastic containers. Detailed spatial coordinates of the sampled soil locations are depicted in Figure 1.



Figure 1. Soil samples collected from the Pb/Zn mining in Dong Hy district, Thai Nguyen province (BT1-BT5: tailing sample; NN1-NN7: agricultural soil sample)

2.2. Analysis procedure

For the determination of copper's total concentration in soil samples, a digestion procedure was conducted following the U.S. EPA method 3051A [14]. This involved utilizing a combination of concentrated nitric acid (HNO₃) and hydrochloric acid (HCl) (in a 1:3 volume ratio) for sample digestion, carried out using a Mars 6 microwave oven manufactured by CEM company, USA. The methodology comprised weighing 0.5 g of the ground dry soil sample, followed by the addition of 8 mL of a mixed acid solution containing 2.0 mL of concentrated HNO₃ and 6.0 mL of concentrated HCl. Subsequently, the sample was transferred into Teflon tubes within the Mars 6 microwave system for digestion. Furthermore, the chemical fractionation of copper in the soil was conducted following the Tessier sequential extraction procedure outlined in Table 1.

Table 1. Tessier's sequential extraction protocol was employed to extract copper from the soil sample under investigation [10]

Code	Chemical fraction	Chemicals	Extracting condition
F1	Exchangeable fraction	CH ₃ COONH ₄ 1 M (pH = 7)	1 h/ 25°C
F2	Carbonate fraction	CH ₃ COONH ₄ (CH ₃ COOH, pH = 5)	5 h/ 25 °C
F3	Fe-Mn oxyhydroxide fraction	NH ₂ OH.HCl 0.04 M/ CH ₃ COOH 25% (v/v)	5 h/ 95°C
F4	Organic matter fraction	CH ₃ COONH ₄ 3.2 M/ HNO ₃ 20%	0.5 h/ 25 °C
F5	Residue fraction	HNO ₃ : HCl (3:1 v/v)	0.5 h/ 25 °C

2.3. Assessment of the analytical method used to determine the total Cu concentration

The precision of copper (Cu) analysis utilizing ICP-MS methodology was evaluated using the MESS-4 sediment standard sample. To mitigate potential interference from ⁶⁵Cu, collision mode with helium (He) gas and kinetic energy discrimination (KED) were employed to selectively reduce polyatomic interferences based on their dimensions. This approach effectively minimized

mass overlap interference, ensuring the accuracy and robustness of Cu analysis via ICP-MS. The MESS-4 standards, characterized by known Cu concentrations provided by the manufacturer (32.90 ± 2.00 mg kg⁻¹), were subjected to digestion and analysis using ICP-MS NexION 2000 (Perkin Elmer, USA) in triplicate. The average Cu recovery, based on the mean total content across three experimental runs, was found to be 97.2%, falling within the acceptable range specified by the AOAC standard (80% ÷ 110% for concentrations < 100 mg kg⁻¹) [15], thus confirming the reliability and accuracy of the analytical method.

2.4. Geo-accumulation Index (Igeo)

The Geo-accumulation Index (Igeo), devised by Muller in 1969, serves as a quantitative tool extensively utilized for the evaluation of heavy metal pollution levels in soils worldwide [16]–[20]. This index is computed using the formula (1):

$$I_{geo} = \log_2 \frac{C_n}{1.5 \cdot B_n} \quad (1)$$

where C_n represents the concentration of Cu in the soil, B_n denotes the geological background concentration (with B_n of Cu set at 55) [21], and 1.5 is a constant adjusting for natural variations in soil element content. The resultant Igeo values are categorized into seven levels: (1) $I_{geo} < 0$, indicating non-contaminated sites; (2) $0 < I_{geo} < 1$, signifying negligible to moderate pollution; (3) $1 < I_{geo} < 2$, reflecting moderate pollution levels; (4) $2 < I_{geo} < 3$, indicating moderate to high pollution; (5) $3 < I_{geo} < 4$, suggesting high pollution levels; (6) $4 < I_{geo} < 5$, representing pollution from very high to extremely severe; and (7) $I_{geo} \geq 5$, denoting extreme pollution [22].

2.5. Risk Assessment Code (RAC)

The Risk Assessment Code (RAC) serves as a pivotal tool for evaluating the degree of heavy metal contamination in soil [23]. Derived from formula (2), RAC integrates the proportions of heavy metals in exchangeable (F1) and carbonate (F2) fractions, determined through the Tessier continuous extraction method [24]. The calculation of RAC is articulated as:

$$RAC = \frac{F1 + F2}{C} \cdot 100\% \quad (2)$$

wherein F1 and F2 denote concentrations of metal forms in the mobile phase (F1) and carbonate-bound phase (F2), respectively, while C represents the total concentration of all five forms (F1 + F2 + F3 + F4 + F5). Soil heavy metal concentrations, assessed via RAC, are categorized as follows: negligible risk - environmentally benign ($RAC < 1\%$); low risk - relatively safe for the environment ($1\% < RAC < 10\%$); moderate risk - posing moderate environmental hazards ($10\% < RAC < 30\%$); high risk - presenting significant environmental dangers ($30\% < RAC < 50\%$); and very high risk - highly detrimental to the environment ($RAC > 50\%$) [23].

3. Results and discussion

3.1. Total concentration of Cu in soil samples

The combined levels of Cu within agricultural soil (NN) and tailing samples (BT) are depicted in Table 3. The tabulated data indicates a range of Cu concentrations in tailing samples spanning from 15.524 to 35.192 mg kg⁻¹, whereas Cu concentrations in agricultural soil samples ranged slightly lower, from 15.359 to 21.198 mg kg⁻¹. All agricultural soil samples fell below the permissible threshold for agricultural land (50 mg kg⁻¹), as stipulated by the Ministry of Natural Resources and Environment of Vietnam [25].

Likewise, the copper levels within the five tailing samples remained within the permissible limits for industrial land (100 mg kg⁻¹), as outlined by the regulations of the Ministry of Natural Resources and Environment of Vietnam [25].

The comparison between the average Cu concentrations of agricultural and tailing samples is depicted in Figure 2. This figure illustrates that the mean Cu concentration in tailing soil (BT:

23.647 mg kg⁻¹) slightly surpassed that of agricultural land (NN: 17.893 mg kg⁻¹). Consequently, it is deduced that the analyzed soil samples comply with Vietnamese standards. Additionally, Table 2 illustrates a comparison of Cu content in this study's soil samples with global results from Pb/Zn mine areas.

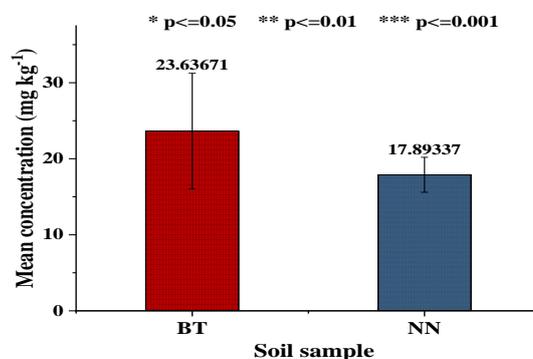


Figure 2. Evaluating the difference in mean copper levels between the tailing (BT) and agricultural (NN) samples

Table 2. Comparing the levels of copper in the Pb/Zn mining observed in this study with data from previous investigations

No	Studied zone	Cu concentration (mg kg ⁻¹)	Analytical method	Reference
1	This study	15.36 ÷ 35.19	ICP-MS	
2	Pb/Zn mining in Isfahan city, Iran	6.70 ÷ 28.20	FAAS	[26]
3	Pb/Zn mining in in the Alcudia Valley, Ciudad Real, Spain	9.56 ÷ 716.58	ICP-AES	[27]
4	Pb/Zn mining in Sidi Kamber, Algeria	10 ÷ 34.20	FAAS	[28]
5	Pb/Zn mining, Oued el Heimer, Morocco	35 ÷ 592	ICP-AES	[29]
6	Pb/Zn mining in Taraba state, Nigeria	7.5 ÷ 32.0	ICP-MS	[30]
7	Pb/Zn mining in Jinding, China	24.3 ÷ 49.3	ICP-MS	[31]
8	Thresholds for copper content in agricultural soil	50		[25]
	Threshold for copper content in industrial soil	100		

ICP-MS: Inductively coupled plasma mass spectrometry; ICP-AES: Inductively coupled plasma atomic emission spectroscopy; AFS: Atomic fluorescence spectroscopy; FAAS: Flame Atomic Absorption Spectrophotometric.

Table 2 illustrates that the copper (Cu) concentrations detected in the soil samples analyzed in this investigation closely resembled those documented in the Pb/Zn mining locales of Sidi Kamber, Algeria [28], and Taraba state, Nigeria [30]. Conversely, the Cu levels observed in the soil samples of this study were notably lower compared to those observed in soil samples from Pb/Zn mining regions in Spain [27], and Morocco [29]. The variance in Cu concentrations across soil samples within Pb/Zn mining sites globally may be attributed to divergent physicochemical properties inherent to each sampled area, historical ore mining activities, and anthropogenic influences during the mining operations.

3.2. Chemical fractions of Cu in soil samples

The determination of copper content in soil samples was conducted employing the Tessier continuous extraction method, with Cu concentrations in the chemical fractions determined through ICP-MS analysis, as detailed in Table 3. The distribution of copper across various chemical fractions in the soil samples is depicted in Figure 3. The content of Cu in the sediment was calculated according to the formula (3): Content of Cu (mg/kg) = C.V/m.1000 (3)

Here: C is the Cu concentration to be determined in the solution obtained after digestion (minus the blank sample) in units of µg/L; V is the normative volume after digestion or volume of reagent solution used for extraction (ml); m is the weight of soil sample weighed for processing and analysis (grams)

The proportion of copper was calculated as the formula (4):

$$Proportion = \frac{F_i}{F_1+F_2+F_3+F_4+F_5} \cdot 100\% \tag{4}$$

Here, F_i is the copper content in the chemical fraction i ($i = 1 \div 5$); F_1, F_2, F_3, F_4 and F_5 are the content of copper in the chemical fractions F_1, F_2, F_3, F_4 and F_5 .

Table 3. The average copper concentration in chemical fractions of tailing (BT) and agricultural soil (NN)

Soil	F1	F2	F3	F4	F5	Total
	mg kg ⁻¹					
BT1	6.260 ± 0.222	12.813 ± 0.372	1.561 ± 0.045	0.612 ± 0.018	13.947 ± 0.405	35.192 ± 1.108
BT2	2.130 ± 0.018	4.225 ± 0.035	4.221 ± 0.035	1.018 ± 0.008	6.687 ± 0.055	18.281 ± 0.180
BT3	1.837 ± 0.012	6.250 ± 0.042	4.321 ± 0.029	0.829 ± 0.006	10.615 ± 0.071	23.853 ± 0.146
BT4	1.639 ± 0.040	3.097 ± 0.195	4.293 ± 0.271	0.884 ± 0.056	5.611 ± 0.354	15.524 ± 0.105
BT5	1.102 ± 0.055	3.531 ± 0.175	6.386 ± 0.316	1.036 ± 0.051	13.277 ± 0.657	25.333 ± 0.245
NN1	1.193 ± 0.008	5.616 ± 0.371	4.653 ± 0.294	1.805 ± 0.102	7.805 ± 0.449	21.071 ± 0.345
NN2	1.086 ± 0.069	5.148 ± 0.296	3.589 ± 0.024	1.484 ± 0.015	5.658 ± 0.366	16.966 ± 0.478
NN3	1.266 ± 0.075	5.790 ± 0.051	4.657 ± 0.038	1.099 ± 0.075	8.386 ± 0.658	21.198 ± 0.438
NN4	1.375 ± 0.068	5.384 ± 0.355	1.346 ± 0.039	1.742 ± 0.094	7.410 ± 0.321	17.256 ± 0.563
NN5	1.443 ± 0.010	5.748 ± 0.379	2.655 ± 0.168	1.354 ± 0.077	5.106 ± 0.294	16.307 ± 0.658
NN6	2.523 ± 0.159	4.706 ± 0.271	2.685 ± 0.018	1.143 ± 0.012	4.302 ± 0.278	15.359 ± 0.656
NN7	2.474 ± 0.206	6.129 ± 0.081	1.737 ± 0.014	1.405 ± 0.096	5.352 ± 0.420	17.097 ± 0.362

F1: exchangeable fraction, F2: carbonate fraction; F3: Fe/Mn-oxihydroxide fraction; F4: organic matter fraction; F5: residue fraction; (n =3);

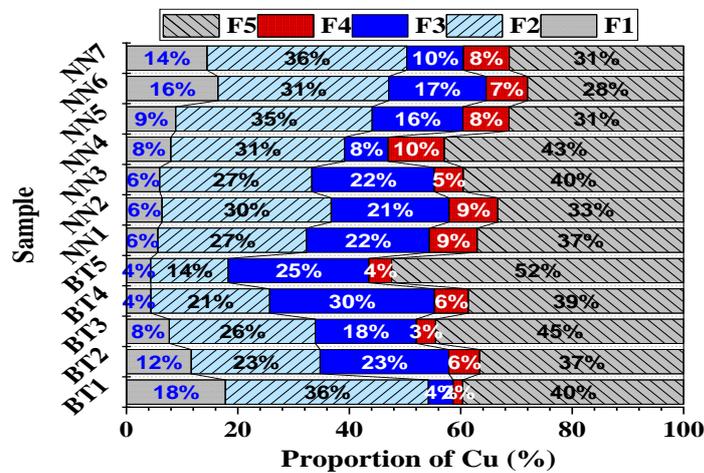


Figure 3. The allocation of Cu across different chemical fractions in the investigated soil (F1: exchangeable fraction, F2: carbonate fraction; F3: Fe/Mn-oxihydroxides fraction; F4: organic matter fraction; F5: residue fraction)

Figure 3 reveals that in the soil samples under investigation, copper was predominantly present in the following descending order of abundance: residual fraction (F5) > carbonate fraction (F2) > Mn/Fe oxide bound fraction (F3) > exchange fraction (F1) > organic fraction (F4). This distribution suggests that copper primarily existed in the stable residual fraction, thereby indicating limited solubility and reduced potential for leaching into groundwater or the surrounding environment. Conversely, copper was found to be minimally present in the exchangeable fraction (F1), which is characterized by higher mobility and greater susceptibility

to leaching into groundwater and the surrounding environment. Soil samples exhibiting elevated copper concentrations in the exchangeable fraction (F1) pose a notable risk of environmental contamination. Consequently, all soil samples examined herein predominantly contained copper within the stable residue fraction (F5) and exhibited minimal presence in the exchangeable fraction (F1), thus indicating a low risk of copper pollution to the surrounding environment. The fact that copper exists mainly in the F5 fraction is because in nature all metals exist mainly in residual form. Due to weathering and human activities, part of the F5 fraction has transformed into other less stable forms such as F1, F2, F3 and F4. The previous study also reported that Cu mainly contributed to the residual fraction (F5) in soil [32], [33]. Cu exists in abundance in the F2 form because the ore in the Pb/Zn mine area in the studied area mainly exists in the carbonate form. Therefore, Cu is widely distributed in carbonate fraction. The distribution of Cu element in soil in this study is slightly inconsistent with the previous studies Gabarrón et al. 2019 reported that the distribution of Cu in agricultural soil near a Pb/Zn mining was $F5 > F4 > F3 > F2 > F1$ [33], when the other study informed that the order was $F5 > F4 > F3 > F1 > F2$ [32]. The disparity was attributed to several factors, including Geological and Geographical Factors, Anthropogenic Activities, Sediment Properties, Redox Conditions and Biological Activity, especially Geological and Geographical Factors and Anthropogenic Activities.

Geological formations and parent materials significantly influence the distribution of heavy metals in soil or sediment. Certain geological formations may contain higher concentrations of specific heavy metals due to natural processes such as weathering and erosion. Geographical factors such as topography, elevation, and proximity to geological features can also influence heavy metal distribution [10].

Human activities, including mining, agriculture, and urbanization, are major sources of heavy metal contamination in sediment. These activities can release heavy metals into the environment through processes such as atmospheric deposition, or the use of contaminated materials (e.g., fertilizers, pesticides) [34].

3.3. Assessment of the pollution level and risk

3.3.1. Geo-accumulation Index (Igeo)

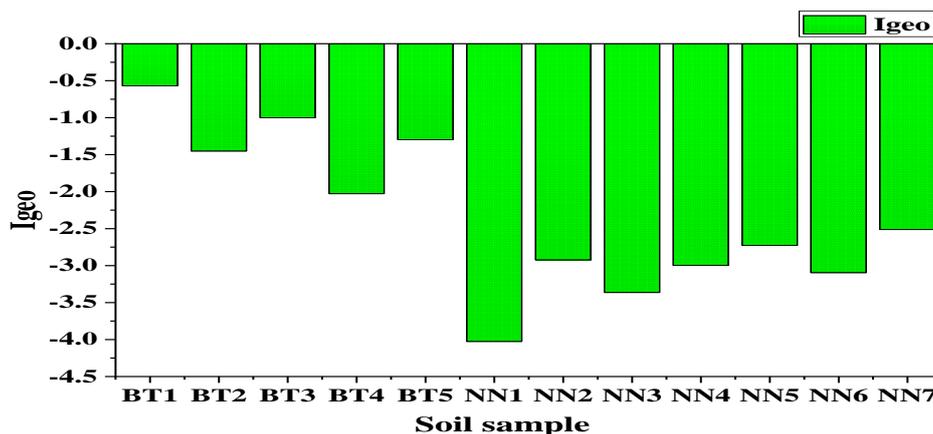


Figure 4. Igeo index for copper in the tailing (BT) and agricultural (NN) soil samples

The average Igeo index values for copper in soil specimens collected from tailing (BT) and agricultural plots (NN) are illustrated in Figure 4. It is evident that the Igeo values of Cu at all sampling locations are less than 0 (Figure 4). Therefore, it can be concluded that there is no indication of Cu pollution in the study area according to the Igeo index. In summary, through the assessment of copper pollution levels using the Igeo index, all soil samples analyzed exhibit no

contamination at any of the study locations, indicating that the study area (including landfills, streams, and agricultural land) is not affected by Cu emissions from mining and disposal activities in the surrounding area.

3.3.2. Risk assessment code (RAC)

Based on the classification table of pollution levels (section 2.5) and the graphical representation in Figure 5, only two soil samples from the landfill area (BT4 and BT5) had RAC values ranging from 10 to 30%, indicating a moderate risk level for the ecosystem. All other samples had RAC values > 30%, with the sample from location BT1 even having a RAC value > 50. Thus, the remaining samples (BT1-BT3) all pose a high to extremely high risk to the ecosystem due to copper contamination. Regarding the agricultural soil samples, all 7 samples have RAC values ranging from 30-50%, indicating a high-risk level for the ecosystem due to the copper content in these soil samples.

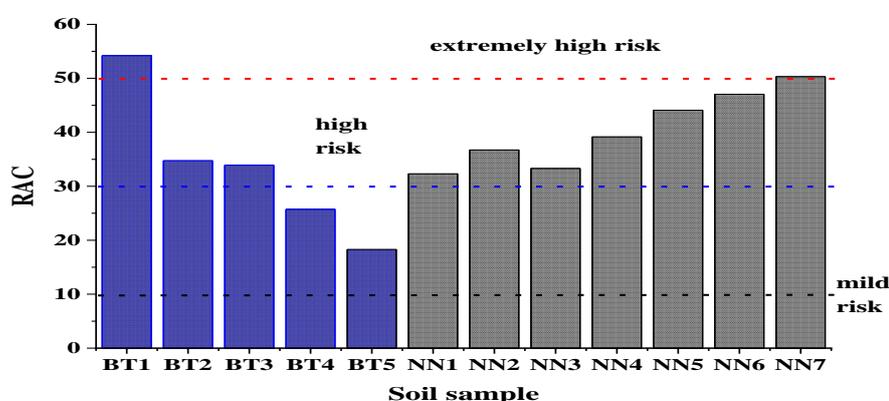


Figure 5. Risk assessment Code (RAC) of copper in the tailing (BT1-BT5) and agricultural (NN1-NN7) samples

The evaluation results indicate that, based on the total copper content and the Igeo index, the soil and sediment samples are not polluted. However, when assessing the level of copper contamination based on the analysis of binding forms using the RAC index, the contamination levels range from low to moderate, with the risk level for the ecosystem mostly being high. This result is attributed to the presence of copper mainly in carbonate form, which is unstable and easily released into the environment when the pH of the soil and sediment is low. I_{geo} bases its evaluation on the overall content of metals, whereas RAC bases its evaluation on the F1 and F2 fractions of metals. This is the distinction between the two methods of evaluation. Since F1 and F2 fractions of metals are the least stable, a high percentage of them will result in high RAC values even though the total content of metals is not high. As a result, Cu in these fractions readily dissolves and enters the environment, endangering the ecological environment. Therefore, immobilizing heavy metals in soil by the composting of biochar or other materials capable of changing into other forms is one of the study approaches to limit the risk of heavy metal contamination to the surrounding environment.

4. Conclusion

The ICP-MS method was employed to ascertain the total concentration of Cu in 12 samples collected from both agricultural land and mine tailings. The mean Cu content in the tailings and agricultural soil samples ranged from 15.524 to 35.192 mg kg⁻¹ and 15.359 to 21.198 mg kg⁻¹, respectively. Subsequently, the concentration of Cu in various chemical fractions was investigated utilizing Tessier's sequential extraction procedure. The findings revealed that Cu distribution in the soil followed this order: F5 > F2 > F3 > F1 > F4. Notably, the majority of

copper was found within the F5 fraction, characterized by high environmental stability, while its presence in the F1 fraction, susceptible to environmental absorption, was minimal. Compliance with Vietnamese standards indicated that the total concentration of Cu in both agricultural and industrial soil samples remained below the permissible threshold. Analysis based on the Igeo index demonstrated that all Igeo values for the soil samples indicated non-contaminated levels, while evaluation using the RAC index revealed a high risk of copper contamination across all samples, particularly in the case of sample BT1, which exhibited an RAC value suggesting an extremely high pollution risk (RAC > 50%). Consequently, the assessed soil samples generally exhibited Cu concentrations within acceptable limits, ensuring environmental safety concerning copper levels in the surrounding area.

REFERENCES

- [1] C. Kamunda, M. Mathuthu, and M. Madhuku, "Health risk assessment of heavy metals in soils from Witwatersrand gold mining basin, South Africa," *International Journal of Environmental Research and Public Health*, vol. 13, no. 7, 2016, doi: 10.3390/ijerph13070663.
- [2] M. Rehman, L. Liu, Q. Wang, M. H. Saleem, S. Bashir, S. Ullah, and D. Peng, "Copper environmental toxicology, recent advances, and future outlook: a review," *Environ. Sci. Pollut. Res.*, vol. 26, no. 18, pp. 18003–18016, 2019, doi: 10.1007/s11356-019-05073-6.
- [3] Y. An, S. Li, X. Huang, X. Chen, H. Shan, and M. Zhang, "The Role of Copper Homeostasis in Brain Disease," *International Journal of Molecular Sciences*, vol. 23, no. 22, 2022, doi: 10.3390/ijms232213850.
- [4] A. Hordyjewska, Ł. Popiołek, and J. Kocot, "The many 'faces' of copper in medicine and treatment," *BioMetals*, vol. 27, no. 4, pp. 611–621, 2014, doi: 10.1007/s10534-014-9736-5.
- [5] G. J. Brewer, "Risks of copper and iron toxicity during aging in humans," *Chem. Res. Toxicol.*, vol. 23, no. 2, pp. 319–326, 2010, doi: 10.1021/tx900338d.
- [6] D. Huang, H. Gui, M. Lin, and W. Peng, "Chemical speciation distribution characteristics and ecological risk assessment of heavy metals in soil from Sunan mining area, Anhui Province, China," *Hum. Ecol. Risk Assess. An Int. J.*, vol. 24, no. 6, pp. 1694–1709, 2018.
- [7] A. Sebei, A. Chaabani, C. Abdelmalek-Babbou, M. A. Helali, F. Dhahri, and F. Chaabani, "Evaluation of pollution by heavy metals of an abandoned Pb-Zn mine in northern Tunisia using sequential fractionation and geostatistical mapping," *Environ. Sci. Pollut. Res.*, vol. 27, no. 35, pp. 43942–43957, 2020, doi: 10.1007/s11356-020-10101-x.
- [8] C. Han, W. Xie, C. Chen, and T. Cheng, "Health Risk Assessment of Heavy Metals in Soils before Rice Sowing and at Harvesting in Southern Jiangsu Province, China," *J. Chem.*, vol. 2020, 2020, doi: 10.1155/2020/7391934.
- [9] Y. Ahn, H. S. Yun, K. Pandi, S. Park, M. Ji, and J. Choi, "Heavy metal speciation with prediction model for heavy metal mobility and risk assessment in mine-affected soils," *Environ. Sci. Pollut. Res.*, vol. 27, no. 3, pp. 3213–3223, 2020, doi: 10.1007/s11356-019-06922-0.
- [10] A. Tessier, P. G. C. Campbell, and M. Bisson, "Sequential Extraction Procedure for the Speciation of Particulate Trace Metals," *Analytical Chemistry*, vol. 51, no. 7, pp. 844–851, 1979, doi: 10.1021/ac50043a017.
- [11] X. T. Vuong, L. D. Vu, A. T. T. Duong, H. T. Duong, T. H. T. Hoang, M. N. T. Luu, T. N. Nguyen, V. D. Nguyen, T. T. T. Nguyen, T. H. Van, and T. B. Minh, "Speciation and environmental risk assessment of heavy metals in soil from a lead/zinc mining site in Vietnam," *Int. J. Environ. Sci. Technol.*, vol. 20, no. 5, pp. 5295–5310, 2023.
- [12] T. K. A. Bui, D. K. Dang, V. T. Tran, T. K. Nguyen, and T. A. Do, "Phytoremediation potential of indigenous plants from Thai Nguyen province, Vietnam," *J. Environ. Biol.*, vol. 32, no. 2, pp. 257–262, 2011.
- [13] V. M. Dang, S. Joseph, H. T. Van, T. L. A. Mai, T. M. H. Duong, S. Weldon, P. Munroe, D. Mitchell, and S. Taherymoosavi, "Immobilization of heavy metals in contaminated soil after mining activity by using biochar and other industrial by-products: the significant role of minerals on the biochar surfaces," *Environ. Technol. (United Kingdom)*, vol. 40, no. 24, pp. 3200–3215, 2019, doi: 10.1080/09593330.2018.1468487.
- [14] EPA, "Method 3051 A: Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oils," 1998. [Online]. Available: <https://www.epa.gov/sites/default/files/2015-12/documents/3051a.pdf>. [Accessed June 4, 2024].
- [15] AOAC - Association of Official Agricultural Chemists, "Appendix F: guidelines for standard method performance requirements," 2016. [Online]. Available: http://www.eoma.aoac.org/app_f.pdf. [Accessed June 4, 2024].
- [16] N. Adimalla, "Heavy metals pollution assessment and its associated human health risk evaluation of urban

- soils from Indian cities: a review,” *Environmental Geochemistry and Health*, vol. 42, no. 1, pp. 173–190, 2020, doi: 10.1007/s10653-019-00324-4.
- [17] H. Li, W. Xu, M. Dai, Z. Wang, X. Dong, and T. Fang, “Assessing heavy metal pollution in paddy soil from coal mining area, Anhui, China,” *Environ. Monit. Assess.*, vol. 191, no. 8, 2019, doi: 10.1007/s10661-019-7659-x.
- [18] A. H. Baghaie and F. Aghili, “Investigation of heavy metals concentration in soil around a Pb-Zn mine and ecological risk assessment,” *Environ. Heal. Eng. Manag.*, vol. 6, no. 3, pp. 151–156, 2019, doi: 10.15171/ehem.2019.17.
- [19] J. Liu, Y. J. Liu, Y. Liu, Z. Liu, and A. N. Zhang, “Quantitative contributions of the major sources of heavy metals in soils to ecosystem and human health risks: A case study of Yulin, China,” *Ecotoxicol. Environ. Saf.*, vol. 164, pp. 261–269, 2018, doi: 10.1016/j.ecoenv.2018.08.030.
- [20] S. Fan, X. Wang, J. Lei, Q. Ran, Y. Ren, and J. Zhou, “Spatial distribution and source identification of heavy metals in a typical Pb/Zn smelter in an arid area of northwest China,” *Hum. Ecol. Risk Assess.*, vol. 25, no. 7, pp. 1661–1687, 2019, doi: 10.1080/10807039.2018.1539640.
- [21] E. I. Hamilton, “Environmental variables in a holistic evaluation of land contaminated by historic mine wastes: A study of multi-element mine wastes in West Devon, England using arsenic as an element of potential concern to human health,” *Science of The Total Environment*, vol. 249, no. 1–3, 2000, doi: 10.1016/S0048-9697(99)00519-7.
- [22] A. Morales-Pérez, V. Moreno-Rodríguez, R. D. Rio-Salas, N. G. Imam, B. González-Méndez, T. Pi-Puig, F. Molina-Freaner, and R. Loredo-Portales, “Geochemical changes of Mn in contaminated agricultural soils nearby historical mine tailings: Insights from XAS, XRD and, SEP,” *Chem. Geol.*, vol. 573, 2021, doi: 10.1016/j.chemgeo.2021.120217.
- [23] J. Latosińska and P. Czapik, “The ecological risk assessment and the chemical speciation of heavy metals in ash after the incineration of municipal sewage sludge,” *Sustain.*, vol. 12, no. 16, 2020, doi: 10.3390/su12166517.
- [24] A. Pejman, G. Nabi Bidhendi, M. Ardestani, M. Saeedi, and A. Baghvand, “Fractionation of heavy metals in sediments and assessment of their availability risk: A case study in the northwestern of Persian Gulf,” *Mar. Pollut. Bull.*, vol. 114, no. 2, pp. 881–887, Jan. 2017, doi: 10.1016/j.marpolbul.2016.11.021.
- [25] Vietnam Ministry of Natural Resources and Environment, *QCVN 03-MT:2015/BTNMT, National technical regulation on the allowable limits of heavy metals in the soils*, (in Vietnamese), 2015.
- [26] M. Nekoeinia, R. Mohajer, M. H. Salehi, and O. Moradlou, “Multivariate statistical approach to identify metal contamination sources in agricultural soils around Pb–Zn mining area, Isfahan province, Iran,” *Environ. Earth Sci.*, vol. 75, no. 9, 2016, doi: 10.1007/s12665-016-5597-2.
- [27] L. Rodríguez, E. Ruiz, J. Alonso-Azcárate, and J. Rincón, “Heavy metal distribution and chemical speciation in tailings and soils around a Pb–Zn mine in Spain,” *J. Environ. Manage.*, vol. 90, no. 2, pp. 1106–1116, 2009, doi: 10.1016/j.jenvman.2008.04.007.
- [28] A. M. Stefanowicz, P. Kapusta, S. Zubek, M. Stanek, and M. W. Woch, “Soil organic matter prevails over heavy metal pollution and vegetation as a factor shaping soil microbial communities at historical Zn–Pb mining sites,” *Chemosphere*, vol. 240, 2020, p.124922.
- [29] S. E. Hasnaoui, M. Fahr, C. Keller, C. Levard, B. Angeletti, P. Chaurand, Z.E.A. Triqui, A. Guedira, L. Rhazi, F. Colin, and A. Smouni, “Screening of native plants growing on a Pb/Zn mining area in eastern Morocco: Perspectives for phytoremediation,” *Plants*, vol. 9, no. 11, pp. 1–23, 2020, doi: 10.3390/plants9111458.
- [30] A. J. Adewumi, T. A. Laniyan, and P. R. Ikhane, “Distribution, contamination, toxicity, and potential risk assessment of toxic metals in media from Arufu Pb – Zn – F mining area, Northeast Nigeria,” *Toxin Rev.*, vol. 40, no. 4, pp. 1–22, 2020, doi: 10.1080/15569543.2020.1815787. (xem lại số vol, số tập)
- [31] X. Cheng, T. Danek, J. Drozdova, Q. Huang, W. Qi, L. Zou, S. Yang, X. Zhao, and Y. Xiang, “Soil heavy metal pollution and risk assessment associated with the Zn-Pb mining region in Yunnan, Southwest China,” *Environ. Monit. Assess.*, vol. 190, no. 4, pp. 1–16, 2018, doi: 10.1007/s10661-018-6574-x.
- [32] M. Jalali and N. Hemati, “Chemical fractionation of seven heavy metals (Cd, Cu, Fe, Mn, Ni, Pb, and Zn) in selected paddy soils of Iran,” *Paddy Water Environ.*, vol. 11, no. 1–4, pp. 299–309, 2013, doi: 10.1007/s10333-012-0320-8.
- [33] M. Gabarrón, R. Zornoza, S. Martínez-Martínez, V. A. Muñoz, Á. Faz, and J. A. Acosta, “Effect of land use and soil properties in the feasibility of two sequential extraction procedures for metals fractionation,” *Chemosphere*, vol. 218, pp. 266–272, 2019, doi: 10.1016/J.CHEMOSPHERE.2018.11.114.
- [34] B. J. Alloway, *Heavy metals in soils: trace metals and metalloids in soils and their bioavailability*, vol. 22. Springer Science & Business Media, 2012.