

CHEMICAL FRACTION ANALYSIS OF LEAD (Pb) IN SEDIMENT AT THE GOLD MINING AREA OF THAN SA COMMUNE, VO NHAU DISTRICT, THAI NGUYEN PROVINCE

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ARTICLE INFO	ABSTRACT
Received: 08/5/2024 Revised: 31/5/2024 Published: 31/5/2024	Mining operations have significantly impacted the environment, soil, water, and sediment within the vicinity of gold mining activities. The objective of this study is to analyze the chemical speciation of Pb in sediment samples from the Than Sa gold mining area to obtain comprehensive information regarding the level of Pb contamination in sediment samples from this area. Employing a sequential extraction procedure, the various forms of lead were extracted from six sediment samples. Using the ICP-MS method, the concentrations of lead and its chemical forms in the sediment samples were quantified. Results indicate that the mean total lead concentration in the sediment samples ranged from $29.16 \div 89.19$ mg/kg, all of which were below the allowable threshold for lead according to Vietnamese regulations for freshwater sediments. The distribution of lead chemical forms in the soil samples predominantly follows the sequence $F5 > F3 > F2 \sim F4 \sim F1$. Assessment based on environmental risk evaluation parameters such as Igeo and RAC reveals that lead concentrations in the sediment samples pose low to moderate levels of risk of pollution.
KEYWORDS Chemical fractionation Lead content Heavy metal Gold mine Sediment	

PHÂN TÍCH DẠNG HOÁ HỌC CỦA CHÌ (Pb) TRONG MẪU TRẦM TÍCH KHU VỰC KHAI THÁC VÀNG XÃ THẦN SA, HUYỆN VÕ NHAU, TỈNH THÁI NGUYÊN

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THÔNG TIN BÀI BÁO	TÓM TẮT
Ngày nhận bài: 08/5/2024 Ngày hoàn thiện: 31/5/2024 Ngày đăng: 31/5/2024	Môi trường, đất, nước và trầm tích ở khu vực mỏ khai thác vàng bị ảnh hưởng nghiêm trọng bởi các hoạt động khai thác. Mục đích của nghiên cứu này là phân tích dạng hóa học của Pb trong các mẫu trầm tích ở khu vực mỏ vàng Thần Sa để có đầy đủ thông tin về mức độ ô nhiễm Pb trong các mẫu trầm tích ở khu vực này. Quy trình chiết tuần tự được áp dụng để chiết các dạng liên kết của chì trong 6 mẫu trầm tích. Hàm lượng của chì trong các mẫu trầm tích và các dạng hóa học được định lượng bằng phương pháp ICP-MS. Kết quả cho thấy, hàm lượng chì tổng số trung bình trong các mẫu trầm tích nằm trong khoảng $29,16 \div 89,19$ mg/kg, và đều thấp hơn giới hạn cho phép của chì theo quy chuẩn Việt Nam đối với trầm tích nước ngọt. Dạng hóa học của bạc trong các mẫu đất phân bố chủ yếu ở dạng $F5 > F3 > F2 \sim F4 \sim F1$. Dựa trên các thông số đánh giá nguy cơ rủi ro môi trường Igeo và RAC cho thấy, hàm lượng chì ở các mẫu trầm tích nằm ở mức độ rủi ro ô nhiễm ở mức thấp hoặc rủi ro vừa phải.
TỪ KHÓA Phân đoạn hóa học Hàm lượng bạc Kim loại nặng Mỏ vàng Trầm tích	

DOI: <https://doi.org/10.34238/tnu-jst.10318>

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1. Introduction

Extracting heavy metals and gold yields considerable economic advantages for the region; however, it invariably results in environmental contamination within the vicinity of the mining site. One of the significant environmental issues rendered by gold mining activities is the contamination of water resources with hazardous substances such as mercury and cyanide, which are commonly used in the gold extraction process. Mercury is particularly concerning due to its bioaccumulative nature, posing risks to human health and wildlife when it enters the food chain [1], [2]. Additionally, the disposal of mining waste, known as tailings, presents a significant environmental challenge. Tailings contain residual metals and chemicals that can leach into the soil and water, contaminating the environment and posing long-term risks to human and ecological health [1]. Therefore, it is necessary to study the total content and chemical fraction of heavy metals such as Pb to evaluate the environmental situation of this area rendered by the mining activities.

Previous studies have often relied on the total content of metals to assess their pollution levels. However, for a more comprehensive evaluation, it is necessary to analyze the chemical forms of these metals in the soil [3], [4]. The Tessier sequential extraction procedure is a commonly used method in many studies to analyze the chemical forms of heavy metals in soil and sediment [5]–[8]. This procedure enables the extraction of five main forms of metals in soil, namely exchangeable form (F1), carbonate form (F2), Fe/Mn hydroxide-oxide bound form (F3), organic matter bound form (F4), and residual form (F5) [9]. Metals in the F1 form are bound to colloidal particles in sediment (clay, iron oxide hydrates, manganese oxide, humic acid) by weak adsorption forces. Metals in this form in sediment are highly mobile and can easily be released back into the water environment with changes in the ion strength of water [9]. Metals existing in the form of carbonate precipitates (F2) are highly sensitive to changes in the pH of the solution. When the pH of the soil solution decreases, metals in this form will be released in a freely exchangeable form). Metals in the F3 form are adsorbed on the surface of Fe-Mn oxide hydroxides and are unstable under reducing conditions. Therefore, the oxidation state of iron and manganese will change under these conditions, causing metals in the soil to be released into the water phase [9]. In the F4 form, metals bound to organic matter are not stable under oxidizing conditions. In this case, these compounds will decompose, and metals will be released into the water phase. In the residual form (F5), naturally occurring mineral salts can trap metal traces in their stable structure. Therefore, metal ions in this form will not dissolve under natural conditions [9].

The gold mining area of Than Sa commune, Vo Nhai district, Thai Nguyen province, Vietnam, is known not only for being a gold mining area in Thai Nguyen but also for the serious environmental pollution in this region. Both authorized and unlicensed gold mining that uses cyanide and mercury can have detrimental effects on people and the environment if left untreated. This region is the site of illicit gold mining. A common method employed in this illicit mining is small-scale manual gold mining that uses mercury amalgam. There are detrimental effects of illegal gold mining on the local ecosystem. Water sources are contaminated when rivers and streams are dug up for gold mining. Certain lush areas have been mostly neglected and are unusable for farming or production. Because of this, there is a significant chance that human mining activities contaminate the water, soil, and sediment in this area with heavy metals such as lead. To date, there has been no research investigating the chemical forms of Pb in sediment in this area. To obtain more comprehensive information on the chemical forms and contamination risk level of Pb in the soil in this area, we conducted this study to (1) analyze the total content and chemical forms of Pb in sediment samples; (2) assess the contamination risk level of Pb in the soil in this area based on environmental assessment indices, including the individual contamination factor (ICF) and the Risk Assessment Code (RAC).

2. Methods

2.1. Sediment samples

The sediment samples analyzed were selected from six different zones within the Than Sa gold mine area. Sediment samples were collected at a depth of 20 cm. The locations of sediment sampling for the study are described in Table 1.

Table 1. The sediment sampling locations in the Than Sa commune gold mine

No.	Sediment Code	Coordinate y	Coordinate x	Description
1	L1	21.8897292	105.9419493	Sediment samples collected from a small stream with clear water
2	L2	21.8871029	105.9413435	Sediment samples were collected from the stream flowing from the Khau Au gold mine located in Kim Ngan, Bac Kan province.
3	L3	21.8866356	105.9416627	Sediment samples collected from the area of a gold mining cave that has been filled, containing gold tailings
4	L4	21.8888930	105.9293818	Sediment samples were collected from the stream area near the entrance of the Thu Do Gio Ngan Trading Company Limited, with two main streams: Khau Au and Kim Ngan, located in Than Sa, where mineral extraction activities are currently taking place
5	L5	21.8834662	105.9288793	Sediment samples collected downstream flowing from the Bai Mo stream, along the same flow path as the sediment sampling area S4
6	L6	21.8746682	105.9306894	Sediment samples were collected from the confluence area of Bai Mo and the streams flowing from the peaks of Giang mountain 1-4, Thuong Kim, Khau Au mountains. In this area, wastewater discharge is characterized by black coloration.

The studied samples were 6 sediment samples located along the stream flowing from Khau Au (Bac Kan province) to Than Sa. Wastewater from gold mining activities is discharged along the stream flowing from Giang 1 and Giang 2 in Khau Au to Ha Kim (Than Sa). Sediment samples at the above locations were collected based on the stratification of sediments of the stream flowing from the Khau Au to the Than Sa area. Six sediment samples were collected along this stream to evaluate the pollution risks and levels resulting from gold mining operations in Khau Au, as well as the effects on the environment in the Than Sa area caused by the discharge of wastewater into the aquatic environment along the stream that runs from Khau Au to Than Sa.

2.2. Analysis of lead in sediment samples

The sediment samples were collected from locations as listed in Table 1. Upon arrival at the laboratory, the sediment samples were dried in a drying cabinet at 45°C for 3 days. Subsequently, the sediment samples were sieved through a 2 mm mesh and stored in polyethylene bags. To analyze the lead content in the soil samples, 0.5 grams of soil samples were treated with 8 ml of aqua regia mixture in a Mars 6 microwave oven following the USEPA 3051A standard [10] and then analyzed using an ICP-MS Nexion 2000 instrument at the Analytical Chemistry Department, Vietnam Academy of Science and Technology. For the analysis of the chemical forms of silver in the soil, the Tessier sequential extraction procedure was applied to extract the chemical forms of silver, and then the silver content in the extracted solutions was analyzed by ICP-MS. Detailed descriptions of the steps of the improved Tessier extraction procedure [9] are presented in Table 2.

Table 2. *The Tessier sequential extraction procedure* [9]

Fractions	Chemical form	Chemicals and extraction conditions
F1	Exchangeable fraction	Extraction with 1M CH ₃ COONH ₄ solution (pH = 7), at 25°C, continuous shaking for 1 hour.
F2	Carbonate fraction	Extraction with CH ₃ COONH ₄ solution (containing CH ₃ COOH at pH = 5), at 25°C for 5 hours.
F3	Fe-Mn oxyhydroxide fraction	Extraction with 0.04M NH ₂ OH.HCl/25% HOAc (V/V) solution. Heating at 95°C, continuous shaking for 5 hours.
F4	Organic matter fraction	Extraction with 3.2M CH ₃ COONH ₄ /20% HNO ₃ solution, at 25°C for 30 minutes.
F5	Residue fraction	Extraction with HNO ₃ :HCl (1:3 V/V) solution at 25°C, continuous shaking for 30 minutes.

2.3. Evaluation of the analysis procedure for the total lead content in sediment samples

To assess the procedure and analytical method, the recovery of silver content in the MESS-4 sediment standard sample was conducted after analyzing the experiment three times by processing the sample and quantifying silver using the ICP-MS method. The standard value of the lead content in the MESS-4 standard sample is 21.5 mg/kg, and the average result after three experiments was 23.49 ± 2.89 . Thus, the recovery of Ag in the MESS-4 standard sample after three repeated experiments is 109.27%, falling within the allowable range according to the AOAC standard of 80-110% [11]. Therefore, the evaluation result of the recovery of silver in the MESS-4 sediment standard sample demonstrates that the analysis procedure for lead content in sediment is highly accurate and reliable.

2.4. Geochemical Accumulation Index (Igeo)

Since 1969, the Geoaccumulation Index (Igeo) has been commonly used as a parameter in geochemistry for evaluating the degree of pollution caused by an element in sediment or soil [12]. Initially introduced by Müller [13], the Geoaccumulation Index (Igeo) is determined by Equation (1):

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

In this equation, C_n denotes the measured concentration of the element in the soil dust, while B_n represents the baseline geochemical value (set at 15 for Pb). The constant 1.5 serves as a factor accounting for the natural fluctuations in metal concentrations in the environment, effectively capturing minor anthropogenic impacts. Müller's classification of Igeo is as follows: (0) $I_{geo} = 0$: no metal contamination; (1) $0 < I_{geo} < 1$: negligible to moderate contamination; (2) $1 < I_{geo} < 2$: moderate contamination; (3) $2 < I_{geo} < 3$: moderate to heavy contamination; (4) $3 < I_{geo} < 4$: heavy contamination; (5) $4 < I_{geo} < 5$: heavy to extremely severe contamination; (6) $5 < I_{geo}$: extremely severe contamination [13].

2.5. Risk Assessment Code (RAC)

The Risk Assessment Code (RAC) is a commonly employed approach for assessing the potential risk associated with metal presence in sediment. This index offers insights into the ecological risk posed by metals, deriving from the ratio of exchangeable and carbonate-bound fractions in soil compared to the total content of 5 forms outlined in formula (2). F1 and F2 forms are recognized as constituents of poorly bound heavy metals in sediment [14], thus their potential release can pose environmental threats. RAC categorizes risk levels into various tiers including none, low, moderate, high, and very high [15]. The RAC calculation formula is expressed as:

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

Risk levels are classified accordingly: $RAC < 1\%$ denotes no risk, $RAC = 1\text{--}10\%$ signifies low risk, $RAC = 11\text{--}30\%$ suggests moderate risk, $RAC = 31\text{--}50\%$ indicates high risk, and $RAC > 50$ implies a potential very high risk associated with metals in sediment samples, particularly concerning their susceptibility to entering the food chain [16].

3. Results and discussion

3.1. Total Pb content in the studied sediment samples

The analysis results in Table 3 indicate that the total Pb content in the sediment samples ranges from 29.16 to 89.19 mg/kg. The highest Pb content was found in the L4 stream sediment sample (89.19 mg/kg), while the lowest was in sample L6 (29.16 mg/kg). The Pb content in the six stream sediment samples was relatively similar, with little variation, except for sample L4, which had a significantly higher Pb content compared to the other sediment samples. This could be explained by the proximity of this area to the gold mining area operated by the Gio Ngan Investment Corporation. Therefore, waste materials during the mining process may be discharged into the stream and accumulate in the sediment, resulting in higher Pb content in this area compared to the other five sediment samples. When comparing the total Pb content in the six sediment samples with the permissible limit for freshwater sediment according to Vietnamese standards (2017), the total Pb content in all sediment samples is below the permissible limit specified in Vietnamese standards 2017 (91.3 mg/kg) [17]. Thus, according to Vietnamese standards, the Pb content in the sediment samples is below the pollution threshold.

3.2. Chemical fraction of Pb in sediment samples

The results of analyzing the chemical fractions of Pb in the sediment samples are presented in Table 3, and the percentage distribution of Pb in chemical fractions is depicted in Figure 1. According to the findings in Table 3 and Figure 1, Pb was predominantly distributed in decreasing order of abundance as follows: $F5 > F3 > F2 \sim F4 \sim F1$ across the sediment samples. In all sediment samples, the content of Pb in the chemical fraction F5 is the highest, accounting for approximately 26.77% to 84.85% of the total of all 5 chemical fractions. Specifically, sample L4 exhibited the highest percentage of Pb in fraction F5, comprising 84.85%, whereas sample L1 showed the lowest percentage of Pb in fraction F5 at 26.77%. The distribution of Pb content in chemical fractions varied among the sediment samples. In sample L1, the distribution order was $F5 > F2 \sim F3 > F1 > F4$, while in samples L2, L3, and L4, it was $F5 > F3 > F4 > F1 > F2$. In sample L5, the distribution order was $F5 > F3 > F4 > F2 > F1$, and in sample L6, it was $F5 > F3 > F2 > F4 > F1$. This disparity was attributed to several factors, including: Geological and Geographical Factors, Anthropogenic Activities, Sediment Properties, Redox Conditions and Biological Activity.

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 [9].

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) [18].

Sediment Properties: Physical and chemical properties of soil or sediment, such as texture, mineralogy, pH, organic matter content, and cation exchange capacity, play a crucial role in determining the distribution of heavy metal fractions. These properties influence the sorption,

retention, and mobility of heavy metals within the soil/sediment matrix, leading to variations in their spatial distribution and availability [19].

Redox conditions (oxidation-reduction potential) in soil or sediment strongly influence the speciation and mobility of heavy metals. Reducing conditions can enhance the solubility and mobility of certain heavy metals, while oxidizing conditions may promote their immobilization. Changes in redox conditions due to factors such as waterlogging, organic matter decomposition, or anthropogenic disturbances can alter the distribution of heavy metal fractions over time [20].

Biological processes, including microbial activity, plant uptake, and organic matter decomposition, can influence the distribution of heavy metal fractions by altering their speciation and bioavailability. Microorganisms can participate in biogeochemical cycling of heavy metals, affecting their transformation, immobilization, or release within soil or sediment environments [21].

The six studied sediment samples had different topography, human activities, properties, biological and redox conditions. Therefore, they might have differences in chemical fractions.

Table 3. The total content and chemical forms of Pb in the sediment samples

Sample	F1	F2	F3	F4	F5	Total content
	mg/kg					
L1	5.33 ± 0.03	8.89 ± 0.07	8.89 ± 0.06	1.67 ± 0.01	9.06 ± 0.74	33.84
L2	1.23 ± 0.01	0.99 ± 0.01	11.82 ± 0.65	2.69 ± 0.05	12.72 ± 0.80	29.45
L3	1.23 ± 0.01	0.99 ± 0.03	14.46 ± 0.14	4.45 ± 0.01	18.58 ± 0.72	39.69
L4	1.81 ± 0.06	0.99 ± 0.02	8.31 ± 0.04	2.40 ± 0.07	75.68 ± 0.50	89.19
L5	0.49 ± 0.03	0.99 ± 0.05	6.84 ± 0.16	1.81 ± 0.09	23.70 ± 0.46	33.84
L6	1.52 ± 0.06	3.92 ± 0.13	5.67 ± 0.27	2.40 ± 0.28	15.65 ± 0.60	29.16
The permissible limit of Pb content in freshwater sediments (QCVN 2017)						91.3

Although there are differences in the distribution order of Pb fractions, the Pb content in the sediment samples is predominantly distributed in fractions F5 and F3. This is consistent with natural conditions where most metals exist in the stable residual fraction due to geological processes in nature and partly in fraction F3. These analytical results are consistent with previous studies on the chemical fractions of Pb in sediments of the Cau River [22] and Tri An Lake in Vietnam [23]. The findings consistently indicate that Pb is predominantly present in fraction F5, with the distribution order typically being F5 > F3 > F4 ~ F2 > F1 [23], [24]. The exceptional dominance of F5-Pb distribution in sample L4 compared to other sediment samples can be attributed to the ongoing gold mining activities in the area, where predominantly residual waste is discharged into streams and accumulates in surface sediments.

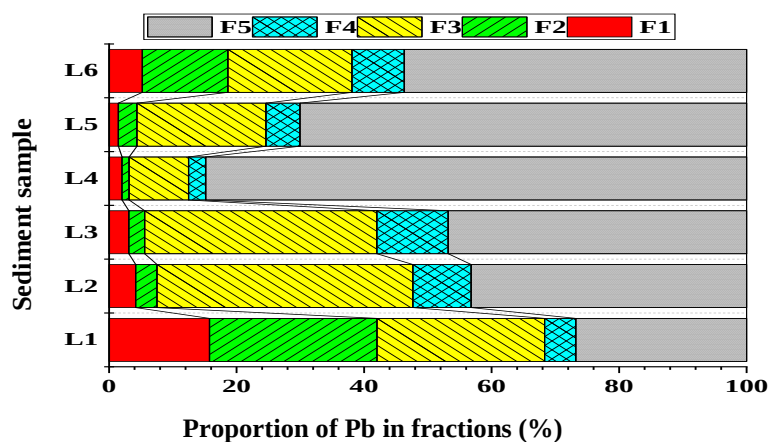


Figure 1. Percentage distribution of chemical fractions of Pb in sediment

3.3. Assessment of pollution risk levels

3.3.1. Geoaccumulation Index (Igeo)

In this study, the calculated Igeo coefficient for silver in the soil samples is depicted in Figure 2.

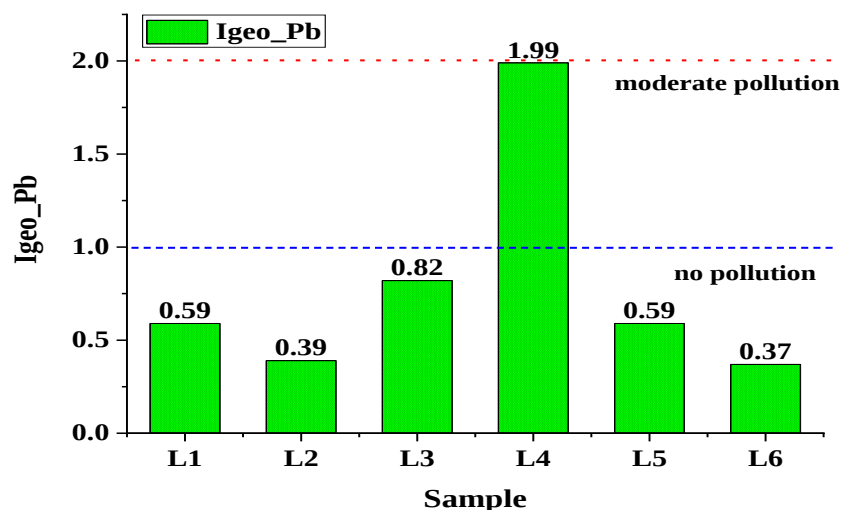


Figure 2. Igeo index of Pb in the studied sediment

The Igeo values of Pb have been calculated and presented in Figure 2. The results indicate that, for Pb, the Igeo values of samples L1-L3 and L5-L6 were below 1, indicating non-pollution levels. However, sample L4 had the highest Igeo value, falling within the range of $1 < \text{Igeo} < 2$, indicating moderate pollution. This can be explained by the fact that the Igeo value is based on the total metal content for assessment. Sample L4 had the highest Pb content, resulting in the highest Igeo value for this sample.

3.3.2. Risk Assessment Code (RAC)

In addition to the Igeo index, the Risk Assessment Code (RAC) is also used to assess the level of pollution risk posed by metals in soil. The RAC values of the soil samples have been calculated according to formula (2) and the results are presented in Figure 3.

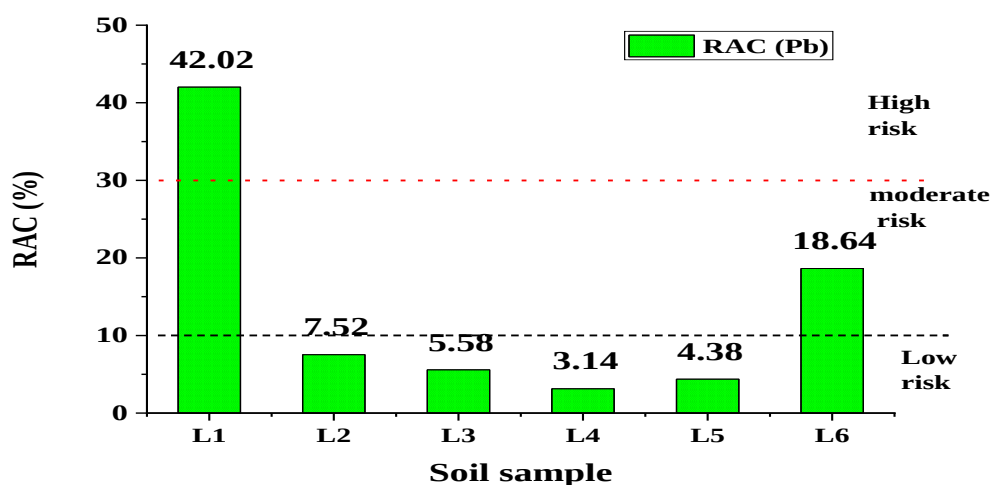


Figure 3. The RAC index of Pb in the sediment samples and the risk levels

The results in Figure 3 show that the RAC values of Pb in the sediment samples ranged from 3.14 to 42.02%. The highest RAC value of Pb was found in sample L1 (42.02%), while the lowest was in sample L4 (3.14%). This can be explained by the distribution of Pb in sample L1, where Pb was predominantly present in forms F1 and F2, especially with F2 being significantly higher compared to the other samples, resulting in the highest RAC value. For sample L4, despite having the highest total Pb content among the six samples, the percentage of Pb distributed in forms F1 and F2 was not high, hence resulting in the smallest calculated RAC value.

Comparing the RAC values of Pb in the sediment samples with pollution risk levels, the results show that samples L2-L5 all had Pb levels posing a low risk, while sample L6 posed a moderate risk, and sample L1 posed a high risk. Thus, although samples L1 and L6 did not have higher total Pb content than the permissible limit, the distribution of Pb in these samples indicates a potential risk of environmental pollution under appropriate conditions (such as low pH).

The contrast in Igeo and RAC results for samples L1 and L4 could be explained by the difference in chemical distribution of Pb in these samples. For sample L1, Pb was distributed mainly in the F1-F4 fractions and to a lesser extent in the F5 form, while in the L4 sample, Pb was primarily distributed in the F5 fraction and to a lesser extent in the F1-F4 form. Therefore, when evaluated according to the RAC index, the RAC value in sample L1 was higher than in L4. However, when evaluated according to the Igeo index, it was the opposite, the Igeo index is based on the total content of metals. For sample L4, the total Pb content was higher than that in sample L1. Therefore, the calculated Igeo value of Pb in sample L4 was much higher than that in sample L1. To sum up, it is necessary to assess the risk level and pollution potential based on both the total content (Igeo) and chemical fractions (RAC) of metals in the sediment samples.

4. Conclusion

This study analyzed the total lead content in sediment samples from the Than Sa gold mining area. The results show that the average total lead content in the sediment samples ranges from 29.16 to 89.19 mg/kg, all of which were below the permissible limit according to Vietnamese standards in 2017. Chemical form analysis of lead in soil samples indicates the presence of lead in the following order: F5 > F3 > F2 ~ F4 ~ F1. The study assessed the risk level of lead in the sediment samples using the Igeo and RAC indices. The results show that, based on the Igeo assessment, 5 out of 6 sediment samples have Igeo values indicating low risk, whereas sample L4 had a higher Igeo value, indicating moderate pollution. When evaluated using the RAC index, 4 out of 6 sediment samples posed no risk for lead, while sample L6 was at a moderate risk level and sample L1 was at a very high-risk level. Therefore, it can be observed that according to environmental risk assessment indices such as Igeo and RAC, the analyzed sediment samples may exhibit pollution levels according to the Igeo index but low-risk levels according to the RAC index and vice versa. Thus, it is necessary to assess the risk level and pollution potential based on both the total content (Igeo) and chemical fractions (RAC) of metals in sediment samples to comprehensively evaluate the level and risk of lead pollution in sediment samples. To fully evaluate the extent of lead and heavy metal pollution in this area, more research should be done by examining water samples. The results could provide environmental managers with vital information to solve the environmental issues of this zone.

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