CHEMICAL FRACTION ANALYSIS AND ASSESSMENT OF ASERNIC IN SOILS SAMPLED IN A Pb/Zn MINING AT HICH VILLAGE IN THAI NGUYEN PROVINCE

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ABSTRACT

The pollution of heavy metals in ore mining areas is severe at present in Vietnam as well as in the world. Assessing the level and risk of contamination of arsenic (As) in the soil in the ore mining area is essential for environmental management. The total content and chemical fractions of As in the soil samples were performed according to Tessier's extraction procedure and using the ICP-MS method. The average concentration of As in the 5 tailing samples ranged from 10.14 ÷ 44.68 mg kg^{-1} and in the 7 agricultural samples was 5.66 ÷ 7.65 mg/Kg. In the investigated soil samples, As was found mainly in the fractions of residues (F5) > carbonate (F2) > Fe/Mn oxides (F3) > Organic carbon (F4) > exchangeable fraction (F1). According to Vietnamese standards, the concentration of As in agricultural soil samples was all lower than the allowable limit, while 3/5 of the tailing samples had As concentrations less than the permissible limit in agricultural soil and the other 2 samples had As concentrations higher than the allowable limit. According to the Igeo index, most soil samples had Igeo values at a mildly contaminated level. According to the Risk Assessment Code (RAC), 10/12 soil samples analyzed were at medium risk.

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

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TÓM TẮT

Tình trạng ô nhiễm các kim loại nặng ở các khu vực khai thác quặng là rất nghiêm trọng hiện nay ở Việt Nam cũng như trên thế giới. Đánh giá mức độ và nguy cơ ô nhiễm của asen (As) trong đất ở khu vực khai thác quặng là rất cần thiết đối với việc quản lý môi trường. Phân tích hàm lượng tổng số và dạng hóa học của As trong các mẫu đất được thực hiện theo quy trình chiết Tessier và thiết bị ICP-MS. Nồng độ trung bình của As trong 5 mẫu đất bãi thải là 10,14 ÷ 44,68 mg/Kg và trong 7 mẫu đất nông nghiệp là 5,66 ÷ 7,65 mg/Kg. As trong 12 mẫu đất phân tích đều tồn tại chủ yếu trong các mẫu đất ở dạng cặn dư (F5) > dạng cacbonat (F2) > dạng oxit Fe/Mn (F3) > dạng hữu cơ (F4) > dạng trao đổi (F1). Theo tiêu chuẩn Việt Nam, nồng độ của As trong các mẫu đất nông nghiệp đều thấp hơn giới hạn cho phép, và 3/5 mẫu đất bãi thải có nồng độ As thấp hơn giới hạn cho phép trong đất nông nghiệp và 2 mẫu đất bãi thải có nồng độ As cao hơn giới hạn cho phép. Theo chỉ số Igeo, hầu hết các mẫu đất đều có giá trị Igeo ở mức ô nhiễm nhẹ. Theo mã đánh giá mức độ rủi ro (RAC) thì 10/12 mẫu đất phân tích nằm ở mức rủi ro trung bình.

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1. Introduction

Heavy metals have existed naturally in the environment and along with human development. However, human activities such as mining have increased pollution levels of heavy metals in the environment [1]. Some heavy metals play a vital role as a source of vitamins and minerals in the functioning of organs in the body (Cu, Zn, Mn, *etc*.) [2]. Humans and plants require small amounts of heavy metals such as Cu, Zn, Mn, and Ni, but these metals become toxic when consumed at higher concentrations which surpass the permissible limits [3]. Other metals, such as arsenic, lead and mercury, have no valuable role in the human body. These elements can be toxic to humans even at low levels of exposure [4]. Heavy metals are resistant in nature and nonbiodegradable [5]. After being delivered into human's body through the four primary ways, such as digestion, inhalation, drinking and skin contact [5], they accumulate in chief organs, including the brain, liver, bones, and kidneys, for a long time and seriously threaten human health [6]. Arsenic is a common element in various compounds in the earth's crust and is the top toxic element on the list of poisonous metals set up by the United States Agency for Diseases and Toxicology. Arsenic is considered a human carcinogen at extremely low levels [7]. Long-lasting exposure to arsenic compounds can induce many serious human diseases, such as nausea, vomiting, abdominal pain, muscle cramps and diarrhea [7], [8].

To assess the pollution level of heavy metals in general and As in particular in soil, it is common to analyze the total concentration of As. However, to fully assess As's level and contamination risk, it is necessary to analyze their chemical fractions in the soil [9]. There are many continuous extraction procedures applied to analyze the chemical fractions of metals in soil, of which the Tessier continuous extraction procedure is a commonly used procedure to extract the chemical forms of metals. This procedure has been applied by many studies [10]–[12]. There are many methods to assess the level and risk of heavy metal contamination in soil, of which the Igeo index and RAC are two methods that have been widely used to evaluate heavy metals in soil.

The Pb/Zn mining area of Hich village has high concentrations of heavy metals in the soil, which has been reported in previous studies [13], [14]. These works mainly studied Pb, Zn and Cd, and there are very few studies focussing on the chemical form of As and assessing the level and risk of As contamination in agricultural soils in this area. Therefore, this study focuses on (1) investigating the chemical fractions of As in the tailing and agricultural land in the Pb/Zn mine area of Hich village, Dong Hy district, Thai Nguyen province, using the Tessier sequential extraction process and ICP-MS method. Besides, this study also assesses the level and risk of As contamination in the soil in this studying zone based on Igeo and RAC.

2. Materials and methods

2.1. Soil samples

12 surface soil samples (0-20 cm), including 5 samples of tailing and 7 samples of farmland near the dump area, were taken in November 2018 at the Pb/Zn mine site in Hich village (21 °43.401′N; 105°51.276′E), in Dong Hy district, Thai Nguyen province. After being delivered to the laboratory, the samples were pretreated by drying naturally in the air, then crushed and sieved through a sieve with a diameter of 2 mm and stored in sealed plastic bags. Information about the location of the investigated soil samples is shown in Figure 1.

2.2. Analysis methods

To determine the total content of arsenic in soil samples, the soil samples were digested according to U.S EPA method 3051A [15] with a mixture of concentrated HNO_3 and HCl acids (1:3 by volume) in a Mars 6 microwave oven (CEM company, USA). The details are briefly described as follows: scaling 0.5g of the ground dry soil sample, then 8 mL of a mixed acid solution consisting of 2.0 mL of concentrated HNO_3 acid solution and 6.0 mL of concentrated HCl solution was added, and transfer to the Teflon tubes of the Mars 6 microwave, then the microwave system was set to digest the soil sample. The extraction procedure for the chemical fractions of As in the soil was performed according to the Tessier sequential extraction procedure described in Table 1.

Figure 1. *Sampling locations of the soil samples in the Pb/Zn mining collected at Hich village, in Dong Hy district, Thai Nguyen province (S1-S5: tailing sample; S6-S12: agricultural soil sample)*

Table 1. *Tessier's sequential extraction procedure applied for As in the investigated soil sample* [17]

Code	Chemical fraction	Chemicals	Extracting time/ Temperature
F1	Exchangeable fraction	CH_3COONH_4 1 M (pH = 7)	1h/ 25^oC
F2	Carbonate fraction	CH_3COONH_4 (CH_3COOH, pH = 5)	5h/ 25 ^oC
F3	Fe-Mn oxyhydroxide fraction	$NH_2OH.HCl$ 0.04 M/ CH_3COOH 25% (v/v)	5h/ 95^oC
F4	Organic matter fraction	CH_3COONH_4 3.2 M/ HNO_3 20%	0.5h/ 25 ^oC
F5	Residue fraction	HNO_3: HCl (3:1 v/v)	0.5h/ 25 ^oC

2.3. Evaluation of the analytical procedure for analyzing the total concentration of As

The sediment standard sample MESS-4 was used to evaluate the accuracy of the As analysis procedure using the ICP-MS method. The analysis of ^{75}As might have interfered with the mass overlap in the presence of ArCl (75). Therefore, the collision mode, which utilized a non-reactive gas (He) and a process called kinetic energy discrimination (KED), was performed to selectively attenuate all polyatomic interferences based on their size to discard the interference of mass overlap, ensuring the reliability and accuracy of the As analysis using the ICP-MS method. The MESS-4 standards with known concentrations of As provided by the manufacturer (21.7 ± 2.8 mg kg^{-1}) were digested and analyzed using ICP-MS NexION 2000 (Perkin Elmer, USA), (repeated three times). The average recovery of As was evaluated based on the analysis of the average total content after three times of experiments. The result of the recovery value of the analytical method obtained was 92.3%. This value was within the allowable range of the AOAC standard (80% ÷ 110% for the concentration value < 100 mg kg^{-1}) [16], ensuring the reliability and accuracy of the analytical method.

2.4. Geo-accumulation Index (Igeo)

The Geo-accumulation Index (Igeo) is a mathematical calculation method introduced by Muller in 1969, which has been widely applied to assess the level of pollution of heavy metals in soils all over the world [18]–[22].

The Igeo index is calculated according to the following equation:

$$\mathrm{Igeo} = \log_2 \frac{\mathrm{Cn}}{1.5.\mathrm{Bn}} \quad (1)$$

Cn is the concentration of As element in the soil; Bn is the geological background concentration (Bn of As = 1.8) and 1.5 is a constant that allows adjusting for natural fluctuations of the element content in the soil. The resulting values are classified into seven categories as follows: (1) Igeo < 0, no contaminated cells; (2) 0 < Igeo < 1, no pollution to moderate pollution; (3) 1 < Igeo < 2, moderately polluted; (4) 2 < Igeo < 3, moderate to high pollution; (5) 3 < Igeo < 4, highly polluted; (6) 4 < Igeo < 5, pollution from very high to extremely severe; (7) Igeo ≥5, extremely polluted [23].

2.5. Risk Assessment Code (RAC)

The Risk Assessment Code (RAC) is used to assess soil's level of heavy metal contamination [24]. The RAC was calculated according to formula (2), taking into account the percentage of heavy metals present in the form of exchangeable fractions (F1) and carbonates (F2) according to the Tessier continuous extraction process [25]. RAC is calculated as follows

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

Where, F1 and F2 are the concentrations of the metal forms in the mobile form (F1) and the form bound to the carbonate (F2). C is the total concentration of 5 forms (F1+ F2+ F3+ F4+ F5).
Concentrations of heavy metals in soil can be classified by the RAC as no risk - environmentally safe (RAC < 1%), low risk - relatively safe to the environment (1%). < RAC < 10%), moderate risk - relatively hazardous to the environment (10% < RAC < 30%), high risk - hazardous to the environment (30% < RAC < 50%), and very high risk - very dangerous for the environment (RAC > 50%) [24].

3. Results and discussion

3.1. Total concentration of As in soil samples

The total concentration of As in the agricultural soil (NN) and tailing samples (BT) is shown in Table 3. Table 3 shows that the total As concentration in the tailing samples ranged from 10.143 ÷ 44.684 mg/Kg, while the total concentration of As in agricultural soil samples was less, in the range of 5.662 ÷ 7.649 mg/Kg. The agricultural soil samples were all below the allowable limit of agricultural land (15 mg/Kg) according to the regulations of the Ministry of Natural Resources and Environment of Vietnam [26].

Meanwhile, there were two of the five tailing samples which had As concentration higher than the permissible standard of agricultural land according to regulations of the Ministry of Natural Resources and Environment of Vietnam (25 mg kg-1), (S1: 44.684 mg kg-1 and S5: 39.389 mg kg-1) (Table 2). The comparison of the average As the concentration of the agricultural and tailing samples is shown in Figure 2. Figure 2 shows that the average concentration of As in the tailing soil (BT: 20.042 mg/Kg) was higher compared to agricultural land (NN: 6.864 mg/Kg) ($p < 0.05$), and 3.5 times higher than that of agricultural land. Thus, it can be said that the analyzed soil samples were below the allowable range according to Vietnamese standards, except for two samples, S1 and S5, which were higher than the permissible limit of the Ministry of Natural Resources and Environment of Vietnam [26]. The comparison of As content in the soil samples of this study with the results of arsenic content in Pb/Zn mine areas around the world is shown in Table 2.

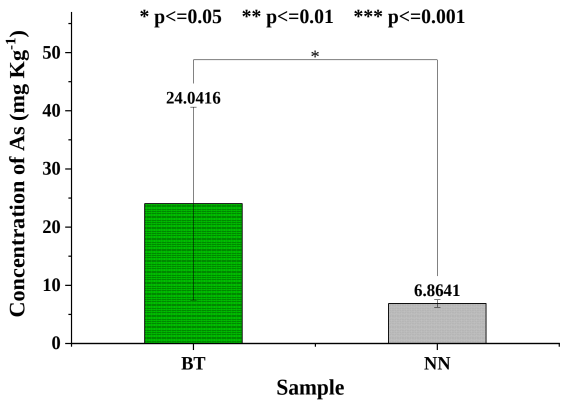

Figure 2. *Comparison of the mean concentration of As in tailing sample (BT) and agricultural sample (NN)*

Table 2. *Comparison of concentration of As in the Pb/Zn mining of this study with other previous studies*

Nr	Studied zone	As concentration (mg kg^{-1})	Analytical method	Reference
1	**This study**	5.6 ÷ 44.7	ICP-MS	
2	Pb/Zn mining in India	9.0 ÷ 367.0	ICP-AES	[27]
3	Pb/Zn mining in Guangxi province, China	11 ÷ 44,6	AFS	[28]
4	Pb/Zn mining in China	1 ÷ 132	ICP-AES	[29]
5	Pb/Zn mining, Ebonyi State, South Nigeria	1.9 ÷ 1333	ICP-MS	[30]
6	Pb/Zn mining, Yunnan, province, China	4.96 ÷ 826	AFS	[31]
7	Pb/Zn mining, Sichuan province, China	1.25 ÷ 50.67	ICP-MS	[32]
8	Permissible limits for As in agricultural soil	15		[26]
	Permissible limit for As in industrial soil	25		

ICP-MS: Inductively coupled plasma mass spectrometry; ICP-AES: Inductively coupled plasma atomic emission spectroscopy; AFS: Atomic fluorescence spectrometry

Table 2 shows that the As concentrations in soil samples reported by this study were close to the As concentrations in the Pb/Zn mine site in Guangxi province, China [28], and Sichuan province, in China [32]. The As concentration in the soil samples in this study was significantly less than in the three soil samples of the Pn/Zn mining area in India [27], South Nigeria [30] and Yunnan province in China [29]. The difference in As concentration in soil samples in Pb/Zn mine areas around the world might be speculated by the difference in physicochemical properties of each soil sample in each studying area, the history of ore mining in those areas, and the human impact in the mining process

3.2. Chemical fractions of As in soil samples

The chemical analysis of arsenic in soil samples was performed using the Tessier continuous extraction procedure and the results of the As concentration in the chemical fractions determined using the ICP-MS instrument are shown in Table 3. The percentage of arsenic species in the soil samples is shown in Figure 3. Figure 3 shows that, in the analyzed soil samples, As existed in the descending sequence of residual fraction (F5) > carbonate fraction (F2) > Mn/Fe oxide bound fraction (F3) > organic fraction (F4) > exchange fraction (F1). It meant that arsenic existed mainly in the residue fraction, which is stable under the influence of the surrounding environment, so As might not be dissolved and enter the groundwater or the surrounding environment. In contrast, As existed very little in the F1 fraction, which is less stable and easily penetrates the groundwater and the surrounding environment. Soil samples with high concentrations of arsenic in the F1 fraction pose a risk of contaminating the surrounding environment. Consequently, all studied soil samples had arsenic that existed primarily in the residue fraction (F5) and very little in the exchangeable fraction (F1), so these soil samples had no risk of As pollution to the surrounding environment.

Table 3. *The mean concentration of As in chemical fractions of tailing (BT) and farming soil (NN)*

Sample	F1	F2	F3	F4	F5	Total
			mg kg^{-1}			
S1	0.064 ± 0.001	16.534 ± 0.005	5.111 ± 0.047	0.721 ± 0.007	22.253 ± 0.045	44.684 ± 0.104
S2	0.003 ± 0.000	2.169 ± 0.003	1.655 ± 0.000	0.300 ± 0.001	7.918 ± 0.045	12.042 ± 0.080
S3	0.015 ± 0.001	2.063 ± 0.002	1.507 ± 0.016	0.173 ± 0.001	6.384 ± 0.130	10.143 ± 0.146
S4	0.003 ± 0.001	2.466 ± 0.001	0.792 ± 0.003	0.079 ± 0.001	10.610 ± 0.051	13.950 ± 0.005
S5	0.005 ± 0.003	15.824 ± 0.015	1.924 ± 0.013	0.374 ±0.001	21.27 ± 0.114	39.389 ± 0.145
S6	0.030 ± 0.002	0.944 ± 0.015	0.628 ± 0.028	0.168 ± 0.010	3.893 ± 0.183	5.662 ± 0.314
S7	0.045 ± 0.002	1.524 ± 0.092	0.686 ± 0.038	0.091 ± 0.006	4.668 ± 0.208	7.013 ± 0428
S8	0.033 ± 0.002	1.538 ± 0.175	1.192 ± 0.137	0.144 ± 0.008	4.741 ± 0.097	7.649 ± 0.336
S9	0.036 ± 0.003	1.929 ± 0.082	0.464 ± 0.038	0.145 ± 0.008	4.036 ± 0.129	6.610 ± 0.260
S10	0.031 ± 0.002	1.730 ± 0.168	0.472 0.021	0.052 ± 0.003	4.428 ± 0164	6.714 ± 0.358
S11	0.022 ± 0.001	1.782 ± 0.204	1.211 ± 0.067	0.049 ± 0.003	4.425 ± 0.081	7.488 ± 0.356
S12	0.039 ± 0.003	1.732 ± 0.074	0.633 ± 0.051	0.073 ± 0006	4.435 ± 0.027	6.912 ± 0.162

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

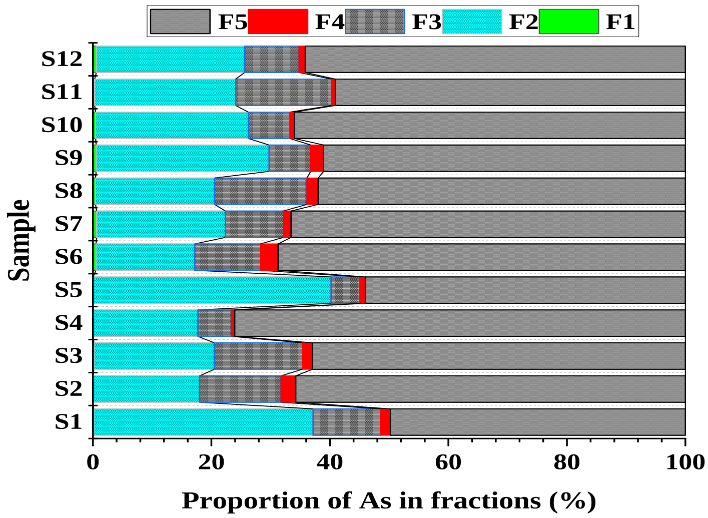

Figure 3. *The distribution of As in chemical fractions in the studied soil (F1: exchangeable fraction, F2: carbonate fraction; F3: Fe/Mn-oxyhydroxides fraction; F4: organic matter fraction; F5: residue fraction)*

3.3. Assess the pollution level and risk

3.3.1. Geo-accumulation Index (Igeo)

The results of calculating the average Igeo index of As in the soil samples from tailing (BT) and agricultural land (NN) are shown in Figure 4. Figure 4 shows that the average Igeo value of BT soil samples is 2.96 which was higher than that of NN soil samples (1.35) ($p < 0.001$). The average Igeo value of the agricultural soil samples ranges from 1 ÷ 3, indicating that they were slightly polluted, while the mean Igeo value of the tailing soil samples (BT) was 2.96, close to the level of heavy pollution. Some tailing samples had Igeo values higher than 3, illustrating that they might be in the heavily polluted level, according to Igeo.

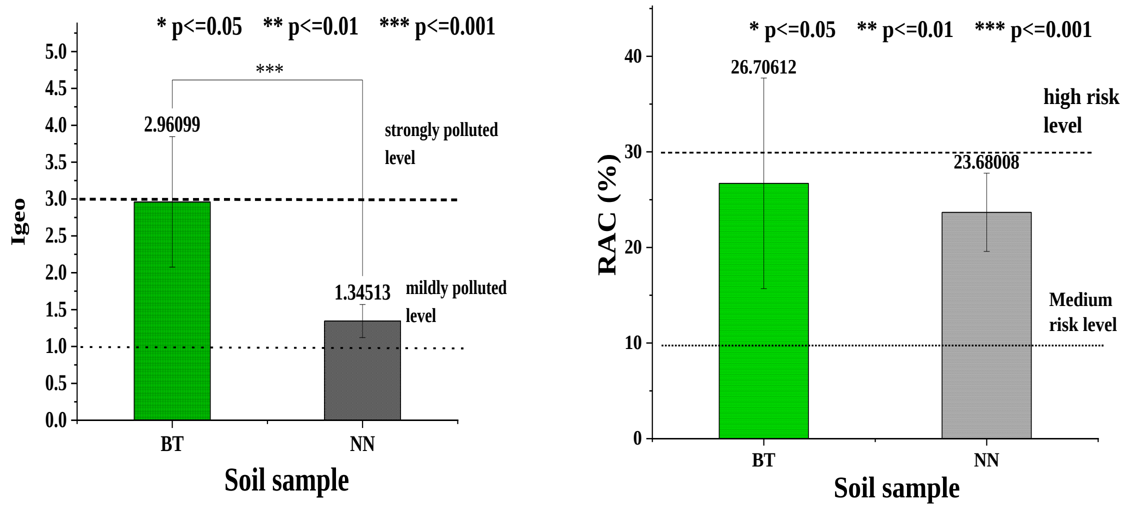

Figure 4. *Igeo index and RAC of As in tailing sample (BT) and agricultural sample (NN)*

3.3.2. Risk assessment code (RAC)

Besides the Igeo index, which is based on total arsenic, the risk assessment code (RAC) was also implemented to evaluate the percentage of exchange form (F1) and carbonate form (F2). The results of the comparison of mean RAC values in samples of tailing and agricultural land (NN) are shown in Figure 4. Figure 4 shows that the average RAC value of BT and NN soil was 26.70 and 23.68, respectively, and there was no statistically significant difference between them ($p > 0.05$). Both RAC values were in the range of 10% ÷ 30%, at medium risk. However, some tailing samples with RAC values higher than 30% were at high risk. Thus, according to Vietnamese standards, most soil samples have arsenic concentrations below the allowable limit, and only two tailing samples (S1 and S5) were higher than the permissible limit for industrial land (25 mg/Kg). According to the Igeo index, the samples of agricultural land (NN) and tailing (BT) had Igeo index at a mildly polluted level, and only a few samples of tailing (BT) had an Igeo index higher than 3, indicating a mildly contaminated level. According to the RAC risk assessment code, all soil samples were at medium risk, and merely some tailing samples (BT) had RAC values higher than 30%, so they were at high risk.

4. Conclusion

The total concentration of As in 12 samples of agricultural land and waste dumps was determined using ICP-MS method. The average content of tailing and agricultural soil samples were 24.04 and 6.86 mg kg^{-1}, respectively. The concentration of As in the chemical fractions was analyzed according to Tessier's sequential extraction procedure. The results showed that As existed in the soil in the following order: F5 > F2 > F3 > F4 > F1. As mainly existed in the F5 fraction, which is very environmentally stable, while it existed minimally in the F1 fraction, which is easily absorbed into the surrounding environment. According to Vietnamese standards, the total concentration of arsenic in agricultural and industrial soil samples was lower than the allowable limit, and only two soil samples of tailing samples (S1 and S5) were higher than the permissible limit. According to the Igeo index, most of the Igeo values of the soil samples were at a mildly polluted level, and according to the RAC index, the soil samples all had the RAC of arsenic at moderate risk, especially for samples S1 and S5, which had Igeo and RAC values located at high pollution (Igeo > 3) and high risk (RAC > 30%). Therefore, the analyzed soil samples generally had As concentrations at the allowable level and were safe regarding arsenic concentrations for the surrounding environment.

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