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Accumulation of Arsenic and Heavy Metals in Native and Cultivated Plant Species in a Lead Recycling Area in Vietnam

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Abstract: This study was conducted to determine the soil contamination and the accumulation of arsenic (As) and heavy metals including chromium (Cr), copper (Cu), zinc (Zn), cadmium (Cd), and lead (Pb) in 15 native and cultivated plant species in a Pb recycling area of Dong Mai village, Hung Yen Province, Vietnam. The analysis of 32 soil samples collected from seven different sites in the study area revealed that the contents of Al, Fe, As, Cr, Cu, Zn, Cd, and Pb in the soils ranged from 6200–32,600, 11,300–55,500, 5.4–26.8, 24.9–290, 66.0–252, 143–455, 0.71–1.67, and 370–47,400 mg/kg, respectively. The contents of As, Cr, Cu, Zn, Cd, and Pb in rice grains and the shoots of 15 plant species ranged from 0.14–10.2, 1.00–10.2, 5.19–23.8, 34.7–165, 0.06–0.99, and 2.83–1160 mg/kg-dry weight (DW), respectively. *Hymenachne acutigluma* (Steud.) Gilliland, a potential hyperaccumulator of Pb (1160 mg/kg–DW), is considered the best candidate for phytoremediation of Pb-contaminated soil. The cultivation of rice and vegetables, and the use of some native plants for food for humans, pigs, and cattle should be managed with consideration of the accumulation of Pb in their aboveground biomass.

Keywords: arsenic; heavy metals; hyperaccumulator; lead recycling; phytoremediation; soil contamination

1. Introduction

Contamination by heavy metals and metalloids is one of the most harmful forms of environmental pollution. Being different from many organic pollutants, heavy metals and metalloids are not biodegradable and are more difficult to remediate. The first half-life of heavy metals in soils under lysimetric conditions varies greatly, e.g. that of lead (Pb) being the longest at 740 to 5900 years [1]. The main sources of metal contamination in soil are the mining and smelting of metalliferous ores, landfill leachate, fertilizers, and pesticides [2,3]. Heavy metals mainly enter plants via the soil or atmosphere [4,5]. Chromium (Cr), copper (Cu), and zinc (Zn) are micronutrients essential for plant growth, but they are toxic when present at high contents [6,7]. Arsenic (As), cadmium (Cd), and Pb are not essential elements [7–10] and are toxic to plants at contents of 5–20, 5–30, and 30–300 mg/kg tissue, respectively [11].

Environmental pollution caused by manufacturing activities in industrial zones is of great concern in Vietnam as well as in other developing countries. A parallel still exists for traditional handicraft villages that are interspersed with residential villages. The activities of these traditional villages in Vietnam heavily pollute the surrounding ecosystem and pose a severe health risk to the local people [12]. The operational model of traditional villages interspersed with residents makes pollution control difficult for many reasons. Most notable is the poor planning, management, and handling of hazardous wastes. In the Chi Dao Commune, Van Lam District, Hung Yen Province, Vietnam, the Pb recycling area has existed for more than 4 decades. Activities such as the collection of old batteries and the processing and smelting of Pb have had negative impacts for a long time. Currently, Dong Mai is still assessed as a typical village in which the local activities are causing serious environmental pollution in Hung Yen Province, with many health harmful effects on the local residents [13–16]. The blood Pb levels in nearly one-fifth of the local children (24 out of 109 children examined) were reported to exceed the allowable limit in 2012 [17]. Therefore, the monitoring and remediation of As and heavy metal contamination in Vietnam are of great interest to many concerned agencies and organizations, but the efficiency of these processes is very limited. Various physical and chemical methods have been developed worldwide for environmental pollution monitoring and remediation with positive results [18–20]. However, the disadvantages of these methods are their high cost and the potential for secondary pollution. This fact is hidden in the application of these technologies for environmental remediation in this seriously contaminated area.

Phytoremediation is a plant-based, cost-effective, and environment-friendly technology for cleanup of the contaminated environment [21,22]. Plant species that can take up and store metals in their tissues at high levels that are a multiple of the content found in nearby plants are hyperaccumulators [23]. Hyperaccumulators can be defined as plants accumulating at least 100 mg/kg-DW of Cd; 1000 mg/kg-DW of As, Cr, Cu, or Pb; or 10,000 mg/kg-DW of Zn [24–26].

In addition to identification of appropriate plant species for use as hyperaccumulator and phytoremediation, the accumulation of As and heavy metals in cultivated plants (such as vegetables and rice) growing in the contaminated environments is also of great concern for public health. Several studies have reported the high levels of As and metal accumulation in cultivated plants which pose a risk to exposed individuals [27–31].

Previous studies in the Dong Mai Pb recycling area showed very high contents of Pb in soil samples [13,15,32]. However, there have been no studies of the As and heavy metal contents in the plants in this area.

In this study, we assessed the soil contamination with As and heavy metals and the accumulation of these elements in both native and cultivated plants growing in the Dong Mai Pb recycling area in Vietnam and recommend potential plants for use in phytoremediation. We also include recommendations for the cultivation of rice and vegetables in this region, and the use of native plants as animal food.

2. Materials and Methods

2.1. Site Description

The Pb recycling area is located in the Dong Mai Village, Chi Dao Commune, Van Lam District, Hung Yen Province, northern Vietnam. The Chi Dao Commune covers an area of 597 ha with 360 ha of agricultural land. In 2015, its population was 8708, including 1874 children of whom 780 were under 6 years old, 716 were 6–10 years old, and 378 were 11–14 years old [33–38]. The study area has a tropical monsoonal climate, and the annual average rainfall is about 1176 mm and the average humidity is 80% [39].

Since the 1970s, the traditional village of Dong Mai in the Chi Dao Commune, Van Lam District, Hung Yen Province, has been developing a professional Pb recycling program, which involves processing old batteries, Pb smelting, and slag sifting. Initially, Pb smelting was performed by individual households within the home and garden areas. Regulation enacted in 1997 improved the recycling management in this village by concentrating the recycling activities at four major Pb smelters located near a paddy field 500 m away from the residential area (old smelters). In 2000, the village started to use a self-contained Pb dust suction system consisting of hundreds of large bags. The suction capacity of this system was 7 tons of Pb dust per one night per one smelter. This groundbreaking technology was very efficient at minimizing the amount of Pb released to the air.

Since 2015, Pb smelting has occurred in 2 new smelter systems operated by two companies located approximately 1 km away from the residential area in Dong Mai village because the old smelters were closed.

2.2. Sampling and Analysis

Sampling was carried out in October 2016. Approximately 200 g of soil per sample was collected from the surface layer within 0–20 cm around the sampled plants at the study sites by using a stainless steel shovel. In total, 32 soil samples were collected at 7 sites (Figure 1) (3–8 samples at each site). These samples were air-dried at room temperature for 5–7 days. The large debris, stones, and pebbles were removed, and the soil samples were then sieved through a 1 mm polyethylene sieve and crushed into fine powder.

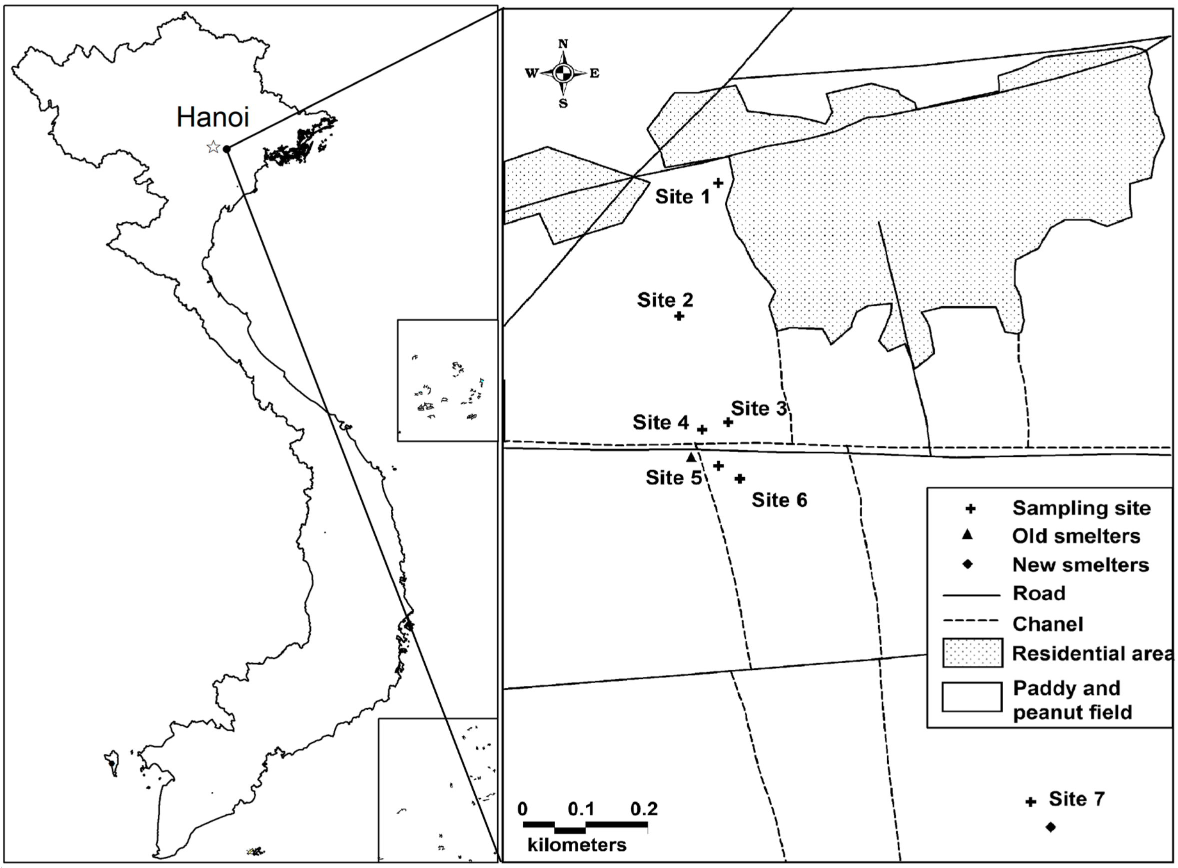

Figure 1. Sampling sites in the Dong Mai Pb recycling area, Hung Yen province, northern Vietnam (Site 1: Peanut field; Site 2: Peanut field; Site 3: Paddy field; Site 4: Path at edge of ditch; Site 5: Path at edge of ditch; Site 6: Path at the edge of the paddy field; Site 7: Paddy field).

A total of 57 native and cultivated plant samples belonging to 15 species (Table 1) were collected in the study area (Figure 1). The scientific names of the plant species were determined by a morphological classification method [40–45]. The aboveground (aerial) tissues of the selected plant samples were washed thoroughly with tap water to remove dust, rinsed 3 times with deionized distilled water, and dried at 60 °C in an oven (Memmert, Germany) for 72 h. The dried samples were ground and cut into very tiny pieces by using a mortar mill and stainless steel scissors.

The soil pH was measured with a glass electrode in a soil: distilled water slurry (1:2.5, w/v). The total contents of nitrogen (N), phosphorus (P), and potassium (K) were determined with the Vietnam Standard methods [46–48]. The soil samples were digested for total N analysis by the addition of 4 mL of a mixed solution of salicylic acid and sulfuric acid (prepared by dissolving 25 g of $C_7H_6O_3$ in 1 L of concentrated H_2SO_4) to each 0.5 g soil sample in a specialized glass bottle for >5 h. To this was added 0.5 g of $Na_2S_2O_3 \cdot 5H_2O$, and the mixture was heated until it stopped bubbling. It was cooled to room temperature, and 1.1 g of the catalysis mixture (200 g K_2SO_4, 6 g $CuSO_4{\cdot}5H_2O$, 6 g TiO_2) was added. The mixture was heated until it became colorless, and then heated gently for a further 5 h. The mixture was cooled and 20 mL of deionized distilled water was added, before N was distilled. The soil samples were digested for the total P analysis by the addition of 10 mL of concentrated H_2SO_4 and 3 mL of 70% $HClO_4$ to each 1.0 g soil sample in a specialized glass bottle. The mixture was heated gently and then boiled for 20 min, after which five drops of 70% $HClO_4$ were added. The mixture was heated until it became colorless, and was then diluted to 100 mL with deionized distilled water. The content (%) of P_2O_5 was calculated as: P_2O_5 (%) = P (%) × 2.31. The soil samples were digested for total K analysis by the addition of 10 mL of HF and 1 mL of 70% $HClO_4$ to each 0.25 g soil sample in a platinum cup. The samples were heated at 200 °C until the fluid had completely evaporated. This procedure was repeated several times until the mixture became colorless. The mixture was cooled, and 5 mL of 6 mol/L HCl and deionized distilled water were added. The mixture was boiled for 5 min, and then diluted to 100 mL with deionized distilled water. The content (%) of K_2O was calculated as: K_2O (%) = K (%) × 1.205. The available Pb content in each soil sample was extracted with 0.5 M NH_4CH_3COO and 0.02 M EDTA solution (1:10, w/v) [49].

Table 1. Plant species collected at the Dong Mai lead recycling area.

N⁰	Latin Name of Plant Species	Native or Cultivated Plant	Family	Common Name	Number of Samples	Sampling Sites
1	*Barleria cristata* L.	Native	Acanthaceae	Bluebell barleria	3	4
2	*Brachiaria distachya* (L.) Stapf.	Native *	Poaceae	Armgrass millet	3	2, 4
3	*Colocasia esculenta* (L.) Schott.	Cultivated	Araceae	Wild taro, dasheen	3	5
4	*Commelina communis* L.	Native *	Commelinaceae	Asiatic dayflower	3	1, 4
5	*Cynodon dactylon* (L.) Press.	Native *	Poaceae	Bermuda grass	3	4
6	*Fimbristylis miliacea* (L.) Vahl	Native	Cyperaceae	Hoorahgrass	3	4
7	*Hymenachne acutigluma* (Steud.) Gilliland	Native *	Poaceae	Dhal grass	3	5
8	*Ipomoea aquatica* Forssk.	Cultivated	Convolvulaceae	Water spinach	6	4, 6
9	*Limnophila chinensis* (Osb.) Merr.	Native **	Scrophulariaceae	Ngo tia	6	4, 5
10	*Ludwigia adscendens* (L.) Hara	Native **	Onagraceae	Water primrose	3	4
11	*Oryza sativa* L.	Cultivated	Poaceae	Rice	6	3, 7
12	*Panicum repens* L.	Native *	Poaceae	Torpedo grass	3	4
13	*Paspalum conjugatum* Berg.	Native *	Poaceae	Buffalo grass	3	4
14	*Polygonum hydropiper* L.	Native **	Polygonaceae	Bite-tounge	6	4, 6
15	*Sida rhombifolia* L.	Native	Malvaceae	Arrowleaf sida	3	4

* Native plants that are used for cattle food; ** Native plants that are used for pig food.

Soil and plant samples were digested following US EPA method 3052 [50], a weighed amount of dried sample (0.200 ± 0.001 mg) was placed into a digestion vessel. Concentrated 65% HNO_3 (9 ± 0.1 mL) and concentrated HF (3 ± 0.1 mL) were added and the mixture was shaken carefully. Small amounts of H_2O_2 (0.1–2 mL) and deionized distilled water (<5 mL) were also added. For samples containing high contents of iron (Fe) and aluminum (Al), about 2 mL of HCl was added. The vessels were then placed in a microwave-accelerated reaction system (Speedwave 4, Berghof, Germany). The contents of As and heavy metals in the plant and soil samples were measured following SMEWW 3125:2012 [51] using an inductively coupled plasma-mass spectrometer (ICP–MS: ELAN 9000, PerkinElmer SCIEX, Waltham, MA, USA). Samples with high Pb contents were analyzed by atomic absorption spectrophotometer (AAS, Perkin Elmer, Waltham, MA, USA). All analyses were performed in duplicate. The certified reference materials BAM–U110 (provided by the Federal Institute for Materials Research and Testing of Germany) and ERM–CD281 (provided by the Institute for Reference Materials and Measurements, European Commission's Joint Research Centre) were used for quality control of the analytical procedure used for the soil and plant samples, respectively. The average recoveries of As, Cd, Cr, Cu, Pb, and Zn from BAM-U110 were 104%, 101%, 105%, 106%, 106%, and 105%, respectively; and those from ERM–CD281 were 113%, 103%, 105%, 105%, 106%, and 103%, respectively.

2.3. Contamination Factor, Enrichment Factor, Pollution Index, Bioaccumulation Factor

The contamination factor (CF), which is calculated as the ratio of the metal content in the soil at each site to the regulatory limit, is used to assess of soil contamination [52]. In this study, the thresholds of As (15 mg/kg), Cr (150 mg/kg), Cu (100 mg/kg), Zn (200 mg/kg), Cd (1.5 mg/kg), and Pb (70 mg/kg) regulated by the Vietnam Ministry of Natural Resources and Environment for agricultural soils [53] were used to calculate the CF.

The enrichment factor (EF) of an element, an indicator of the intensity of anthropogenic contamination of the surface soil, was determined with the following equation [54,55]:

$$EF = (C_i/C_{ref})_{sample}/(C_i/C_{ref})_{background} \quad (1)$$

where $(C_i/C_{ref})_{sample}$ is the ratio of the content of interested element and reference element in soil sample, and $(C_i/C_{ref})_{background}$ is the ratio of the content of interested element and reference element in the background. In this study, Fe was selected as reference element [54]. The contents of Fe, As, Cr, Cu, Zn, Cd, and Pb in shale in the Earth's crust were used to calculate the background values which were 47,200, 13, 90, 45, 95, 0.3, and 20 mg/kg, respectively [56].

The pollution index (PI) was calculated for each sampling site using Equation (2) [57]:

$$PI = \sqrt{\frac{(CF_{aver})^2 + (CF_{max})^2}{2}} \quad (2)$$

where CF_{aver} and CF_{max} represent average value of CF and maximum value of CF at each sampling site, respectively.

The bioaccumulation factor (BAF) is calculated as a ratio of metal in the harvestable part of the plants (aboveground biomass) to that in the soil [58].

2.4. Statistical Analysis

Statistical analyses of data were performed using the SPSS 20.0 package (IBM Corp., Armonk, NY, USA). All data were tested for goodness of fit to a normal distribution. Data were log transformed where necessary to achieve homogeneity of variance. Evaluation of significant differences among different treatments was performed using one-way ANOVA (Analysis Of Variance) followed by Tukey's post-hoc test, with $p < 0.05$ indicating statistical significance. Pearson product moment correlation coefficients (r) were used to express the associations of quantitative variables.

3. Results and Discussion

3.1. Contents of N, P, K, As, and Heavy Metals in Soils

The soil sample pH ranged from 4.8 to 7.1 which is in the range of the pH value index of the soils in Vietnam [59] (Table 2). The range of pH values of the soil samples collected from peanut fields (Sites 1 and 2) was 6.3–7.1 and was significantly higher than those of samples collected at all other sites ($p < 0.05$) (Table 2). The Pb recycling activities, particularly the disposal of old batteries, in Dong Mai have caused the acidification of the soil. The results of this study are consistent with a previous report of the low soil pH in the study area [32].

Table 2. pH values and contents of N, P, K, Al, As, and heavy metals in soils in the Dong Mai lead recycling area.

Parameters	Sites							Allowable/Index Values *
	1	2	3	4	5	6	7	
pH	7.1 ± 0.6 ^{b}	6.3 ± 0.5 ^{b}	4.9 ± 0.4 ^{a}	4.9 ± 0.2 ^{a}	5.0 ± 0.4 ^{a}	5.2 ± 0.7 ^{a}	4.8 ± 0.4 ^{a}	4.11–7.57 [1]
Al (mg/kg)	6200 ± 1300 ^{b}	32,600 ± 5600 ^{a}	21,500 ± 6700 ^{a}	25,200 ± 6700 ^{a}	23,300 ± 4400 ^{a}	14,300 ± 4900 ^{a,b}	23,400 ± 4200 ^{a}	-
Fe (mg/kg)	22,000 ± 4500 ^{b}	42,300 ± 11,100 ^{a}	34,600 ± 15,400 ^{a}	29,100 ± 3700 ^{a}	55,500 ± 7800 ^{a}	32,100 ± 5600 ^{a}	11,300 ± 1600 ^{b}	-
As (mg/kg)	10.9 ± 0.5 ^{a,b}	15.3 ± 0.5 ^{a,b}	10.9 ± 9.0 ^{a,b}	11.6 ± 4.1 ^{a,b}	26.8 ± 0.8 ^{a}	16.0 ± 6.9 ^{a,b}	5.4 ± 0.3 ^{b}	15 [2]
Cr (mg/kg)	60.7 ± 22.9 ^{a}	43.4 ± 11.0 ^{a}	84.8 ± 49.2 ^{a}	49.6 ± 32.5 ^{a}	290 ± 83 ^{a}	114 ± 79 ^{a}	24.9 ± 1.4 ^{a}	150 [2]
Cu (mg/kg)	143 ± 19 ^{a,b}	101 ± 12 ^{a,b}	105 ± 58 ^{a,b}	84.0 ± 4.4 ^{a,b}	251 ± 56 ^{a}	104 ± 71 ^{a,b}	66.0 ± 12.0 ^{b}	100 [2]
Zn (mg/kg)	455 ± 117 ^{a,b}	333 ± 97 ^{a,b}	223 ± 101 ^{a,b}	228 ± 25 ^{a,b}	392 ± 75 ^{a}	223 ± 90 ^{a,b}	143 ± 48 ^{b}	200 [2]
Cd (mg/kg)	1.24 ± 0.17 ^{a}	1.35 ± 0.35 ^{a}	0.71 ± 0.48 ^{a}	0.87 ± 0.27 ^{a}	1.67 ± 0.24 ^{a}	0.76 ± 0.32 ^{a}	0.93 ± 0.23 ^{a}	1.5 [2]
Pb-Total (mg/kg)	370 ± 126 ^{b}	834 ± 234 ^{b}	5050 ± 2200 ^{a}	47,400 ± 43,100 ^{c}	12,800 ± 4200 ^{a,c}	977 ± 257 ^{b}	419 ± 123 ^{b}	70 [2]
Pb-Extractable (mg/kg)	3.17 ± 0.17 ^{b}	84.0 ± 5.7 ^{a,c}	536 ± 252 ^{a}	869 ± 213 ^{a}	870 ± 83 ^{a}	77.7 ± 60.0 ^{c}	11.9 ± 1.0 ^{b}	-
Total N (%N)	0.19 ± 0.08 ^{a}	0.19 ± 0.05 ^{a}	0.23 ± 0.08 ^{a}	0.34 ± 0.21 ^{a}	0.27 ± 0.06 ^{a}	0.23 ± 0.02 ^{a}	0.29 ± 0.11 ^{a}	0.095–0.27 [3]
Total P (%P_2O_5)	0.37 ± 0.11 ^{b}	0.24 ± 0.06 ^{a}	0.13 ± 0.02^{c}	0.30 ± 0.08 ^{a}	0.19 ± 0.03 ^{a,c}	0.17 ± 0.0 5 ^{a,c}	0.16 ± 0.08 ^{a,c}	0.03–2.35 [4]
Total K (%K_2O)	1.23 ± 0.2 ^{b}	2.25 ± 0.53 ^{a,c}	1.90 ± 0.11 ^{a,c}	1.66 ± 0.18 ^{c}	1.84 ± 0.13 ^{a}	2.17 ± 0.17 ^{a,c}	2.27 ± 0.45 ^{a,c}	0.03–2.35 [5]

Note: Figures followed by different letters (a,b,c) in the same row are significantly different at $p < 0.05$. * Values are for agricultural soil; [1] TCVN 7377: 2004 [59]; [2] QCVN 03-MT:2015/BTNMT [53]; [3] TCVN 7373: 2004 [60]; [4] TCVN 7374: 2004 [61]; [5] TCVN 7375: 2004 [62].

The total N, P (P_2O_5), and K (K_2O) contents of the soils were 0.19%–0.34%, 0.13%–0.37%, and 1.23%–2.27% (Table 2), respectively, whereas the index values for the total N, P (P_2O_5), and K (K_2O) contents in the soils of Vietnam are 0.095%–0.27%, 0.03%–2.35%, and 0.03%–2.35%, respectively [60–62]. Thus, only the soil samples collected from the ditches in front of one old Pb smelter (Site 4) contained total N contents exceeding the index values of total N given in the Vietnam Standard [60].

The contents of Al, Fe, As, Cr, Cu, Zn, Cd, and Pb were 6200–32,600, 11,300–55,500, 5.4–26.8, 24.9–290, 66.0–252, 143–455, 0.71–1.67, and 370–47,400 mg/kg, respectively (Table 2). The contents of Pb in an extractable form were 3.17–870 mg/kg, which were significantly lower than those of total Pb ($p < 0.05$). The ratio of the content of extractable Pb to that of total Pb in the present study was lower than that reported by Rodríguez-Seijo et al. [63] and Ngoc et al. [64], but higher than that reported by Zhang et al. [65] and Lenart and Wolny-Koładka [66]. The differences in the proportions of extractable Pb in different studies may be attributable to the total Pb contents in the soils and the different properties of the soils (e.g., soil pH, soil texture, organic carbon content, cation exchange capacity, calcium carbonate equivalents, and nutrient balance) [11,63–68]. Extractants also play an important role in the amounts of extractable metals detected [63,64,69]. The effects of the recycling of old batteries on the disturbance of the natural properties of the soil in the study area may have also altered the proportion of extractable Pb.

The results of this study also demonstrate that the contents of Pb (both total and extractable forms) in the soil samples collected at the edges of ditches (Sites 4 and 5) and a paddy field (Site 3) were significantly higher than those at other sites ($p < 0.05$). The high Pb contents in the paddy field may pose a high risk of Pb accumulation in rice.

The CF for As in approximately 40% of the collected soil samples (three out of seven sites) varied from 1 < CF < 2, indicating moderate contamination according to the classification of Brady et al. [52] (Table 3). The CF values for Cr and Cd were <1, with the exception of Site 1, indicating that the soils in the study area were not contaminated with these metals. The CF values for Cu (0.7–2.5) and Zn (0.7–2.3) indicated uncontaminated to moderately uncontaminated soils (Table 3).

By contrast, the contents of Pb were significantly higher than those of As, Cr, Cu, Zn, and Cd in the soils, except at Site 2 ($p < 0.05$) (Table 2). The contents of total Pb were 5–677-fold higher than the maximum allowable limit for agricultural soils in Vietnam [53]. The highest contents of Pb were found in the samples collected at the edges of ditches, indicating the release of contaminants into the surrounding environment via the ditch systems and the poor control and management of these hazardous wastes in the study area.

The EFs for As, Cr, Cu, Zn, and Cd were within the range of 1.4–5.3, indicating uncontaminated to moderately uncontaminated soils [52] (Table 3). By contrast, the EFs for Pb varied from 40 to 3850, with an average of 712, indicating extreme contamination of the soils with Pb. The pollution index (PI) ranged from 4 to 492, implying heavily polluted soil according to the classification of Nemerow et al. [57].

The correlations between the contents of each pair of metals (As, Cr, Cu, Zn, and Cd) were moderately to strongly positive ($p < 0.01$): $r(32)$ was 0.68–0.91 for As, 0.55–0.91 for Cr, 0.55–0.86 for Cu, 0.66–0.88 for Zn, and 0.55–0.69 for Cd. These findings suggest that the As, Cr, Cu, Zn, and Cd were derived from similar sources [70,71]. By contrast, Pb showed no correlation ($p > 0.05$) with As or other heavy metal, implying that the source of Pb in the soil was the Pb recycling activities in the study area. This result is consistent with the findings of previous studies that Pb occurs naturally in the earth's crust [72] at levels below 50 mg/kg [73] and that the amounts and types of Pb species in soils are often modified by anthropogenic activities [9]. Iron also correlated ($r = 0.45$–0.80, $p < 0.001$) with As and heavy metals, reflecting the role of Fe-compounds in binding these elements in soils [74,75].

Previous studies have also reported high contents of Pb in the soils collected in the study area [13] which were more than 214-fold higher than the maximum allowable limit for agricultural soils in Vietnam [53]. An analysis performed in 2007 showed Pb contamination in the agricultural soils at two sites in Dong Mai village with total Pb contents of 864 and 3352 mg/kg [32]. Recent research reported that the agricultural soil in Dong Mai was heavily contaminated with Pb, with total Pb contents ranged from 250 to 7070 mg/kg [15]. High contents of Pb in the soils have also been reported in other battery recycling areas which were as high as 122,404 mg/kg [76], 140,500 mg/kg [77], 24,600 mg/kg [78], 5657 mg/kg [69], and 640.71 mg/kg [79].

Table 3. Soil quality classification for CF (contamination factor) and EF (enrichment factor).

Class.	Qualification	CF	EF
0	Uncontaminated	CF < 1	EF < 2
1	Uncontaminated to moderately contaminated		
2	Moderately contaminated	1 < CF < 3	2 < EF < 5
3	Moderately-heavily contaminated		
4	Severely contaminated	3 < CF < 6	5 < EF < 20
5	Heavily contaminated	CF >6	20 < EF < 40
6	Extreme contaminated		EF > 40

Note: Adapted from Brady et al. [51].

3.2. Bioaccumulation of the Studied Elements in Plant Species

Our survey of the study area in Dong Mai village showed that wild flora was abundant and grew well, displaying no morphological abnormalities in soil contaminated with some heavy metals and heavily contaminated with Pb, indicating the tolerance of these species.

The contents of As and heavy metals in rice grains and in the shoots of 15 native and cultivated plant species are shown in Table 4. The greatest number of plant species belonged to the family Poaceae (six of the 15 species) (Table 1), which is consistent with the dominant distribution of Poaceae in other areas highly contaminated with Pb, Zn, and As in mining regions in northern Vietnam [80].

The contents of As, Cr, Cu, Zn, Cd, and Pb in the rice grains and the shoots of the 15 plant species tested were within the ranges of 0.14–10.2, 1.00–10.2, 5.19–23.8, 34.7–165, 0.06–0.99, and 2.83–1160 mg/kg-DW, respectively. Therefore, the contents of As, Cr, Cu, Zn, and Cd in most of the plant species studied were lower than the toxic levels for plant growth [11] (Table 4), possibly because of the low contents of these metals in the soils. By contrast, the contents of Pb in these plant species were significantly higher ($p < 0.01$) than those of As and the other heavy metals, reflecting the impact of the high contents of Pb in the soils on its accumulation in these species. Eight of the 15 plant species studied had Pb contents higher than the toxic level for plant growth (Table 4), indicating the capacity of these species to tolerate heavily Pb-contaminated soils and to accumulate Pb in their tissues. In this study, the hyperaccumulation of Pb (1160 mg/kg-DW) was observed in *H. acutigluma*. In a previous laboratory experiment, Chu [81] reported the hyperaccumulation of Pb in *P. hydropiper* (4650 mg/kg-DW) and *H. acutigluma* (3161 mg/kg-DW) after 2 months growth in soils containing 192,185 mg Pb/kg. In the present study, we detected lower contents of Pb in *P. hydropiper* and *H. acutigluma* than were reported by Chu [81] (Table 4), possibly resulting from the growing conditions and higher contents of Pb in the soil in the previous study. This was supported by the strong correlation between the contents of Pb in the plant shoots and the contents of total Pb ($r = 0.80$, $p < 0.001$) and extractable Pb ($r = 0.81$, $p < 0.001$). This result also implies the strong effect of the bioavailability of Pb in the soil on the uptake and accumulation of Pb in plant shoots, consistent with previous studies [65,82]. Our results also showed higher contents of Pb in the shoots of *I. aquatica* (586 mg/kg-DW) than those reported (179 and 232 mg/kg) when the plants were growing in soil containing 864 and 3352 mg Pb/kg, respectively [32], possibly because of the differences in the Pb contents in the soil. At other Pb battery-recycling sites, Pichtel et al. [77] showed that the contents of Pb in the shoots of nine plant species were higher than the toxic level for plant growth [11]. González-Chávez et al. [76] reported that the maximum Pb content in the shoots in *Ricinus communis* was 293 mg/kg.

Plants considered important components of ecological systems transfer metals from abiotic to biotic environments. Although more than 400 plant species have been identified as hyperaccumulators, most are nickel hyperaccumulators which occur in ultramafic areas throughout the world [83–87], or hyperaccumulators of other elements such as Al, Mn, Cu, Cr, Co, Ni, or Zn [88], whereas only a few hyperaccumulators of Pb have been reported. Jiang et al. [88] reported the hyperaccumulation of Pb in *Brassica juncea.* Wan et al. [89] found a hyperaccumulation of Pb (2350 mg/kg-DW) in the shoots of *Viola principis* H. de Boiss. Hyperaccumulation levels (mg/kg-DW) were also reported in *Ageratum houstonianum* Mill. (1130), and *Pteris vittata* L. (1020) [90]. Diep and Zarli [91] showed that *Lantana camara* L. was a hyperaccumulator of Pb.

Table 4. BAF values, contents of As and heavy metals in the shoots of native and cultivated plants collected at the Dong Mai Pb recycling area.

Plant Species	Contents in the Shoots (mg/kg-DW)						BAF Values						
	As	Cr	Cu	Zn	Cd	Pb	As	Cr	Cu	Zn	Cd	Pb	Pb ***
Native Plant													
B. cristata	1.41	1.72	13.8	56.5	0.20	293	0.17	0.06	0.17	0.25	0.32	0.01	0.33
B. distachya *	2.90	1.87	16.9	89.0	0.31	213	0.35	0.07	0.21	0.40	0.49	0.01	0.24
C. communis *	1.18	1.80	11.0	96.6	0.26	594	0.14	0.06	0.14	0.43	0.41	0.02	0.68
C. dactylon *	3.49	1.80	15.0	70.7	0.32	193	0.42	0.06	0.19	0.32	0.50	0.01	0.22
F. miliacea	0.90	1.00	5.19	34.7	0.13	70.0	0.11	0.04	0.07	0.16	0.20	0.01	0.08
H. acutigluma *	1.96	10.2	14.9	85.0	0.99	1160	0.07	0.04	0.06	0.22	0.59	0.09	1.34
L. chinensis **	1.20	2.20	10.1	165	0.50	600	0.13	0.07	0.12	0.77	0.68	0.01	0.69
L. adscendens **	0.94	1.30	14.5	63.2	0.44	308	0.09	0.04	0.17	0.31	0.55	0.01	0.36
P. repens *	8.17	1.82	17.9	90.4	0.43	825	0.98	0.06	0.23	0.40	0.68	0.03	0.94
P. conjugatum *	2.61	1.71	16.1	83.4	0.32	214	0.31	0.06	0.20	0.37	0.50	0.01	0.24
P. hydropiper **	10.2	2.20	23.8	92.4	0.68	798	1.10	0.07	0.29	0.43	0.92	0.02	0.92
S. rhombifolia	1.09	1.09	14.1	44.4	0.21	269	0.13	0.04	0.18	0.20	0.33	0.01	0.31
Cultivated Plant													
C. esculenta	1.10	5.47	12.0	85.4	0.93	726	0.04	0.02	0.05	0.22	0.56	0.06	0.83
I. aquatica	3.18	2.14	23.6	91.9	0.49	586	0.34	0.07	0.29	0.43	0.66	0.01	0.68
O. sativa (rice grains)	0.14	1.32	3.73	39.4	0.06	2.83	0.03	0.06	0.06	0.27	0.11	0.01	0.09
Hyperaccumulation [1]	1000	1000	1000	10,000	100	1000							
Normal range [2]	1.0–1.7	-	5–30	27–150	0.05–0.2	5–10							
Toxic range [2]	5–20	-	20–100	100–400	5–30	30–300							

* Native plants that are cattle food; **Native plants that are harvested for pig's food; *** Ratio of Pb content in the plant to the extractable Pb content in the soil; [1] Brooks, 1998 [83]; Reeves and Baker, 2000 [84]; [2] Kabata-Pendias, 2011 [11].

In general, metal toxicity mechanisms have not been well studied. However, metal toxicity in plants related to an oxidative stress approach has raised much concern in recent years [82,92,93]. It has been reported that a tolerance of metals may be attributable to changes in the content of nonprotein thiols in plants. For example, increased levels of peroxidase activity and higher proline contents in the stems and/or leaves of *Vicia faba* plants treated with different metals (Pb, Cd, Ni, or Zn) have been established [82]. Heavy metal stress usually promotes the excessive accumulation of reactive oxygen species in plant cells, which induce cell damage or death. However, some hyperaccumulator plants develop cellular strategies whereby their endogenous antioxidant enzymes provide them with increased protection against the harmful effects of the oxidative stress induced by heavy metals [92]. It has been reported that the uptake of Pb and Cd is enhanced in the presence of cysteine and glutathione, and that there may be specific transporters for these thiol ligands [94]. The cytoplasmic and intravacuolar sequestration of Pb is predominant in the cells of the root tip, whereas no endocytosis of Pb at the plasma membrane has been observed. Therefore, a membrane transport protein may be involved in the sequestration of Pb. Plants respond to the toxic effects of Pb in various ways [95]. For example, abundant cell-wall thickening could be a common response of plant cells to Pb [96]. The thickening of the plasma membrane almost certainly protects the plant cell from the return of Pb to the protoplast [97].

3.3. Potential Risks Associated with the Consumption of Contaminated Plants

The high contents of Pb in the soil in the study area (370–47,400 mg/kg) could cause high contents of Pb in cultivated vegetables and food. It was reported that total Pb contents from 23.51 to 44.81 mg/kg-DW in agricultural soil caused Pb accumulation in water spinach to levels exceeding the maximum level [98] for Pb in fresh vegetables [99].

Among the cultivated plants analyzed, the contents of As and some other heavy metals in the grains of rice (*O. sativa*) were lower than those in shoots of wild taro (*C. esculenta*) and water spinach (*I. aquatica*) (Table 4). In the study area, these three plant species were cultivated as human food and pig food (wild taro). The contents of Pb in *C. esculenta* and *I. aquatica* were approximately twofold higher than the maximum toxic level of Pb in plant species (300 mg/kg-DW) [11], representing a health risk to the local people through the potential biological amplification of Pb accumulation in the upper levels of the food chain, even direct and indirect consumption of these plants. It is noteworthy that although *L. chinensis*, *L. adscendens*, and *P. hydropiper* were not cultivated in the study area, they are sometimes harvested together with *C. esculenta* as a source of pig food in Vietnam. *Brachiaria distachya, C. communis*, *C. dactylon*, *H. acutigluma*, *P. repens*, and *P. conjugatum* are also potential sources of food for cattle. Therefore, the high contents of Pb in these plant species, ranging from 193 to 1160 mg/kg-DW (Table 4) may pose a great risk to human health through the food chain. It is noteworthy that the numbers of pigs and cattle in the Chi Dao Commune were 1300–5200 and 25–250, respectively, during the period 2010–2015 [33–38].

The data in Table 4 also show that the content of Pb in grains of rice (*O. sativa*) was 14-fold higher than the maximum permitted level (0.2 mg/kg) for food and feed [100,101]. Accumulation of Pb in rice to levels higher than 0.2 mg/kg has been reported [102,103], indicating that the uptake of Pb by roots and its accumulation in rice present a considerable risk. The contents of As and Pb in spinach (*I. aquatica*) were approximately 3- and 293-fold higher, respectively, than the standard allowance for vegetables [101] (1.0 and 2.0 mg/kg-DW, respectively). These findings highlight the need to manage the cultivation of rice and vegetables appropriately in these environments and to use native plant species (*B. distachya*, *C. communis*, *C. dactylon*, *C. esculenta*, *H. acutigluma*, *L. adscendens*, *L. chinensis*, *P. conjugatum*, *P. hydropiper*, and *P. repens*) to reduce the risk of As and heavy metal toxicity in pigs, cattle, and humans via the food chain.

3.4. Phytoremediation Potential of Plant Species

An ideal plant for phytoremediation must meet the following criteria: it must be a hyperaccumulator, have a large, fast-growing biomass, have an AF value >1, be widely distributed, have a highly branched root system, and be easy to cultivate and harvest [21,70,104].

Of the 15 plant species examined in this study, Pb was hyperaccumulated only in *H. acutigluma*. Although this plant species has a medium biomass, it grows endemically, widely, and very rapidly, and has a highly branched root system. *Panicum repens* and *P. hydropiper* also had higher contents of Pb in their shoots than the other species studied, although their biomasses are lower than that of *H. acutigluma*.

The BAF value for As and the heavy metals tested are shown in Table 4. BAF was >1 in *P. hydropiper* for As and in *H. acutigluma* for Pb (extractable Pb in the soil), indicating the capacity of these plants to accumulate these metals in their aboveground biomass. However, the BAF of *H. acutigluma* for Pb (total Pb in the soil) was only 0.09. Among the species studied, Pb was only hyperaccumulated in *H. acutigluma*, although high contents of Pb were also found in other species (Table 4). Therefore, this plant species is considered a potential hyperaccumulator of Pb, and warrants further experimental cultivation to confirm a hyperaccumulator [105].

It is notable that very low BAF values for Pb (total Pb contents in soils) were obtained (0.01–0.09), possibly due to the very high contents of Pb in the soils and the ability of Pb to bind strongly to organic and/or colloidal materials. Many other parameters also strongly affect the interactions of trace elements with soils and plants, and therefore influence the efficiency of phytoremediation [11,67,68]. For example, metals are more bioavailable at acidic pH, whereas organic matter and clay with a high cation-exchange capacity reduce metal availability and toxicity [106]. Therefore, only a small amount of the Pb in soil is soluble and available for plant uptake [107,108].

The BAF value of 1.34 (Table 4) calculated from the extractable Pb data may indicate the capacity of *H. acutigluma* to accumulate Pb in its shoots. Therefore, *H. acutigluma* is the best candidate species for the phytoremediation of soils contaminated with Pb in the study area. However, considering the very high contents of Pb in the soil, a long period of phytoremediation would be required to achieve the allowable limits of Pb in the soils [53].

4. Conclusions and Recommendations

The total contents of As, Cr, Cu, Zn, Cd, and Pb in soil samples collected in the Dong Mai Pb recycling area in the Chi Dao Commune, Van Lam District, Hung Yen Province, northern Vietnam, exceeded the allowable limits [53] at three, one, five, six, one, and seven of the seven sites tested, respectively. The role of soils for human health, in particular, the effects of soil contamination on human health, is well recognized by some world organizations [108]. The serious contamination of soil with Pb and its contamination with As and other heavy metals endanger the health and livelihoods of local residents. This metal contamination in food and vegetable crops, especially the high Pb contents in rice grains (*O. sativa*) and the shoots of water spinach (*I. aquatica*), is higher than the permitted levels [100,101].

Arsenic and heavy metals had accumulated in 15 plant species growing in the study area. *Hymenachne acutigluma* showed the greatest ability to accumulate Pb from the soil into its shoots (1160 mg/kg-DW), and this species grows rapidly and has a dense root system.

Based on the available evidence, we do not recommend field cultivation of rice or vegetables in the area of Dong Mai village. The local authorities should be informed about the status and risk of food and vegetable contamination by Pb and should take measures to remediate the Pb-contaminated soil in Dong Mai village as soon as possible. In this study, *H. acutigluma* is recommended as the best candidate for the phytoremediation of soil heavily contaminated with Pb. Detailed laboratory and field experiments are required to assess the feasibility of this plant species in the phytoremediation of Pb-contaminated soils.

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