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HUMAN HEALTH RISK IMPLICATION FROM CADMIUM AND LEAD CONTAMINATION AT LEAD-ZINC MINE AREA, NORTHERN VIET NAM

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ABSTRACT

This study was conducted to investigate cadmium (Cd) and lead (Pb) accumulation in soil, vegetables, and residential hair in the vicinity of Cho Dien mine. Health risk assessment of those was also evaluated based on vegetables contamination, including the average daily dose (ADD) and hazard quotient (HQ) calculation. The concentration of Cd and Pb in soil was 2.1 and 8.4 times higher than QCVN 03-MT:2015/BTNMT. The highest concentrations of both metals were found at 56.2 mg/kg and 23.266 mg/kg near mine areas and tailings dam. Among eight vegetables investigated, the common leafy species consumed by local people, *Sauropus androgynous* and *Ipomoea aquatic*, were the most contaminated plants. *Sauropus androgynous* tended to be accumulated higher Cd (10.8 mg/kg) while *Ipomoea aquatic* was accumulated more Pb (17.3 mg/kg). Health impact monitoring revealed that Cd and Pb concentrations in hair samples were up to 0.93 and 84.2 mg/kg, respectively. Consumption of vegetables would lead to potential health risks especially for children, since the values of HQ of Cd and Pb for vegetables would sum up to almost 1. Thus, long-term Cd and Pb exposure by regular consumption of locally grown vegetables poses potentially health problems to the local population.

Keywords: lead/zinc mine, transfer factor, health risk, lead contamination, daily intake.

1. INTRODUCTION

Cadmium and lead have known to be very toxic substances, which were derived widely in the environment due to natural and anthropogenic emissions. Nonferrous metallurgy was reported as one of the most important anthropogenic Pb and Cd emission sources. The reasons for high levels of those in and around non-ferrous metals mine because of dispersion of mine wastes in to nearby soil, vegetables, crop and stream networks. Numerous studies related to metal contamination from smelting and the mining activities have been conducted in China, Australia and in Korea [1-3]. Vegetables can uptake both elements via roots from contaminated soils and surface water, or direct deposition of contaminants from the atmosphere onto plant surfaces. Cultivation of crops for human or livestock consumption can potentially lead to the uptake and accumulation of metals in edible plant parts with a resulting risk to human and animal health [4, 5]. The human health risks due to vegetable ingestion enriched by Pb were greatly concerned. Increased absorption of lead, cadmium and other metals has been determined in population, especially in children living near nonferrous metal smelters in China, Malaysia and Italy [6-9]. The levels of heavy metals accumulated in vegetables grown in contaminated soils were higher than those in uncontaminated sites that reflected the more serious exposure as well as human health burden effects in these areas [10, 11]. The sources, distribution of Pb in Cho Dien Bac Kan province, Vietnam) lead/zinc mine was known to be mainly derived from tailings dam and mining activities [12, 13]. Heavy metal occurrence in Cho Dien Pb-Zn mine was evident in water and soil [13]. However, there is no research data reported on the biological monitoring of heavy metal levels in human hair and vegetables. Thus, the main objectives were (1) to investigate cadmium and lead contamination in soil, vegetables and human hair; (2) to assess health risk to residents through oral exposure route at Cho Dien lead/zinc mine.

2. MATERIAL AND METHOD

2.1. Sample collection

Sampling of tailing, soil, vegetables and water was conducted around the Pb-Zn mining areas (22^{0}11’50’’N, 105^{0}32’00’’E), Bac Kan Province, North Vietnam in March, 2013. Surface soils (0-15 cm in depth) were sampled by trowel, from the tailings, forest, and paddy fields. Uncultivated soil on the mountain in near the mining sites and at different elevations was selected. Paddy and farmland soils located near the mining area and in the valley below the slope of the mountain were also investigated. All the soils were sampled, preserved and stored in polyethylene bags under QCVN 03-MT: 2015/BTNMT.

Eight full edible vegetables selected for this study were *Barassica Juncea, Ipomoea aquatic, Corchorus, Pumpkin, Sauropus Androgynus, Basella Alba, Eggplant, and Sechium edule,* accompanying with soil in which the plants were grown on. Soil samples and vegetables were stored in polyethylene bags in the field, then treated as well analyzed at the laboratory

Human hair was also collected from the inhabitants living near lead-zinc mine. The study group consisted of 109 subjects (2-72 year olds), without colored or treated hair. Hair samples were cut by a stainless steel scissors from the nape of the neck, preserved in a sealed plastic bag, labeled and stored in a dry environment before analysis.

2.2. Analytical and quality control

Tailing and soil samples were dried at room temperature (approximately 30 ^{o}C) and ground to pass 0.15 mm. Then, 0.25 g of sample was digested using aqua regia (HCl/HNO_3 = 3:1) (USEPA, 2001a) by the microwave digestion method. The digested samples were then filtered by Whatman GF/C filter papers and these solutions were analyzed by atomic absorption spectrometry (AAS 800 Perkin Elmer) and inductively coupled plasma mass spectrometry (ICP-MS ELAN 900-Perkin Elmer).

Vegetables were taken from the farmlands, rinsed with tap water and washed with deionized water to remove dust and soil particles adhered to the surface. Then, the samples were air-dried at 40^{0}C for 48 h before being milled to 200 mesh sieve, digested with concentrated nitric acid and hydro peroxide H_2O_2 (USEPA, 2001b). The digested solutions were treated as soil samples.

Approximately 0.5 g of hair samples was cut into small pieces no longer than 1 cm, thoroughly washed with a mixture of ethyl ether and acetone (3:1,v/v) under continuous stirring for 10 minutes. Then, samples were dried at 85 ^{0}C for 1 hour, treated with a dilute aqueous solution of EDTA (5 %) for 1 h and repeatedly rinsed with double-distilled water several times before dried at 85 ^{0}C for 12 hour in an oven to determine the dry weight. 0.25 g of each the dried hair was digested in microwave oven Milestone (USA) with the high-purity of HNO_3 (68 %) and H_2O_2 (30 %) [14] . After digesting by microwave, the digested samples were filtered through Whatman GF/C filter papers and analyzed by ICP/MS ELAN. Blank samples were proceed for each batch digestion with same way with real samples. Blank samples were analyzed and subtracted every tenth sample. The Merck standard solutions were used to ensure the measurement precision and accuracy in the whole analytical procedure. Triplicate analyses were in the range 5-10 % for all analyzed elements.

2.3. Health risk of inhabitants via vegetables consumption

In this study, potential health risks of heavy metal exposure to the inhabitants by local vegetable-fruit consumption via digestion pathway were assessed. A daily intake dose (ADD) is used to quantify the oral exposure dose. The health risk through consumption of vegetables was characterized using the hazard quotient (HQ). Reference dose (RfD) is defined as a daily intake rate that is evaluated to cause no appreciable risk to adverse health effects, even to sensitive populations, over a specific exposure duration. If HQ is excessive to 1, there is a potential risk associated with that metals and inverse [15].The oral reference dose for Cd and Pb in food is at 1 µg/(kg.d) and 3.5 µg/(kg.d), respectively [15-16]. The value of ADD and HQ were computed as follows:

$$ADD = \frac{C \times IR \times EF \times EF}{BW \times AT} \quad (1)$$

$$HQ = \frac{ADD}{RfD} \quad (2)$$

where: C (µg/g fw) is an average weight of contaminant (this study); IR is ingestion rate: 160 g/day (this study); ED is exposure duration: 30 years [15]; EF is exposure frequency: 350 days/year [15] BW is the average body weight for adult: 60 kg [this study]; AT is averaging time: 30 years for non-carcinogen [15]. The concentration of metals in vegetables was converted from dry weight to fresh weight with a factor of 0.085 of these vegetables [17].

3. RESULT AND DISCUSSION

3.1. Cadmium and lead contamination in tailing and soils

The total concentrations Pb and Cd in tailing and soil showed large variation in Cho Dien lead/zinc mine. The elevated levels of Cd (11.4 mg/kg) and Pb (10.002 mg/kg) are measured in tailing samples which significantly exceeded QCVN 03-MT:2015/BTNMT (the Vietnamese Standard on the allowable limits of heavy metals in the soils). These heavy metals were more enriched comparing the world's normal soil composition (0.35 mg/kg and 35 mg/kg), respectively [17]. Besides, Cd and Pb were detected in surface layer of the soil, in which, Pb exceeded the Vietnamese standard in all samples. Overall, the highest concentrations of heavy metals were found in mining areas and tailing dams. Especially, whereas the levels of Cd reached 22.47 mg/kg and 11.4 mg/kg, those of Pb were 13.42 mg/kg and 10.02 mg/kg in mining areas as well as tailing dams, respectively. The concentrations of Cd and Pb in the 28 cultivated soils from Cho Dien lead/zinc mine with a mean value of 4.2 mg/kg and 839 mg/kg, which was about 2.1 and 8.4 times higher than QCVN 03-MT/2015/BTNMT, respectively. These results were also consistent with previous studies that the levels of Pb and Cd were mainly derived from mining activities and smelting [5,13]. Due to complex original soil characteristics as nature of ore deposits in Cho Dien Pb/Zn mine, the main minerals of this region are Sphalerite (ZnS) and Galena (PbS) that may release much amount of Pb and other heavy metals through washing and weathering process [13].

3.2. Concentrations of cadmium and lead in vegetables

Heavy metal concentrations showed variations among different vegetables collected in the local gardens in Cho Dien Lead-Zinc mine were shown Table 1. The variations in Pb and Cd concentrations in vegetables of the same site may be ascribed to the differences in their morphology and physiology for heave metal uptake exclusion, accumulation and retention [6,11]. Comparing to safe limits given by WHO/FAO 2007, the concentration of Pb and Cd in leafy vegetables were higher. According to Kabata-Pendias and Pendias [17], toxic elements as Pb and Cd are natural constituents of the earth’s crust, which are taken up from the soil by plants and transferred to the food chain. Although metal concentrations of plant tissues are generally results of the metal concentration in the growth solution or soil, the relationship differs according to the plant species and tissues.

Table 1. Average metals concentration of vegetables around Cho Dien lead-zinc mine (mg/kg dw).

Plant species		Cd	Pb
Barassica Juncea (5)	Mean	0.72	10.4
Leaf specie	Range	N.d-1.38	4.7-20.2
Basella alba (n = 2)	Mean	0.62	13.3
Leaf specie	Range	0.44-0.93	8.1-18.4
Corchorus (n = 6)	Mean	1.06	4.42
(Leaf specie)	Range	N.d-2.22	0.46-9.0
Ipomoea aquatic (n = 5)	Mean	0.32	17.3
(Leaf specie)	Range	0.01-0.5	8.4-29.8
Sauropus androgynus	Mean	10.8	14.9
(n = 7) (Leaf specie)	Range	0.46-16.4	N.d-67.0
Sechium edule (n = 4)	Mean	N.d	N.d
Fruit specie	Range		
Pumpkin (n = 5)	Mean	0.14	1.53
Fruit specie	Range	N.d-0.71	N.d-6.58
Eggplant (n = 2)	Mean	0.007	0.017
Fruit specie	Range	N.d-0.013	0.001-0.034
All vegetables (n = 36)	Mean	2.478	8.45
	Range		
Normal value (*)		0.05-2.0	5.0-10.0
WHO/FAO (2007)		0.2	5

N.d: Not detected: Kabata-Pendias and Pendias 1984.*

Comparing to the normal values suggested by Kabata-Pendias and Pendias, the average concentration of Cd in the vegetable samples was fallen in range of the Normal Value, except for *Sauropus androgynus* with the highest level of 10.8 mg/kg, whereas, the levels of Pb exceeded in four leafy vegetables such as *Barassica Juncea; Basella alba; Ipomoea aquatic; Sauropus androgynus*. The concentration of Pb was less than the normal values in all observed fruity vegetables. The enrichment of heavy metals among vegetables were different due to different bioavailability of metals, difference in uptake capability and growth rate of different plant species that was consistent with previous studies in Shaoguan city, Guangdong, southern China and New South Wales, Australia [6,11]. The concentrations of Pb and Cd in the leaves of *Ipomoea aquatic* and *Sauropus androgynus* were all higher than those of *Barassica Juncea and other vegetables*. *Ipomoea aquatica* had the highest concentration of Pb (17.3 mg/kg) followed by *Sauropus androgynus* (14.9 mg/kg) which was approximately 2 and 1.5 times than permissible levels offered by Kabata-Pendias and Pendias [17]. Among the edible portions, *Ipomoea aquatic* appeared to the most bioaccumulation on Pb, whereas *Sauropus androgynus* indicated to the most bioaccumulation on Cd. The all plants could uptake Pb higher than Cd in this study. It suggests that transfer of Pb from soil to plant is higher in all vegetable than Cd that was also appeared in South China [10].

It is noticeable that *Sauropus androgynous and Ipomoea aquatic* was locally consumed, were the most contaminated plants among observed vegetables. The concentration of Cd in vegetables near the smelter was significantly higher than those at other areas ($P < 0.05$). These high accumulations of Cd and Pb in vegetables near the smelter may be attributed to the adsorption of aerial deposited on vegetable leaves from the stack of smelters that was corresponding with previous study in Australia [2]. The leafy and fruiting vegetables in studied area were enriched by Cd and Pb apparently. Among observed plant species, the leafy vegetables can uptake Cd and Pb more than fruity vegetables. Leafy edibles (*Barrassica Juncea, Corchorus, Ipomoea aquatic, Sauropus androgynus)* accumulated Pb and Cd much than fruiting edibles (*sechium edule species, pumpkin and eggplant*). The higher uptake of heavy metals in leafy vegetables may be due to higher transpiration rate to maintain the growth and moisture content of these plants [8]. These results revealed the corresponding with previous study to confirmed that metal concentrations in leafy crops are much higher than those on fruit crops [2, 10].

3.3. The accumulation of lead and cadmium in human hair

The concentrations of Pb in the hair samples ranged from 5.5 to 687 mg/kg (with an average of 84.2 mg/kg), whereas those of Cd and N.d-11.5 mg/kg (with an average of 0.93 mg/kg) in the whole individuals, respectively. In this study, Pb were elevated in hair of the residents higher than in Holland, which the lead concentration of residents living within 1 km of a lead smelter ranged from 0.8 to 114 mg/kg [18]. However, The values of Pb in hair samples of this study was lower than in Brazil that found lead in hair of fishermen living in Santo Amazo near lead smelter, The levels of Pb in fisherman's hair ranged from 2-1168 mg/kg with average value of 90.3 mg/kg [19. Comparing to other studies, the levels of Cd of hair samples of habitants in Cho Dien Pb/Zn mine showed higher than those in Poland and Italy [14, 20]. This variation of levels for different heavy metals from different individuals were related to the cumulative behavior of metals, life style, dietary habits [18, 20, 21]. High heavy metal accumulation in human body affected on the nervous system development, particularly toxic to children, causing potentially permanent learning and behavior disorders. Potential health effects for residents and burden of lead in hair need to be concerned [4, 9]. The Spearman'correlation coefficient was applied to identify the association between the concentration of Pb and Cd in hair samples. The relationship between Pb and Cd in hair specimens was consistent with study in Holland reporting that the significant correlation in hair between lead and cadmium with R^2 of 0.66 ($p < 0.001$) [20]. It would be explained that close relationship between Cd and Pb levels in hair samples can be result of possibly same source that was corresponding with findings in Malaysia and Brazil [7, 19]. Others suggested that the persistent correlations were due to similarities in the physicochemical properties of the metals [22]. These characteristics may be found through the geochemical composition of metals in the crust, surface water, food sources, general metabolism, disposition and absorption in the human body.

3.4. Health risk of inhabitants via vegetables consumption

Soil-to-plant transfer is one of the key components of human exposure to metals through the food chain. Dietary exposure to Cd and Pb has been identified as the risk on human health through the consumption of local vegetables. The results of average daily dose of inhabitants in the Cho Dien mine were shown in Table 2. The ADD of Cd and Pb from vegetable consumption in Cho Dien was 0.56 μg/kg*day and 1.915 μg/kg*day for adults, respectively. These findings were higher than other studies in Beijing of China, Samta of Bangladesh [22, 23]. However, the intake of Cd and Pb from vegetables in Cho Dien was lower than in Hunan Province, China [24].

*Table 2***.** Estimated metals intake of inhabitants in Cho Dien mine in comparison with other regions via vegetables ingestion (μg/kg.d).

	Cd	Pb
This study	0.56	1.915
Beijing, China	0.062	0.283
Bombay, India	0.009	0.035
Samta, Bangladesh	0.158	1.25
Hunan Province, China	1.66	2.67

The individual hazard quotient (HQ) of health risk to the habitants in Cho Dien Pb/Zn mine of cadmium and lead was calculated at 0.56 and 0.54, respectively. The values of HQ of each heavy metal derived due to consumption of vegetables around Cho Dien mine was estimated to be less than 1. Thus, the habitants in this region were exposed to minimal risks associated with consumption of leafy-fruity vegetables. However, long-term metal exposure by regular consumption of locally grown vegetables may pose potentially health problems to the residents in the vicinity of the mine, although no adverse health effects have been observed yet.

4. CONCLUSION

Soils and plants around Cho Dien lead/zinc mine area have been contaminated by mining activities. Elevated concentrations of Cd and Pb were also found in surface soils near the mining site, with mean values of 24.5 and 13,423 mg/kg, respectively. Soils from uncultivated and cultivated sites contained higher lead and cadmium concentrations than QCVN 03-MT/2015/BTNMT. The study indicated that cadmium and lead burden in samples as a result of their contamination in environment. High environmental and hair lead levels were identified in specific areas, from the smelter and the mining zones. Cadmium and lead concentrations in vegetable varied among plant species. *Sauropus Androgynus and Ipomoea aquatica* growing on heavily contaminated soil accumulated high levels of Cd and Pb, posing a potential health risk on the inhabitants. In order to reduce the health risk, the consumption of these vegetables should be avoided. Fruit vegetables appear to be relatively low accumulation of Cd and Pb in their edible parts and so would be more suitable species to grow. Thus, the regular consumption of these crop plants could pose potential health problem from long-term metal exposure.

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