HEAVY METALS ACCUMULATION OF FOOD-CROPS GROWN IN AGRICULTURAL AREAS AFFECTED BY INDUSTRIAL WASTEWATER, DA NANG, VIETNAM

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Abstract - Heavy metal pollution of agricultural soils resulting from wastewater irrigation has been causing major concern due to the potential risk involved. In the present study, food-crops (*Chrysanthemum coronarium; Ocimum basilicum; Coriandrum sativum*), irrigation water, and corresponding agricultural soil were assessed for Pb and As contamination. Study results reveal that contents of Pb and As in agricultural soils are lower than their permissible values in comparison with Vietnam technical regulations on the allowable limits of heavy metals for agricultural soils. By contrast, the concentration of Pb and As in water samples are higher than its allowable level for irrigation water. Besides, most of As values in food-crops grown surrounding Hoa Khanh industrial zone (IZ) are lower than its permissible level in vegetables. Meanwhile, a vast fraction of Pb contents in food-crops have exceeded its allowable level for both leafy and spice vegetables. The associated risk was assessed using HI index. The results indicate that there is a health risk associated with the ingestion of contaminated food-crops (HI > 1).

Key words - Hoa Khanh IZ; heavy metals; health risk assessment; food-crops; I_{geo}.

1. Introduction

Heavy metals occur as natural constituents of the earth crust, and are persistent environmental contaminants since they cannot be degraded or destroyed by natural processes [1]. Besides, with the rapid development of economy and society, pollution caused by industrial activities has been and continues to be a major cause of environmental deterioration. Slow depletion of heavy metals also takes place through leaching, plant uptake, erosion and deflation. This activity adversely affects the quality of environment so much that it becomes a subject of serious concern worldwide [2]. Plenty of studies have already concluded that areas in close proximity to industrial activities are marked by noticeable contamination of air, soil, and water.

The effects of metal pollution on local environments and organisms may therefore be substantial and long lasting in spite of extensive remediation efforts [3]. Heavy metals can be enriched via the food chain. Once the soil and water suffer from heavy metal contamination, it is difficult to be remediated and moreover, it was transferred and accumulated in food crops [4]. Food consumption contaminated with heavy metals is a major contributor pathway to human exposure than any other pathway such as inhalation and dermal contact. Heavy metal contamination is a known causative of various disorders such as genomic instability, endocrine disruption, neurotoxicity, carcinogenicity, immunological problems and also impaired psycho-social behavior.

Lead and arsenic are known as two of the most toxic heavy metals. The most sensitive targets for Pb toxicity are the developing nervous system, the hematological and cardiovascular systems, and the kidney. However, due to the multi-modes of action of lead in biological systems, lead could potentially affect any system or organs in the body [5]. Consequently, Pb is responsible for elevated blood pressure, renal and tumor infection, improper hemoglobin synthesis and reproductive system. Exposure to lead produces various deleterious effects on the hematopoietic, renal, and reproductive and central nervous system, mainly through increased oxidative stress [6]. While, As is a potent toxicant that may exist in several oxidation states and in a number of inorganic and organic forms. Acute arsenic poisoning is associated initially with nausea, vomiting, abdominal pain, and severe diarrhea. Encephalopathy and peripheral neuropathy are also reported. Chronic arsenic toxicity results in multisystem disease. Arsenic is a well-documented human carcinogen affecting numerous organs [7].

Da Nang is considered as a region of strong industrialization, especially steel industry. The unplanned development of this industry has led to many environmental consequences. Though most of the places surrounding steel factories were reported being polluted, the level of the pollution and the impact on humans have not been assessed. With the expansion of urbanization, there has been a decrease not only in quality of soil and water in agricultural areas surrounding the industrial zones but also in agricultural production acreage. Meanwhile, the demands of food stuffs such as vegetables, cereals, and meat for daily meals are more and more increasing in both quantity and quality. Consuming unsafe products will put the consumers at risk, thus, an assessment of Pb and As in food crops is very necessary.

Absorption and elimination of contaminants by the plants depend on several factors such as climate conditions, soil characteristics, kind of pollutants, and especially physiological characteristics of each plant [8]. Therefore, this study is conducted to evaluate the absorption of heavy metals in different parts of the food crops (especially the edible parts). Thence, we did: (1) Measure the Pb and As contents in soil and some food crops; and (2) Assess the human health risk caused by heavy metals via using food-crops in daily meal of local people.

2. Material and methods

2.1. Description of study site

Hoa Khanh IZ was established in 1998 with a total area of 395.72 hectares, of which 298.25 hectares have been used for hire. In 2004, expanded-Hoa Khanh IZ - one of the new industrial zones of the city was built in Lien Chieu district with a total area of 216.52 hectares; in which 132.6

hectares of land are used for factories construction, the rest are for public buildings, plant trees and services-areas for the project. Before the expansion, all waste water of old-Hoa Khanh IZ was treated by wastewater treatment Plant with capacity of 2000 m^3/day. Although in 2004 city government decided to extent more, the Wastewater Treatment Plant did not elevate the treatment capacity. At the end of 2013, the capacity of wastewater collection overall Hoa Khanh IZ was 95%. Therefore, about 600 m^3 of untreated wastewater pour into surrounding agricultural areas per day [9].

The farm land vicinity of Hoa Khanh IZ has about 400 households having subsistence mainly relying on agricultural activities with an area of approximately 52 hectares for cultivation. However, because of the influences of wastewater from this site in recent years, agricultural land was seriously polluted, cultivatable area decreased to just over 25 ha. In the past, this area was paddy field and this was also the main livelihood of the local people who lived around Hoa Khanh IZ. Now most of the people have switched to plant vegetables instead of rice (*Oryza sativa*) because agricultural land was seriously polluted.

2.2. Soil sampling and analysis

Soil at agricultural area surrounding Hoa Khanh IZ was collected by digging a monolith of 10 cm x 10 cm x 20 cm size by using a plastic scooper. Non soil particles such as stones, wooden pieces, rocks, gravels, organic debris were removed. Soil was oven dried and then it was sieved via a 2 mm sieve and stored in the labeled polythene sampling bags (According to the guideline of TCVN 7538-2:2005).

Soil samples had been natural-dried by sunlight before it were oven-dried at 60^0 C by Oven (Model: UNE500) until constant weight. Take 3 g of soil samples which were digested by 15 ml tri acid mixture namely, HNO_3, $HClO_4$ and H_2SO_4 at 5:1:1 ratio (volume - mL) at 180^0C until the transparent solution appeared. Water samples were filtered via Whatman No. 42 filter papers. The filtrate was adjusted to 100 mL by adding distilled water and stored for further analysis. Concentrations of Pb and As in the digested samples were determined using a graphite furnace atomic absorption spectrophotometer (GFAAS – Zenit 700P). Each preparation of sample was repeated in triplicate.

2.3. Food crops sampling and analysis

Standing food crop samples including Japanese-green (*Chrysanthemum coronarium*), Basil (*Ocimum basilicum*), and Chinese parsley (*Coriandrum sativum*) were also collected from the same sites where soils were collected. At harvest, plants were divided into leaves and roots, and properly washed with deionized water to remove all visible soil particles. Leaves were rinsed briefly in deionized water while roots were properly washed with tap water and finally with deionized water to remove all visible soil particles. The washed plant samples were oven-dried at 60°C to a constant weight. The dried samples were ground and sieved via 2mm mesh size (According to guideline of TCVN 9016:2011). 3 g of vegetable samples were subsequently digested in HNO_3 and HCl in 3:1 ratio at 180^0C. After cooling down, the suspensions were filtered and filtrate was adjusted to 100 mL with distilled water. Concentrations of Pb and As in the digested samples were determined using a graphite furnace atomic absorption spectrophotometer (GFAAS – Zenit 700P) (According to the guideline of TCVN 6496: 2009). With water-hyacinth samples, the pretreatment and analysis are conducted like vegetable samples but they are not divided into leaves and roots.

2.4. Index of geoaccumulation

Originally, the index of geo-accumulation (Igeo) was proposed by Muller (1969) to assess the heavy metal contamination in bottom sediments by comparing current and preindustrial concentrations. Danuta Wiechula (2004) [10] applied this index to assess the soil contamination by heavy metal in farming soil. It can be calculated by using the following equation:

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

Where C_n referred to the total concentration of heavy metals in soil samples, and B_n referred to the concentrations of heavy metals in the Earth's crust [11]. The B_n values of Pb and As in Earth's crust were 20 mg/kg and 1.5 mg/kg, respectively. Factor 1.5 is used because of natural fluctuations in background values for a given heavy metal in the environment as well as very small anthropogenic influences.

According to Gong Qingjie (2008), Muller has distinguished six classes of the geoaccumulation index as in the following table:

Table 1. *Igeo values and classes with corresponding to soil quality*

Class	Value	Soil quality
0	Igeo ≤ 0	practically uncontaminated
1	0 <Igeo ≤ 1	uncontaminated to moderately contaminated
2	1 <Igeo ≤ 2	moderately contaminated
3	2 <Igeo ≤ 3	moderately to heavily contaminated
4	3 <Igeo ≤ 4	heavily contaminated
5	4 <Igeo ≤ 5	heavily to extremely contaminated
6	Igeo> 5	extremely contaminated

2.5. Health risk assessment

Health risk index (HRI) was used to determine the health risks of consuming food crops by local inhabitants. The method was provided by US EPA (2007). HRI is expressed as the ratio of determined dose of a pollutant to a reference dose. An index more than 1 is considered not safe for human health and versus, the exposed population is unlikely to experience obvious adverse effects if the ratio is less than 1. The health risk index for Pb and As by consumption of contaminated food crops was calculated by the following equation [12]:

$$HRI = \frac{EF \times ED \times FI \times C \times 10^{-3}}{R_fD \times BW \times AT} \quad (2)$$

Where EF (365 days/year) is exposure frequency; ED is exposure duration (70 years); FI (g/person/day) is vegetable ingestion (157 g/person/day for adult Vietnamese); C (mg/kg on fresh weight basis) is heavy metal concentration in food crops (edible part – leaves); R_fD (mg/kg/day) is the oral reference dose; BW is the average body weight, which are considered to be 54 kg and 46 kg for adult males and females (applied for Vietnamese), respectively; AT is average time for noncarcinogens (365 days/year × number of exposure years, assuming 70 years in this study). R_fD values for Pb and As were 0.004 mg/kg/day and 0.0003 mg/kg/day), respectively (US EPA, 2000). R_fD is measured heavy metals dose that a person can be exposed in a day without being at any health risk in the whole life.

3. Results and Discussion

3.1. The concentration of Pb and As

The range and mean concentration of Pb and As in surface soil, water, and water-hyacinth (*Eichhornia crassipes*) samples surrounding Hoa KhanhIZ are summarized in Table 2.

Table 2. *The concentration of Pb and As in soil (mg/kg), water (mg/L), and water-hyacinth (mg/kg-FW)*

Elements	Samples	Minimum	Maximum	Median	Mean	Permissible level
Pb	Soil (n=19)	2.04	30.05	6.01	8.88±1.86	70 (a)
	Water (n=5)	0.76	3.13	1.95	1.96±0.39	0.1 (b)
	Water-hyacinth (n=3)	16.21	27.87	17.48	20.52±3.70	
As	Soil (n=19)	0.00	1.52	0.35	0.44±0.09	12 (a)
	Water (n=5)	0.04	0.58	0.30	0.29±0.09	0.1 (b)
	Water-hyacinth (n=3)	0.22	4.04	1.36	1.87±1.13	

QCVN 03: 2008/BTNMT: Vietnam technical regulation on the allowable limits of heavy metals for agricultural soils

Decision No. 106/2007/Dec-BNN: The permissible level of heavy metal in irrigation water for agriculture

Lead contaminated soil can pose a risk through direct ingestion or uptake in vegetable gardens and the common use of Pb makes its concentration in all environmental media elevated [13]. In this study, the mean value of Pb in surface soils samples were 8.88 mg/kg with a range of 2.04 mg/kg - 30.05 mg/kg, much lower than the permissible limit of lead content in Vietnam agricultural soil (70 mg/kg). Meanwhile, the mean content of Pb in water samples was 1.96 mg/l with a range from 0.76 mg/l to 3.13 mg/l – 20 times more than the permissible level of lead concentration for irrigation water (0.1 mg/l).

Ferric hydroxide generally plays an important role in controlling the concentration of As in soils and soil solutions. Significant anthropogenic sources of As are related to industrial activities (metal processing, chemical works based on S and P minerals) and to the use of arsenical sprays, particularly in orchards. The As contamination of paddy soils resulted from both high sorption capacity of these soils and the As transportation through irrigation. In the tested soils of this study, it ranged from 0 to 1.52 mg/kg with the mean value of 0.44 mg/kg, very lower than the values in the allowable limits of heavy metals for agricultural soils of Vietnam (12 mg/kg). Meanwhile, the mean concentration of As in water sample (0.29 mg/l) was three times higher when compared to the permissible level of As in irrigation water for agriculture of Vietnam (0.1 mg/l).

Farmers in the vicinity of Hoa Khanh IZ not only use the chemical fertilizers in agricultural production, but also often have a habit of using organic fertilizer made from water - hyacinth (*Eichhornia crassipes*) - the popular plant in this area is considered as a super-absorbent and hyper-accumulated heavy metal species. This was demonstrated by the mean Pb and As in water-hyacinth values, those were 20.5 mg/kg and 1.87 mg/kg respectively, much more higher than the mean contents in corresponding soil and water samples.

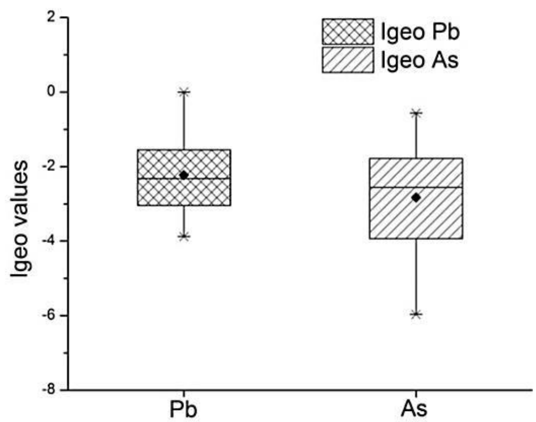

Figure 1. *Indexes of geo-accumulation of Pb and As in soil samples*

The Igeo values of Pb and As were mostly negative, indicated that nearly all the examined soil samples were not contaminated for Pb and As (Figure 1).

3.2. Pb and As contents in different parts of food-crops

Food-crop samples of this study included 3 vegetables named Japanese-green (*Chrysanthemum coronarium*), Basil (*Ocimum basilicum*), and Chinese parsley (*Coriandrum sativum*). The contents of heavy metals (mg/kg) in different part of food-crop samples are given in Table 3. The concentrations of metals varied greatly among food-crop species. In general, the mean concentrations of Pb and As in roots were found higher than in corresponding leaves samples. The Pb contents were at 8.85 mg/kg and 10.11 mg/kg in roots and 5.13 mg/kg and 5.14 mg/kg in leaves of Japanese-green and Basil, respectively. The As contents were at 0.11 mg/kg and 0.28 mg/kg in roots and 0.1 mg/kg and 0.05 mg/kg in leaves of Japanese-green and Basil, respectively.

Table 3. *The content of Pb and As in food-crops*

Plant species	Portion	Pb (mg/kg-FW)			As (mg/kg-FW)		
		Range	Median	Mean	Range	Median	Mean
Chrysanthemum coronarium(n=11)	Roots	2.62-39.96	6.48	8.85±3.17	0.00-0.23	0.12	0.11±0.02
	Leaves	0.83-18.06	3.33	5.13±1.60	0.00-0.21	0.08	0.10±0.02
Ocimumbasilicum(n=8)	Roots	3.36-42.13	5.35	10.11±4.62	0.00-1.79	0.03	0.28±0.22
	Leaves	2.64-7.13	5.22	5.14±0.62	0.00-0.11	0.06	0.05-0.02
Coriandrumsativum(n=10)	Leaves	2.21-43.69	4.11	15.01±5.66	0.00-0.34	0.06	0.13±0.04
	Permissible level*			1.0			1.0

** Decision No. 106/2007/Dec-MARD: The permissible level of heavy metal in vegetables (Vietnam Agriculture and Rural Development Ministry)*

Chinese parsley is the spice food-crop that is used popularly in daily food processing by Vietnamese in particular and Asia in general. Study results showed that, the mean Pb content in leaves (15.01 mg/kg) of Chinese parsley were 1.5-2 times higher than the ones in Japanese-green and Basil. On average, the Pb contents in edible part (leaves) of all food-crops in the current study have exceeded the Vietnam permissible level of heavy metal in vegetables (1.0 mg/kg).

According to Xiangdong Li [14], one of major factors contributing to high metal accumulation in food-crops could be ascribed to atmospheric deposition. When fuels were burned, heavy smoke containing various kinds of heavy metals, metalloids, and organic pollutants were discharged into the air, and the food-crops growing in those areas might be the first recipients of *Pb* and *As* as well. The foliar uptake of atmospheric Pb has been proved to be the dominant pathway for Pb entering the leaf grown in nearby industrial zone.

3.3. Uptake and translocation of Pb and As in food crops

The capacity of food crops to uptake heavy metals from soils can be assessed using the bio-concentration factor (BCF), the BCF values of Pb and As were calculated by dividing the concentration of a metal in a food crops (dry weight) by the total soil metal concentration, defined in the following equation:

$$BCF = \frac{\text{Heavy metal content in root (mg/kg)}}{\text{Heavy metal content in soil (mg/kg)}} \qquad (3)$$

The higher BCF reflects the poorer retention in soil or greater efficiency of plants in absorbing heavy metal, and low BCF reflects the strong sorption of metal to the soil colloid.

The translocation capacity of Pb and As between the roots and aerial parts (shoot, leaves or grain) of food-crops can be defined by the translocation factor (TF), defined in the following equation:

$$TF = \frac{\text{Heavy metal content in leaves (mg/kg)}}{\text{Heavy metal content in roots (mg/kg)}} \qquad (4)$$

Translocation factor is one of the main components of human exposure to heavy metals via the food chain. The BCF and TF values of Pb and As were calculated and given in Table 4.

As seen from Table 4, there was a relative difference in BCF and TF values that was observed among different food-crops and heavy metals. The BCF values for Pb and As in Japanese-green were given in descending order as Pb (0.997) > As (0.012) and Pb (1.138) > As (0.032) in Basil respectively.

Table 4. *The BCF and TF values across the sampling sites*

Food crops	Elements	BCF (soil to root)	TF (root to leaves)
Chrysanthemum coronarium	Pb	0.997	0.579
	As	0.012	0.938
Ocimumbasilicum	Pb	1.138	0.508
	As	0.032	0.180

The TF values for Pb and As in *Chrysanthemum coronarium* were 0.579 and 0.938, whereas the TF values for Pb (0.508) in *Ocimum basilicum* were higher than As (0.18). According to Li, Xiangdong (2011), the TF of heavy metals can be used to assess the potential capacity of plants in transportation of heavy metals from soil to plant or from root to aerial parts. Heavy metals with high TF are transferred easily from soil to plant and/or from root to aerial parts of plant than ones with low TF [14].

3.4. Potential risk of Pb and As to human health

HRI is a complex index which has been used for the evaluation of potential human health risks associated with long term exposure to pollutants such as heavy metals. Values of this index for investigated heavy metals Pb and As were presented in table 6. Individual HRI values of Pb and As almost exceeded 1 for both males and females in the study area (HRI values of Pb and As were at 6.21 and 0.93 for males; 7.29 and 1.09 for females respectively).

Table 5. *Health risk assessment of Pb and As by HRI index*

Inhabitants	Elements	RfD (mg/kg/day)	HRI	HI
Male	Pb	0.004	6.21	7.14
	As	0.0003	0.93	
Female	Pb	0.004	7.29	8.38
	As	0.0003	1.09	

According to Hye-Sook (2008), non-cancer risk is represented in terms of HRI for a single substance; in this case we assume that the additive effects, HRI can be summed across constituents to generate a hazard index (HI) for a specific pathway combination. The HI is a measure of the potential risk of adverse health effects from a mixture of chemical constituents. Whether or not a particular chemical mixture poses an additive risk depends on the targets (tissue, organ, or organ system) and the mechanisms of action of each chemical [15].

HI values through diet for males and females in the present study were 7.14 and 8.38, respectively. This suggests that male and female local people live in the vicinity of Hoa Khanh IZ may experience adverse health effects. The HI for males via diet is quite close to that for the females; this indicates that their levels of health risk are similar.

According to Qichao Wang (2007), the HI is a measure of the potential risk of adverse human health effects from a mixture of chemical pollutants. Whether or not a particular chemical mixture posed an additive risk not only depends on the targets (tissue, organ, or organ system) but also on the mechanisms reaction of the individual chemicals [16].

4. Conclusions

Based on the heavy metals concentrations, we conclude that nearly all the contents of Pb and As in agricultural soils in the vicinity of Hoa Khanh IZ are lower than their permissible values in comparison with Vietnam technical regulation on the allowable limits of heavy metals for agricultural soils. Most of the As values in food-crops grown around Hoa Khanh IZ are lower than its permissible level in vegetables. Meanwhile, a vast fraction of Pb contents in food-crops have exceeded its allowable level for both leafy and spice vegetables.Food-crops consumption were identified as the major pathway of human exposure to heavy metals. Food-crops in the vicinity of Hoa Khanh IZ are the main source of Pbs and As intake from foodstuff for adult males ans females. The HI values of the studied metals > 1 indicated that there is a health risks associated with the ingestion of contaminated food-crops.

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