Status of heavy metal (Pb, Cd) pollution in agricultural soil in Dong Mai lead recycling craft village in Hung Yen, Vietnam

Hien trang o nhiem kim loai nang (Pb, Cd) trong dat ong nghiep tai lang nghie t’ai che chi thon Dong Mai, tinh Hung Yen, Viet Nam

Research article

Pham, Thi Thao Trang; Phan, Thi Phuong; Nguyen, Khanh Linh; Nguyen, Thi Kim Oanh; Ha, Thi Thu Thuy; Ho, Thi Oanh; Nguyen, Kieu Bang Tam; Nguyen, Thi My Trang; Do, Thi Thu Trang; Nguyen, Thi Hue; Vu, Van Tu; Chu, Thi Thu Ha

1. Hanoi University of Science, 334 Nguyen Trai, Hanoi, Vietnam; 2. Vietnam Academy of Agricultural Science, Vinh Quynh, Thanh Tri, Hanoi, Vietnam; 3. Institute of Environmental Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam; 4. Institute of Ecology and Biological Resources, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam

The newly planned lead recycling zone in Dong Mai village has been operating with primary treatment systems using lime to neutralize acid in wastewater is a good sign for the local environment, yet the real problem that needs further attention and proper solutions is the accumulation of heavy metals typically lead (Pb) and cadmium (Cd) in agricultural land near the old Pb recycling area. In this context, 27 soil samples were collected and analyzed by AAS method to assess the situation and the quality of the agricultural soil. The results showed that the levels of Cd in the soil were still in acceptable level according to National Regulation. However, the lead contents in all of the soil samples exceeded National Regulation. The level of Pb pollution in soil was inversely proportional to the distance with old lead melting zone. The lead content in the soil sample collected at the distance of 50 m radius to the old melting zone reached 7070 ppm, which was 100 times higher than the allowable value of National Regulation.

Khu tai che chi one tai thon Dong Mai da duoc quy hoach va di vao hoat dong cung het thong xuly so bo vo voi biet la mot tin hieu dung mong cho moi truong noi day, nhung van de dan quan tam va giai quyet triet de la su tich huy mot luong lon kim loi nang dien hinh la chi (Pb) va cadmi (Cd) trong dat ong nghiep gan nhung khu tai che chi cu. 27 mau dat da duoc thu thap va phan tich hang phuong phap AAS de danh gia tinh trang, chat luong dat ong nghiep tai day. Ket qua cho thay hams luong Cd trong dat van trong muc do cho phap theo Quy chuan quoc gia. Tuy the, 100% cac mau dat dau co ham luong chi vuot qua muc cho phap theo Quy chuan quoc gia. Muc do o nhiem Pb trong dat tuy li nghiep voi khoang cach toi khu lo nau chi cu. Mau dat cach 50 m so voi khu vuc lo cua co ham luong chi len toi 7070 ppm, gap hon 100 lan so voi Quy chuan quoc gia.

Keywords: agricultural soil, lead contamination, cadmium contamination, lead recycling

1. Introduction

Craft villages play an important role in rural socio-economic development and contribute to industrialization and modernization process. Besides the positive impacts on the economic development, the evolution of craft villages brought plenty of shortcomings, especially in term of environmental issues. One of the environmental problems that need to be concerned today is heavy metal contamination in the agricultural soil that cause the food crops accumulated heavy metals and make poisoning to people when eating these food crops.

On a molecular level, proposed mechanisms for heavy metal’s toxicity involve fundamental biochemical processes. These include lead’s ability to inhibit or mimic the actions of calcium, which can affect calcium-dependent or related processes, and to interact with proteins (including...
those with sulphhydryl, amine, phosphate and carboxyl groups) (ATSDR, 2005). Children are vulnerable to risk. While the immediate health effect of typically concern in children is neurological, it is important to remember that childhood lead poisoning can lead to health effects later in life including renal effects, hypertension, reproductive problems, and developmental problems with their offspring.

Recently, traditional soil environmental restoration technologies are expensive and reveal several weaknesses, such as robbing the nutrients and microbiology structure of soil lead to plants cannot survive. While phytoremediation that defines the use of plants to extract, sequester, and/or detoxify various kinds of environmental pollutants (Salt et al., 1998) have advantages on recovering soil quality when plants continue grow during the recovery process. The plant’s growth on processing place also reduces soil erosion by wind and water, therefore, prevent the spread of pollutants.

2. Materials and methods

2.1 Materials

27 agricultural soil samples (0 - 20 cm at surface layer) were collected nearby the old lead recycling zone in Dong Mai village, Chi Dao commune, Van Lam district, Hung Yen province, Vietnam to analyze Pb and Cd contents.

2.2 Methods

Direct interviewing representatives of Chi Dao commune and households about the lead recycling status, as well as its effects on the local people in the past and at the present was performed in November and December 2015.

Soil samples were air-drying at room temperature for 5-7 days. Some impurities such as large-size debris, small stones and pebbles were removed. In the next step, soil samples were ground and sieved to obtain the small, smooth form for analysis. After that, the soil samples were treated with 65% HNO₃ solution and some droplets of H₂O₂ at 100°C - 110°C during 3 hours to mineralize. Lastly, the lead and cadmium contents were measured by Atomic Absorption Spectroscopy method (ASS).

3. Results and discussion

3.1 Lead recycling operation in Dong Mai lead recycling village

Lead recycling activities in East Village Mai have been taking place for decades since 1978. From the early days, people were not aware of the toxicity of this manual work, which were considered as lifesaver for the economic pressure. The people participating to Pb recycling were usually in direct contact with the used batteries to take out the lead to recycle. The development of production was the top priority, while the environmental protection, however, was overlooked without any waste and wastewater treatment system Therefore, the environmental pollution in Dong Mai craft villages increased seriously, especially soil pollution.

![Figure 1. Waste from old batteries nearby the old lead recycling furnace](image)

Facing this situation, in 2010, Hung Yen Province People's Committee promulgated Decision No. 491 QDUB about building industrial zone in order to minimize sources of lead pollution in the village. Most households that have Pb recycling activities moved into the lead recycling industry zone, however, there were still about 30 households (in a total of 637 households) continued to demolish old batteries, smelt lead and keep a large amount of lead slag, lead powder in the area of living house and at public sites.

3.2 Lead contamination levels in agricultural soils in Dong Mai lead recycling village

Analysis results of 21 soil samples collected at the paddy field nearby old lead recycling furnaces indicated lead pollution situation in paddy soil of the Dong Mai village (Table 1).

The level of lead concentrations in agricultural soil samples were inverse proportional to the distance from the points of collecting sample to the old Pb recycling area. At the sites having distance of 50 m from the old Pb recycling furnaces, Pb contents in soil samples ranged from 2,732 mg.kg⁻¹, dry weight to 7,070 mg.kg⁻¹, dry weight. At the distance of 100 m and 200 – 300 m from the old Pb recycling furnaces, Pb contents in soil samples ranged from 950 mg.kg⁻¹, dry weight to 3600 mg.kg⁻¹, dry weight and from 250 mg.kg⁻¹, dry weight to 880 mg.kg⁻¹, dry weight, respectively. All of these 21 soil samples collected near the old Pb recycling furnaces contained Pb levels exceeding the allowable value given in the National technical regulation on the allowable limits of heavy metals in the soils (QCVN 03:2008 BTNMT) from 3.5 to 100 times.
For soils used in other purposes such as vegetable planting, acacia planting we took 4 and 2 soil samples respectively to measure Pb contents. The soils for planting vegetable were collected at the distance of 200 m from the old Pb recycling area that included samples namely 22, 23, 24, 25. The soils used for planting acacia were collected at the distance of 100 m from Pb recycling area that included samples namely 26, 27. The results are shown in table 2.

Table 2. Lead contents in soils planted vegetable and acacia near the old lead recycling furnace in Dong Mai village

| Soil sample (200m) | Pb (mg.kg⁻¹ dry) | Soil sample (100m) | Pb (mg.kg⁻¹ dry) |
|--------------------|------------------|-------------------|------------------|
| 22                 | 700              | 26                | 479              |
| 23                 | 1,269            | 27                | 972              |
| 24                 | 1,300            |                   |                  |
| 25                 | 3,500            |                   |                  |

QCVN 03: 2008/BTNMT

The analysis results of soil samples for the purpose of vegetable and acacia planting showed excessively high concentrations of Pb. Soil samples namely from 22 to 25 contained Pb at levels from 700 mg.kg⁻¹, dry weight to 3,500 mg.kg⁻¹, dry weight. While, Pb contents in soils planted acacia ranged from 479 mg.kg⁻¹, dry weight to 972 mg.kg⁻¹, dry weight.

In fact, soils for planting acacia were collected at the closer distance from Pb recycling area in comparison to the distance of soils for planting vegetable but they contained lower levels of Pb. The reason was that because in 2014 the local people transported new soils from other place to cover the soils in this area and started to plant acacia.

The concentrations of Pb in soils planted vegetable and acacia were higher than the allowable value given in the National technical regulation on the allowable limits of heavy metals in the soils (QCVN 03: 2008/BTNMT) from 7 to 50 times.

The above data of Pb concentrations in agricultural soils demonstrated Pb pollution in Dong Mai lead recycling craft village at serious level, especially near old Pb recycling furnace zone. The scope of pollution does not stop at around furnace zone, it also spreads to areas of agricultural land and the land of living of Dong Mai village and other villages of Chi Dao commune. This situation requires the concern from local authorities to remediate pollution because Pb is a highly toxic heavy metal that can have adverse effect on human health. When penetrating into living organism, Pb is accumulated in bone, blood and kidneys. Some initial signs of Pb poisoning are digestive upset, vomiting, diarrhea, abdominal pain, decreased red blood cell by interfering with the synthesis of hemoglobin, decreased blood to the kidneys causing kidney failure. Half-life for lead emissions from kidney is 7 years, from bone is 32 years (Nies and Silver, 1995).

### 3.3 Cadmium contamination levels in agricultural soils in Dong Mai lead recycling village

Because of low Cd concentrations in soils in Dong Mai village, only a few representatives of agricultural soil samples were measured Cd content. Table 3 shows the levels of Cd in 12 paddy soil samples taken at the sites of distance 50 m, 100 m and 200-300 m from the old Pb recycling area.

Analysis results showed that paddy soils collected near the old Pb recycling area were slightly contaminated by Cd with the contents ranged from 0.05 mg.kg⁻¹, dry weight to 1.37 mg.kg⁻¹, dry weight. Although the concentrations of Cd in paddy soil samples were under the limit value given in National technical regulation on the allowable limits of heavy metals in the soils (QCVN 03: 2008/BTNMT), the risk of Cd accumulation in the agricultural crops should be concerned. Among the heavy metals, Cd has no benefit to the human and is potentially very toxic (WHO, 1992). Actually this is extremely hazardous element even at low concentration, and it will be bio-accumulated in the organisms as well as in the ecosystems. According to International Agency for Research on Cancer, Cd is classified as a Class 1 human carcinogen (IARC, 1993). One of the most likely reasons for the toxicity of Cd is it interferes in reactions of the enzymes containing zinc (Zn). Zn is an important element in biological systems, but Cd is although very similar to Zn in chemical terms cannot replace Zn in the biological role. Cd can also interfere with biological processes containing magnesium and calcium in a similar way. Compounds containing Cd is also carcinogenic substances that could arise immediate poisoning and damage to the liver and kidney of infected persons.
Table 3. Cadmium contents in paddy soil samples near the old lead recycling furnace in Dong Mai village

| Soil sample (50m) | Cd (mg.kg⁻¹ dry) | Soil sample (100m) | Cd (mg.kg⁻¹ dry) | Soil sample (200-300m) | Cd (mg.kg⁻¹ dry) |
|------------------|------------------|-------------------|------------------|------------------------|------------------|
| 1                | 1.28             | 8                 | 1.37             | 15                     | 0.20             |
| 3                | 1.37             | 9                 | 0.20             | 16                     | 0.05             |
| 5                | 1.28             | 11                | 0.20             | 19                     | 0.05             |
| 7                | 1.28             | 14                | 1.37             | 21                     | 0.13             |
| QCVN 03: 2008/BTNMT | 2              |                   |                  |                        |                  |

Soil planted vegetable and acacia were also slightly contaminated by Cd concentrations (Table 4). 6 soils samples were collected including 4 soil samples taken at sites of planting vegetable namely 22, 23, 24, 25 (in the distance of 200 m from the old Pb recycling area) and 2 soil samples taken at sites of planting acacia namely 26, 27 (in the distance of 100 m from the old Pb recycling area).

Table 4. Cadmium contents in soils planted vegetable and acacia near the old lead recycling furnace in Dong Mai village

| Soil sample (200m) | Cd (mg.kg⁻¹ dry) | Soil sample (100m) | Cd (mg.kg⁻¹ dry) |
|--------------------|------------------|-------------------|------------------|
| 22                 | 0.20             | 26                | 0.55             |
| 23                 | 0.20             | 27                | 0.75             |
| 24                 | 0.52             |                   |                  |
| 25                 | 0.20             |                   |                  |
| QCVN 03: 2008/BTNMT | 2              |                   |                  |

In general, Cd concentrations of 6 soil samples where people planted vegetable and acacia were lower than the limit value of National technical regulation on the allowable limits of heavy metals in the soils (QCVN 03: 2008/BTNMT). The Cd contents ranged from 0.20 mg.kg⁻¹, dry weight to 0.75 mg.kg⁻¹, dry weight. In the soils planted vegetable, the highest Cd value was only 0.52 mg.kg⁻¹, dry weight. However, due to the mechanism of heavy metal accumulation and amplification in organisms, the risk of effect by Cd on human eating vegetable in long term is reasonable.

Dong Mai lead recycling village currently do not have efficient wastewater treatment plants. All wastewater from households and firms recycling Pb was discharged into 3 compartment tank built from bricks and cement. People used lime to neutralize acid in wastewater then it was directly discharged into the irrigation channel system at the adjacent paddy field. Besides, the lead slag and dust were not thoroughly treated.

Manual activities on lead recycling at residential areas in the past and near the paddy field at the present led to seriously polluted environment by Pb in Dong Mai village. That is a great risk to local people because of the toxicity of Pb.

3.4. Recommendation

Nowadays, after on long way on socio-economic development, people have left countless contaminated lands back, and heavy metal pollution is no exception. In these lands with high content of toxic metal, some plant species not only can adapt but also can strongly grow. Although heavy metals are endangered substances which have no known biological function, these plants may accumulate toxic metals in their bodies, even with high level contaminated than soil (Hanna and Grant, 1962; Baker and Brooks, 1989). Some decades ago it was a newly evolving field of biotechnology that uses plants to remediate polluted soil, water, and air (Salt et al., 1998). This field proposed great excitement because it may offer a reasonable cost effective means to restore hundreds of thousands of square miles of land and water that have been polluted by human activities (Salt et al., 1995; Cunningham and Ow, 1996; Salt et al., 1998).

Face with serious situation of heavy metal pollution on a large scale in Dong Mai village, phytoremediation technology is realized with high feasibility of applying to clean heavy metal contaminated soil. A bunch of previous studies have shown a number of local plant species having remarkable ability to resistant to heavy metal contamination especially Pb and Cd through accumulating in the roots, stems and other parts. Using phytoremediation technology can reduce significantly the concentrations of heavy metals in the soil. Two important characteristics of plants chosen for phytoremediation include: they are hyperaccumulators of pollutants and they produce high biomass. Previous research results showed some indigenous plant species possessing both of the above mentioned characters that can be used in phytoremediation to clean up Pb pollution in paddy soil soil in Dong Mai lead recycling craft village (Chu Thi Thu Ha, 2014).

4. Conclusion

All of the agricultural soil samples taken near the old Pb recycling furnaces in Dong Mai village contained high concentrations of Pb level that exceeded the limit given by National technical regulation on the allowable limits of heavy metals in the soils (QCVN 03: 2008/BTNMT). Concentrations of Cd in the agricultural soil samples were under the allowable limit. However, the risk of being affected by not only Pb but also Cd is reasonable because both of these heavy metals are very toxic.

Therefore, improvement of the agricultural soil in the Dong Mai village is extremely urgent. Phytoremediation method is proposed as one of the optimal methods in terms of both economic efficiency and remediation of heavy metal pollution without destroying soil structure.
Acknowledgement: The authors thank to the financial support from Vietnam Academy of Science and Technology for the research project that has code: VAST07.03/16-17.

5. References

[1] ATSDR (2005) www.atsdr.cdc.gov.

[2] Baker AJM, Brooks RR (1989) Terrestrial higher plants which hyperaccumulate metallic elements- A review of their distribution, ecology and phytochemistry. Biorecovery 1: 81-126.

[3] Chu Thi Thu Ha (2014) Study on the growth and tolerance ability of Polygonum hydropiper L.and Hy menachne acutigluma (Steud.) Gilliland on Pb and Cd polluted soil. Journal of Vietnamese Environment, Vol.6 No.3, pp. 298-302.

[4] Cunningham SD and Ow DW (1996) Promises and prospects for phytoremediation. Plant Physiol 110: 715-719.

[5] Dang Thi An, Tran Quang Tien (2008) Pb-Cd contamination in agricultural soils and in produces in Van Lam, Hung Yen. Vietnam Soil Science 29, 56-58 (In Vietnamese).

[6] Hanna W J, Grant CL (1962) Spectrochemical analysis of the foliage of certain trees and ornamentals for 23 elements. Bull Torrey Bot Club 89: 293-302.

[7] IARC (1993) Beryllium, cadmium, mercury, and exposures in the glass manufacturing industry, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans and their Supplements 58, 1–444.

[8] Nies, D. H., and S. Silver (1995) Ion efflux systems involved in bacterial metal resistances. J. Ind. Microbiol. 14:186-199.

[9] QCVN 03: 2008/ BTNMT. National technical regulation on the allowable limits of heavy metals in the soils (In Vietnamese).

[10] Salt DE, Rauser WE (1995) MgATP-dependent transport of phytochelatins across the tonoplast of oat roots. Plant Physiology 107: 1293-1301.

[11] Salt DE, Smith RD, Raskin I (1998) Phytoremediation. Ann Rev Plant Physiol Plant Mol Biol 49: 643-668.

[12] WHO (World Health Organization) (1992) Cadmium, Environmental Health Criteria 134, 1–280.