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A survey of arsenic and other heavy metals in vegetation from markets or mine tailings

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Abstract: This research includes two investigations. The first one is a market basket survey of the levels of arsenic (As) and trace elements in bracken fern (*Pteridium aquilinum*) originated from three countries: South Korea, China and North Korea. The results showed that the mean As concentrations in stems of samples were significantly higher than those in leaves. As concentrations in all samples did not exceed food safety limits for vegetables. Generally, concentrations of Fe, Mn, Cu and Zn in leaves were higher than those in stems. The second investigation is a survey on the levels of As and other heavy metals in vegetation in the vicinity of Myoungbong mine tailings. The results demonstrated that As, Pb and Cu concentrations and bioaccumulation factors (BCF) in seedlings of the fern(*Asplenium achilleifolium*) were the highest, whereas Marsh horsetail(*Equisetum palustre*) accumulated the highest levels of Zn. Concentrations of As, Pb, Zn and Cu in vegetable-cress (*Lepidium sativum*) and the edible herb-aromatic madder (*Elasholtzia splendens*) were higher than food safety limits. Therefore, a risk assessment of As and other heavy metals in vegetables and herbs on local human health should be conducted in the future.

Keywords: arsenic; heavy metals; ferns; bioaccumulation factors

Introduction

Arsenic (As) is a toxic and carcinogenic element that occurs widely in soil environments around the world. Soil contamination with As occurs through both natural and anthropogenic pathways (Abedin *et al.*, 2002). Accumulated As in plants will eventually be transferred to animals or humans, which results in health problems throughout the food chain.

Recent diet studies that included evaluations of total arsenic in foods had been reported for Canada, U. S., Japan, India and Bangladesh (Das *et al.*, 2004; Roychowdhury *et al.*, 2002; Dabeka *et al.*, 1993). The mean arsenic levels ranged from 20.9 to 21.2 μg/kg in vegetables from markets, and from 91.73 to 123.22 μg/kg in vegetables and edible herbs from local villages located in As contaminated area of West Bengal(Roychowdhury *et al.*, 2002).

Approximately 1000 abandoned metal mines exist in South Korea. Recently, arsenic and heavy metal contamination of agricultural soils and crops surrounding the mining areas have been identified as some of the most serious environmental problems in South Korea(Kim and Davis, 2003).

Phytoremediation (phytoextraction in particular) had generated increasing research interests worldwide. Different studies on the environmental impacts of heavy metals and arsenic on mining areas have identified some plant species with the ability to develop tolerance to these pollutants, such as *Agrostis castellana* and *Agrostis deliculata*(De Koe and Jaques, 1993), *Cynodon dactylon* and *Amaranthus hybridus* (Jonnalagadda and Nenzou, 1997), *Bidens cynapiifolia* (Bech *et al.*, 1997), and *Pteris vittata*(Ma *et al.*, 2001). Therefore, collecting plant species from contaminated soils may be effective for identifying potential plants for phytoremediation.

Bracken fern(*Pteridium aquilinum*) is a species in fern family and a common vegetable in Korea and China. The present market survey is intended to analyze As concentrations in this edible fern and to investigate the potential effect of arsenic in this fern on human health through the food chain. The objectives of the survey for As and other heavy metals in vegetation in the vicinity of Myoungbong mine tailings were to investigate As, Pb, Cu and Zn concentrations in these plants and to identify plant species that accumulate or tolerate arsenic and these metals, and to know if their concentrations in edible vegetation exceeded food safety limits.

1 Materials and methods

1.1 Sample collection and preparation

A market basket survey of As and trace elements in bracken fern (*Pteridium aquilinum*) samples (dry) were collected from three large markets in Gwangju city during September 2004. Two samples were from South Korea, two samples from China and three samples from North Korea. After collection, each sample was divided into two parts: stems and leaves

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with stainless steel scissors. All samples were washed with deionized water in an ultrasonic cleaner for 10 min (Model 3510, Branson, USA)(Roychowdhury *et al.*, 2002), then rinsed with deionized water for three times. The samples were air-dried at room temperature for 72 h. Leaves were ground with a mortar and stems were ground with a mill to fine homogenized powders.

A survey of As and other heavy metals in vegetation in the vicinity of Myoungbong mine tailings. Plant samples were collected during October 2004. Different plant species (n=3) were randomly sampled in Myoungbong mine tailings and areas close to the tailings (Table 1). Aromatic madder(*Elasholtzia splendens*), a local common edible herb was divided into two parts: flowers and leaves.

Table 1 Sampling sites and plant species

Sampling sites	Plant species
Tailings site	*Woodsia ilvensis*, *Athyrium thelypteroides*, *Equisetum palustre*
Shore of pond next to tailings	*Pteridium aquilinum*, *Athyrium thelypteroides*, *Asplenium achilleifolium*, *Dicranopteris linearis*, *Equisetum palustre*
Hill near tailings	*Thelypteris hexagonoptera*, *Dryopteris campyloptera*
Farmland near tailings	*Lepidium sativum*, *Elasholtzia splendens*
Pond near farmland	*Typha Latifolia*

All the samples were thoroughly rinsed with tap water and then with deionized water in an ultrasonic cleaner for 20 min followed by thorough rinse with deionized water three times. The samples were air-dried at room temperature for 5 d then ground with a smaller mill to homogeneous powders. All the samples were stored in sample bags in a drier before digestion.

1.2 Digestion procedures and analysis of samples

Approximately 0.5000 ±0.0003 g of dry and finely powdered sample was weighed into a dry, clean TFM digestion vessel. Concentrated nitric acid 8 and 2 ml of hydrogen peroxide were added. The vessel was placed in the microwave oven(Milestone, Italy) to be digested. The microwave procedures for digestion are summarized in Table 2. After digestion in the microwave oven, the vessel with digestion solution was directly placed on the heating block to heat again at 95℃ for 1.5 h in order to drive off the residual H_2O_2. Each digested solution was transferred quantitatively to a 20 ml volumetric tube and made up with ultra-water (Milli-Q). Finally it was filtered through a membrane filter (0.45 μm, MFS, USA) and kept in a clean plastic tube for analysis. A reagent blank and standard reference plant material (Tomato leaves: SRM 1573a, National Institute of Standard and Technology, USA) were digested under the same conditions to verify the accuracy and precision of the digestion procedures and subsequent analysis.

Table 2 Microwave program for grass digestion(recommended by Milestone incorporation)

Step	Time, min	Temperature, ℃	Microwave power, W
1	3	85	≥1.000
2	9	145	≥1.000
3	4	200	≥1.000
4	14	200	≥1.000

Arsenic concentrations in digested solutions were determined using atomic absorption spectrophotometer coupled with hydride generation (HG-AAS) (Model 5100, Perkin Elmer, USA). Fe, Mn, Cu , Pb and Zn were measured by Flame-AAS.

1.3 Data analysis

As, Pb, Zn and Cu concentrations in soil and plants were used to estimate the ability of plant species to accumulate these elements. The ability of accumulation was expressed by the bioaccumulation factor (BCF), which is the ratio of arsenic and heavy metal concentrations in the plants to extractable fractions in the soil(EPA 3050b method).

Data on As concentrations in ferns from markets were tested by analysis of variance (ANOVA) using Matlab 5.2.

2 Results and discussion

2.1 As and other micronutrient element concentration in bracken fern

Bracken fern (*Pteridium aquilinum)* is a plant species within the fern family and a common vegetable in Korea and China. The results showed that arsenic concentrations in bracken fern ranged from 30.7 to 125.3 μg/kg in stems, and from 15.4 to 79.3 μg/kg in leaves(Fig.1a). Furthermore, arsenic was not detected in leaves of samples from South Korea. The result also showed that mean concentrations of As in stems of fern were significantly higher than leaves (P<0.001). The ranking of arsenic concentrations in fern samples among three countries was China ≈ North Korea > South Korea. Arsenic levels in the fern originated from South Korea were significantly lower than those of other countries (Fig.1b; P<0.001). Total concentrations of As in bracken fern were lower than food safety limits reported by some countries(China, Chile: 500 μg/kg for vegetables), so bracken fern in markets is safe for human consumption (Queirolo, 2000). However, experimental studies with vegetables grown under soil-less culture conditions of contaminated nutrient solutions showed that arsenic uptakes by tomato, radish, and turnip plants may reach unacceptable limit for human consumption (Burlo *et al.*, 1999; Carbonell-Barrachina *et al.*, 1999). We did not determine arsenic species (organic and inorganic arsenic compounds) in fern samples, since inorganic arsenic may be the major contributor of total arsenic in many foods, especially for vegetables(Schoof *et al.*, 1999).

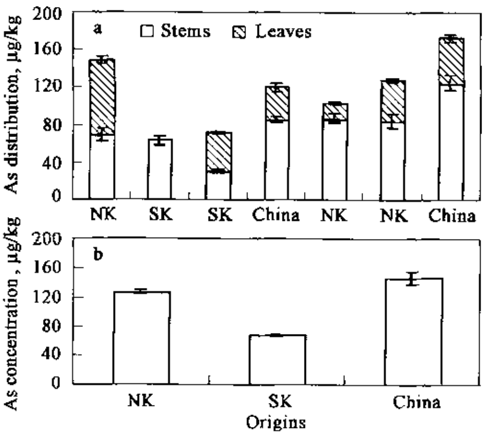

Fig.1 As concentrations in bracken ferns (*Pteridium aquilinum*) from markets and originated from three countries(North Korean(NK), South Korean(SK), China)

2.2 Trace elements of Fe, Mn, Cu and Zn in edible fern

Trace elements (Fe, Mn, Cu and Zn) are usually beneficial to human health. Meanwhile, concentrations of trace elements were also analyzed in the fern. Generally, Fe, Cu and Zn concentrations in leaves are higher than those in stems of all samples, which is a normal situation for plants. The ranking of Fe concentrations in samples was North Korea≈China > South Korea(Fig.2a). There was little difference in Cu and Zn concentrations in stems among different origins. The tendencies of Cu and Zn concentrations in leaves from three countries were similar to that of Fe (Fig.2c and Fig.2d). It might depend on the characteristics of different trace elements and soil conditions. In general, the concentrations of trace elements in the ferns from South Korea were lower than those from North Korea and China. There was little difference between stems and leaves in Mn concentrations(Fig.2b).

2.3 Concentrations of As and other heavy metals in vegetation from the vicinity of Myoungbong mine tailings

To assess the level of contamination of the mine

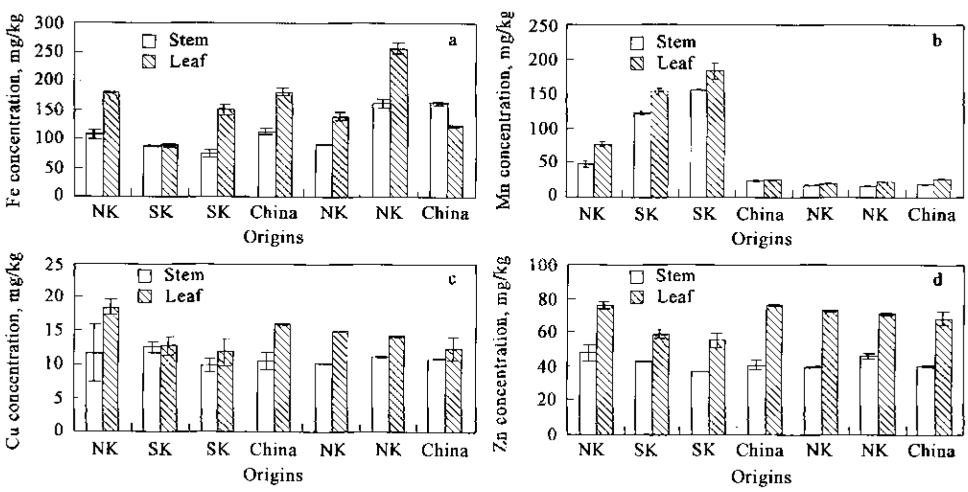

Fig.2 Fe(a), Mn(b), Cu(c), Zn(d) concentrations in bracken fern(*Pteridium aquilinum*) from market originated from three countries(North Korean (NK), South Korean(SK), China)

tailings and to select and identify plant species that might be useful in remediation of As and other heavy metal-contaminated environments, the levels of As, Pb, Zn and Cu in common vegetables, herbs and ferns were determined (Table 3). The results demonstrated that As concentrations in seedlings of the fern (*Asplenium achilleifolium*) was the highest (63.20 mg/kg), followed by the concentration found in the marsh horsetail(*Equisetum palustre*). As concentration in marsh horsetail was 15.03 mg/kg from tailings, and 11.86 mg/kg from the shore of pond near the tailings.

The As concentrations of two ferns that grew in the uncontaminated soils were less than 1.0 mg/kg. These results indicated that the concentrations of arsenic in vegetations might depend on As concentrations in soils of the sampling locations and the abilities of vegetations to take up arsenic from growth medium (Queirolo *et al.*, 2000). The popular vegetable to the local farmers, cress (*Lepidium sativum*), contained 1.05 mgAs/kg. It was higher than the food safety limits (0.5 mg/kg) (Das *et al.*, 2004; Queirolo *et al.*, 2000). Therefore, ingestion of cress may cause a risk to human health if it is consumed over a long period of time. In addition, As concentration was also high in the edible herb aromatic madder (*Elasholtzia splendens*)(1.27 mg/kg in flowers, 1.62 mg/kg in leaves and stems). The concentrations of arsenic in edible parts of vegetables and herbs in this study were in agreement with that reported by Queirolo *et al*.(2000) in samples of potato and broad bean from Chile. Therefore, a risk assessment of As in vegetables and herbs on local farmer health should be conducted in the future.

Table 3 As, Pb, Zn and Cu concentrations in plants from Myoungbong tailings site(means±*SE*)

Plant species	Concentrations of heavy metals, mg/kg			
	As	Pb	Zn	Cu
Pteridium aquilinum(spore)	6.26±0.40	7.63±1.36	64.35±7.88	49.81±3.25
Pteridium aquilinum(frond)	5.48±0.29	7.62±1.65	102.20±10.28	22.59±3.68
Woodsia ilvensis	2.20±0.10	12.12±2.61	101.48±10.91	20.59±4.73
Athyrium thelypteroide(t)*	5.29±0.13	6.52±1.59	110.28±10.53	35.02±6.19
Athyrium thelypteroide(p)*	3.71±0.05	6.07±1.73	113.83±9.86	27.90±5.81
Thelypteris hexagonoptera	0.80±0.02	2.92±1.08	16.30±2.43	33.10±6.05
Dryopteris campyloptera	0.51±0.01	2.76±0.85	23.03±3.11	17.99±4.02
Asplenium achilleifolium	63.2±15.4	34.84±4.79	91.67±10.98	103.37±12.25
Dicranopteris linearis	1.37±0.63	5.39±0.68	47.64±5.65	13.78±3.80
Equisetum palustre(t)*	15.0±0.13	12.80±1.60	151.96±23.96	24.24±7.37
Equisetum palustre(p)*	11.89±0.44	14.01±1.93	149.59±19.46	16.47±4.10
Elasholtzia splendens(flower)	1.22±0.16	6.42±1.03	52.19±18.86	17.93±3.65
Elasholtzia splendens(shoot)	1.62±0.13	8.81±1.44	103.88±21.28	21.51±3.61
Lepidium sativum	1.05±0.13	11.74±3.06	78.91±4.87	25.74±4.49
Typha Latifolia	0.40±0.01	7.68±1.66	20.45±4.87	12.36±4.21

Notes: * t: plant samples from mine tailing; p: plant samples from the side of pond next to mine tailing

Table 4 Bioaccumulation factors of As, Pb, Zn and Cu in samples from Myoungbong tailings site

Plant species	Bioaccumulation factors in plant species(BCF)*			
	As	Pb	Zn	Cu
Pteridium aquilinum(spore)	0.04	0.15	9.19	5.53
Pteridium aquilinum(frond)	0.04	0.15	14.60	2.51
Woodsia ilvensis	0.01	0.24	14.50	2.29
Athyrium thelypteroide(t)*	0.03	0.13	15.75	3.89
Athyrium thelypteroide(p)*	0.02	0.12	16.26	3.10
Thelypteris hexagonoptera	0.08	0.16	2.33	3.68
Dryopteris campyloptera	0.05	0.15	3.29	2.00
Asplenium achilleifolium	5.95	1.94	13.10	11.49
Dicranopteris linearis	0.01	0.30	6.81	1.53
Equisetum palustre(t)*	0.11	0.36	21.57	2.69
Equisetum palustre(p)*	0.15	0.49	21.37	1.83
Elasholtzia splendens(flower)	0.01	0.71	7.46	1.99
Elasholtzia splendens(shoot)	0.01	0.78	14.84	2.39
Lepidium sativum	0.27	0.65	11.27	2.86
Typha latifolia	0.10	0.43	2.92	1.37

Notes: * t: plant samples from mine tailing; p: plant samples from the side of pond next to mine tailing; bioaccumulation factor (BCF): the ratio of concentration of As and other heavy metals in the plants to extractable fraction in the soil

Moreover, concentrations of heavy metals(Pb, Cu and Zn) were also analyzed in plant species. The results showed that concentrations of Cu and Pb were the highest in seedlings of the fern (*Asplenium* *achilleifolium*) (Cu: 103.37 mg/kg, Pb: 34.84 mg/kg). Pb and Cu levels in this edible herb (*Elasholtzia splendens*) were also high (7.6 mg/kg for Pb and 19.7 mg/kg for Cu). Furthermore, Pb, Cu, Zn concentrations in cress (*Lepidium sativum*) were higher than the results reported in other studies (Queirolo *et. al.*, 2000).

The BCF values for As, Pb and Cu were the highest in seedlings of the fern (*Asplenium achilleifolium*) (Table 3 and Table 4), however, this was not the case for Zn. This indicated that the fern (*Asplenium achilleifolium*) had a stronger ability of accumulating As, Pb, Cu than other plant species. Moreover, BCF value for Zn reached the maximum in marsh horsetail (*Equisetum palustre*) and significantly exceeded the food safety limits reported in China and Chile(Table 3).

3 Conclusions

The market basket survey demonstrated that As concentrations in bracken fern was lower than food safety limits. This edible fern from markets are safe for human consumption. Another survey for As and other heavy metals in vegetation in the vicinity of Myoungbong mine tailings showed *Asplenium achilleifolium* among all the plants sampled was potentially useful in the remediation of the mine tailings. More attention should be paid to the contamination of As and other heavy metals in vegetables and edible herbs due to the potential adverse effects on the residents in the vicinity of tailings sites.

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