Lim, H., Lee, J., Chon, H., Sager, M., Environmental contamination and geochemical behaviour of heavy metals around the abandoned Songcheon Au-Ag mine, Korea. International Symposium on the Fusion Technology of Geosystem Engineering, Rock Engineering and Geophysical Exploration
Seoul, Korea, Nov. 18-19, 2003

Environmental contamination and geochemical behaviour of heavy metals around the abandoned Songcheon Au-Ag mine, Korea

Hye-sook Lim[1], Jin-Soo Lee[1], Hyo-Teak Chon[1], Manfred Sager[2]
[1]School of Civil, Urban and Geosystem Engineering, Seoul National University, Seoul, Korea
[2]Austrian Agency for Health and Food Safety and Federal Office for Food Safety, Vienna, Austria

Abstract: The objective of this study is to investigate the contamination levels and dispersion patterns of arsenic and heavy metals and to estimate the bioaccessible fraction of the metals in soil and plant samples in the vicinity of the abandoned Songcheon Au-Ag mine. Tailings, soils, plants (Chinese cabbage, red pepper, soybean, radish, sesame leaves, green onion, lettuce, potato leaves, angelica and groundsel) and waters were collected around the mine site. After appropriate preparation, all samples were analyzed for As, Cd, Cu, Pb and Zn by ICP-AES and ICP-MS. Elevated levels of As and heavy metals were found in tailings. Mean concentrations of As in agricultural soils were higher than the permissible level. Especially, maximum level of As in farmland soil was 513 mg/kg. The highest concentrations of As and Zn were found in Chinese cabbage (6.7 mg/kg and 359 mg/kg, respectively). Concentrations of As, Cd, and Zn in most stream waters which are used for drinking water around this mine area were higher than the permissible levels regulated in Korea. Maximum levels of As, Cd and Zn in stream waters were 0.78 mg/L, 0.19 mg/L and 5.4 mg/L, respectively. These results indicate that mine tailings can be the main contamination sources of As and heavy metals in the soil-water system in the mine area. The average of estimated bioaccessible fraction of As in farmland soils were 3.7% (in simulated stomach) and 10.8% (in simulated small intestine). The highest value of bioaccessible fraction of metal in farmland soils was 46.5% for Cd.

1. Introduction

A number of metal mine operations have been closed up to now, and a mound of contaminated mining wastes remained near the abandoned mine sites without any environmental treatment. Heavy metal contamination has been one of serious problems in the vicinity of abandoned mine sites. These heavy metals and metalloids have a potential to contaminate soil and water. They can be dispersed and accumulated in plants and animals, and finally taken in by human beings as consumer.

The potential toxicity of contamination is strongly determined by the speciation of the element. In risk assessment, oral exposures are typically stated in terms of the external dose or intake, instead of in terms of absorbed dose or uptake. Intake is typically defined as the process by which an agent crosses the outer exposure surface of a human without passing an absorption barrier, while uptake is the process by which an agent crosses an absorption barrier into human or animal. Bioavailability of a compound can be defined as the fraction of an administered dose that reaches the central (blood) compartment, whether through the gastrointestinal track, skin, or lungs. Bioaccessibility is the fraction of a chemical in an environmental medium that is available for absorption based on in vitro extraction but not necessarily absorbed. The term "bioaccessible" will be used to indicate the in vitro fraction of the chemical intake that is directly available for absorption. Exposure assessment of the oral route of exposure considers ingestion of food, water and soil. Therefore, bioaccessible metal concentrations are more important for risk assessment than total metal contents in the environment.

The purpose of this study is, firstly, to investigate the contamination levels and dispersion patterns of As and heavy metals, secondly, to estimate the bioaccessible fraction of the metals in soil and plant and, thirdly, to assess the possible entry of As and heavy metals into human body in the vicinity of the abandoned Songcheon Au-Ag mine. The Songcheon mine is located in Gangneung-Si, eastern habour city of South Korea. The Songcheon mine was Au and Ag producer, and working period was from 1939 to 1995.

2. Material and methods

Sampling and analysis

Soil and water samples were collected during three different seasons (October of 2002, March and May of 2003). Plant samples were collected during two seasons (October of 2002 and May of 2003). Soil samples were air-dried and sieved by 2-mm and 0.2-mm screen. Plant samples were washed in deionized water, and air-dried. Dry plant material was ground in a stainless steel blender. Collected water samples were filtered through 45 ㎛ membrane, then samples for cation analysis were acidified by conc. HNO_3. Water samples were maintained under 4°C until they analyzed.

Two grams of dried soil sample were digested with aqua regia. One gram of dried plant sample was digested with $HNO_3/HClO_4$. Trace elements concentration in soil and plant extracts were determined by ICP-AES. Water samples were analyzed by IC and ICP-MS.

In vitro Bioaccessibility Testing

EHS (Extraction of Heavy metals in Stomach and Small intestine) test means the in vitro simulation of the human digestive system-stomach and small intestine. In this method bioaccessibility was estimated by amount of metal extracted from the soil and plant samples using the simulated digestion system. EHS test consist of two steps. In the first step, presence of food in the stomach was simulated by using a glycin-HCl buffer of pH 1.5 containing pepsin as an artificial gastric fluid. In the second step, the small intestinal environment was simulated, and the digestive solution was simulated by phosphate-carbonate buffer pH 8 containing pancreatin. All extractions were performed in the dark system and experimental temperature was maintained at 37°C (human body temperature). All extracted solutions were analyzed by ICP-AES.

3. Results

Metals in Soil, Plant and Water

The average total amount of As and heavy metals in soil samples were shown in Table 1.

Table 1. The average total amount and range of As and heavy metals in soil [mg/kg].

Elements		Tailing	Mountain soil	Farmland soil	Stream sediment	Control soil
As	Range	3584 – 143813	695 – 3082	6.6 – 626	32 – 445	19 – 26
	Mean	51413	1910	161	138	22
Cd	Range	2.0 – 20	0.61 – 1.8	0.15 – 1.4	0.32 – 1.5	0.07 – 0.20
	Mean	9.4	1.32	0.71	0.68	0.14
Cu	Range	30 – 749	36 – 89	13 – 673	16 – 80	30 – 36
	Mean	385	67	76	48	33
Pb	Range	125 – 50803	63 – 428	23 – 290	14 – 231	26 – 38
	Mean	20323	291	89	82	32
Zn	Range	580 – 7541	115 – 795	83 – 362	63 – 399	94 – 96
	Mean	3059	477	175	164	95
Hg	Range	0.090 – 1.007	0.189 – 0.551	0.092 – 4.903	0.019 – 0.258	0.015 – 0.050
	Mean	0.451	0.389	1.124	0.103	0.033

Except for the roots, the highest levels of heavy metals in plant were 6.7 As mg/kg, 1.0 Cd mg/kg, 359 Zn mg/kg (in Chinese cabbage), 13.74 Cu mg/kg (in red pepper leaves), 2.9 Pb mg/kg (in potato leaves). Concentration levels of heavy metals in leaves are much higher than those in grain products.

The highest levels of As and heavy metals in water were 0.78 As mg/L, 0.19 Cd mg/L , 0.02 Cu mg/L, 0.001 Pb mg/L and 5.4 Zn mg/L.

Bioaccessibility Testing

The average of estimated bioaccessible portions in the simulated human digestion system are shown in Fig. 1. The estimated bioaccessible fraction of plant was up to 96% in the first step, and was up to 76% in the second step. The highest bioaccessible fractions were found in Chinese cabbage (1st step) and potato leaves (2nd step).

Except for As, extracted amounts of heavy metals in 1st step (acid environment) were higher than those in 2nd step(neutral or weekly alkaline environment). The average rate of extraction was 4% As, 41% Cd, 17% Cu, 34% Pb 23% Zn in 1st step and 13% As, 1% Cd, 6% Cu, 1% Pb, 1% Zn in 2nd step.

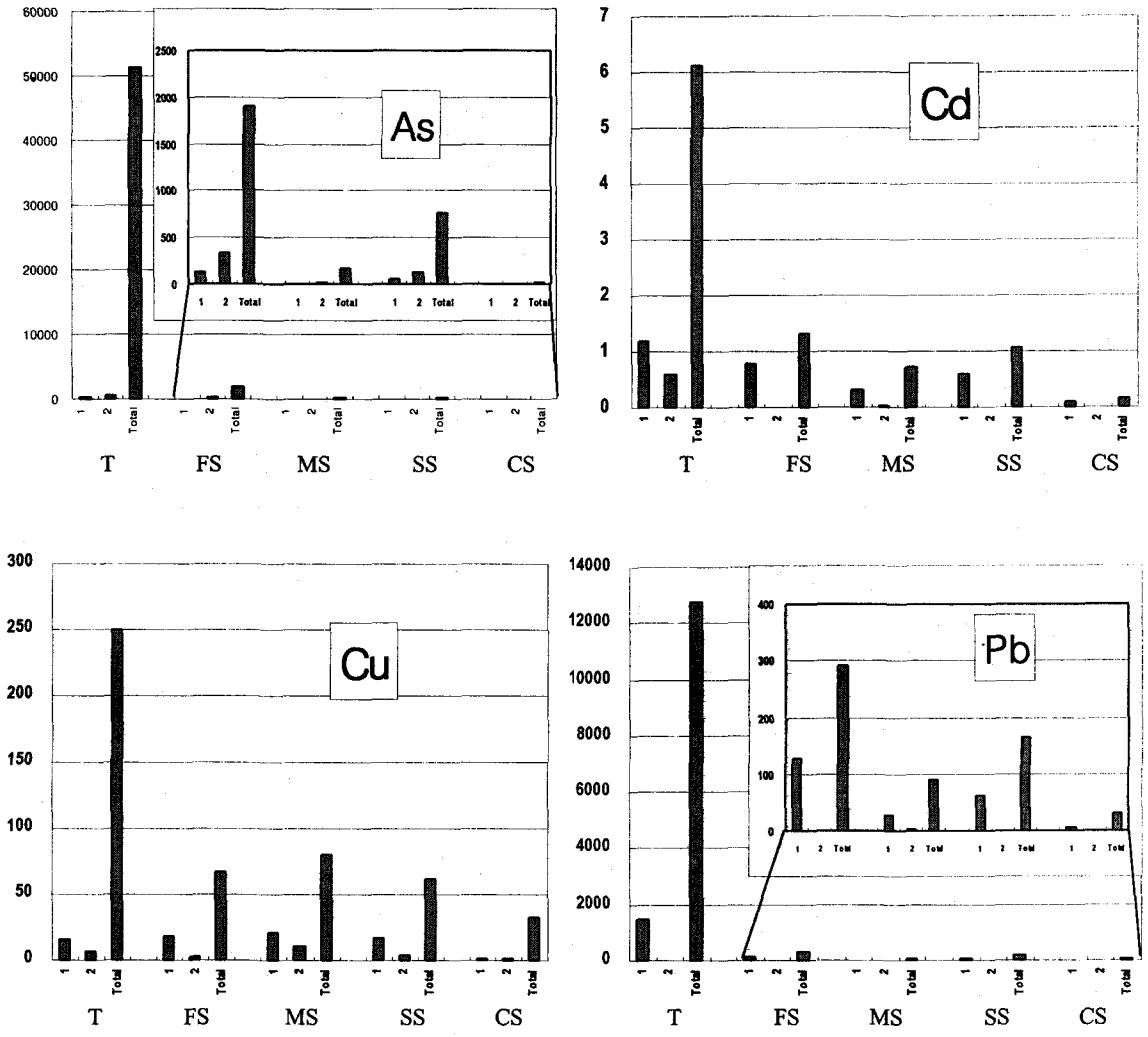

Fig 1. The average amount of bioaccessible As and heavy metals in soil samples [mg/kg].

(1: 1st step, 2 : 2nd step, T : tailing , FS : farmland soil, MS : mountain soil, SS: stream sediment, CS : control soil)

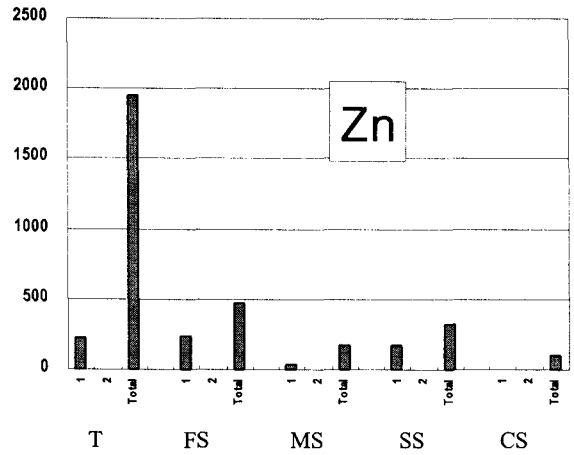

Fig. 1. Continued.

4. Conclusions

Concentration levels of heavy metals in tailings from the Songcheon Au-Ag mine were 141,550 As mg/kg, 20.4 Cd mg/kg, 754 Cu mg/kg, 51,331 Pb mg/kg and 7,959 Zn mg/kg. Mean concentrations of As, Cd, Cu, Pb and Zn in agricultural soils were higher than the permissible level. Especially, maximum level of As in farmland soil was up to 513 mg/kg. The highest levels in plant were 6.7 As mg/kg, 1.0 Cd mg/kd, 359 Zn mg/kg (in Chinese cabbage), 13.74 Cu mg/kg (red pepper leaves), 2.9 Pb mg/kg (potato leaves). Concentration levels of heavy metals in leaves are much higher than those in grains and stalk. Vegetable grown on contaminated soils were rich in As and heavy metals. The highest levels of heavy metals in water were 0.78 As mg/L, 0.19 Cd mg/L , 0.02 Cu mg/L, 0.001 Pb mg/L and 5.4 Zn mg/L The levels of As, Cd, and Zn in most stream waters which is used for drinking water around the mine area were higher than the permissible levels regulated in Korea. The seasonal variation of As in stream water shows that concentration levels of As in water samples collected in May were the highest, and in October were the lowest. These soils, plants and waters are the possible sources of As and heavy metals entry into human body.

These results indicated that mine tailings can be the main contamination sources of As and heavy metals in the soil-water system in the vicinity of mine site.

The average of estimated bioaccessible fraction of As in farmland soils in simulated stomach and in simulated small intestine was 3.7% and 10.8%. The bioaccessible fraction in soil samples decreased in the order of Cd > Pb > Zn > Cu > As in stomach environment, and As > Cu > Cd > Pb = Zn in small intestine environment. The highest value of bioaccessible fraction of metal in farmland soils was 46.5% for Cd.

References

Hoehmann A., 1994, In vitro-Untersuchungen zur enzymatischen Abbaubarkeit von Futtermitteln fuer Hunde, Hannover.

Human Health Risk Assessment Appendix 5, 2002, Bioaccessibility and Bioavailability of Metals Following Ingestion of Rodney Street Community Soils/Dusts and Oter Environmental Media, Rodney Street Community.

Kolluru R. V., Bartell S. M., Pitblado R.M. and Stricoff R.S., 1976, Risk assessment and management handbook, McGraw-Hill.

Sager M., Pucsko R., Belocky R., 1989, Evaluation of the speciation of inorganic constituents in sediments of the Reservoir at Altenworth of the River Danube, Arch. hydrobiol. suppl. 84, 37-72.

Sager M., Belocky R., Pucsko R., 1990, Zur Ermittlung der Bindungsformen von haupt und Spurenelementen in Sedimenten durch sequentielle Löseverfaren, Acta hydrochim. Hydrobiol. 18, 12-139.