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Arsenic and heavy metal contamination in the vicinity of the abandoned Dongjung Au-Ag-Cu mine, Korea

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Abstract: The Dongjung Au-Ag-Cu mine area was seriously contaminated with As and heavy metals - Cd, Cu, Hg, Mn, Pb and Zn etc. Those elements were highly accumulated in plants grown at farmland as well as farmland soil. Stream waters and groundwater which has been used as drinking water around the mine site contain high levels of heavy metals, especially As. As a result of human health risk assessment using EHS(Extraction of Heavy metals in Stomach and Small intestine) test for bioaccessible contents of heavy metals, there is a potential of cancer and adverse effects on human health for the residents of the mine area.

1. Introduction

There are some elements known as toxic - As, Cd, Cu, Hg, Mn, Pb and Zn etc. These elements have adverse effect on growth of animals or plants and human health by accumulation through various pathways. Most of abandoned mine sites in Korea have not been under any environmental treatment for remediation, and ecosystem around the mine sites has been threatened.

The purpose of this study is to find the source of various toxic elements, and to investigate the levels of contamination, transfer routes and dispersion patterns within stream water, groundwater, soil and plant around the Dongjung Au-Ag-Cu mine area. Finding pathway of toxic heavy metals to human body, exposure assessment, dose-response assessment and calculating risk for carcinogenic risk and toxic risk were performed around the mine site. For risk calculation, bioaccessibility contents of heavy metals in soil and plant were measured by EHS(Extraction of Heavy metals in Stomach and Small intestine) test.

The Dongjung Au-Ag-Cu mine is located in Ocheon-Ri, Jipum-Myeon, Yeongdeok-Gun, Gyeongsangbuk-Do, Korea. The ore deposit of the mine is hydrothermal veins. The mine was gold producer, and 105 tons of Au ore were produced in 1975 and 1976. The environmental impacts are due to tailings and rock files of Au mining. There are residential land and farmland along the stream near to mine and rock files.

2. Sampling and Analysis

In order to investigate the contamination level and geochemical behaviour of heavy metals around the abandoned Dongjung mine, tailing, soil, crop plant (lettuce, radish, Chinese cabbage, bean leaves and roots) and water samples were collected along a distance of about 2 km in October, 2002 and in May, 2003.

Tailings and soils were dried and sieved under 10 mesh(<2 mm) for domestic regulation, the quarter of those samples was sieved -80 mesh(<180 ㎛) for aqua regia analysis. To meet domestic regulation, 0.1 N HCl 50 ml was added to -10 mesh dried soil 10 g, and shaken for 1 hour. For decomposition with aqua regia, 21 lm of conc. HCl and 7 ml of conc. HNO_3 were added to 2 g of -80 mesh dried soil, heated at 60 ℃ /30 min. and 140 ℃/90 min. After filtration, water was added to 100 ml. Plant samples were washed with distilled water, dried, milled. For digestion of plant sample, 16 ml of conc. HNO_3 and 4 ml of conc. $HClO_4$ were added to 1 g of dry plant sample. Samples were heated at 80 ℃ and up to 150 ℃ gradually. After cooling, 25 ml of distilled water were added. All soil and plant samples were analyzed for 22 main and trace elements by ICP-AES and ICP-MS. Arsenic, Cd, Cu, Mn, Pb and Zn showed highly contaminated levels. Sodium and K in water samples were analyzed using AAS, and other cations such as Mg, Ca, Al, Si, Cr, Mn, Fe, Cu, Zn, Cd, Ba, Pb were by ICP-AES. Anions in water samples (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) were analyzed by Ion Chromatography(IC).

All chemical analytical results of this study were performed by quality control system using duplicated and reference samples, and precision and accuracy were less than 10 %.

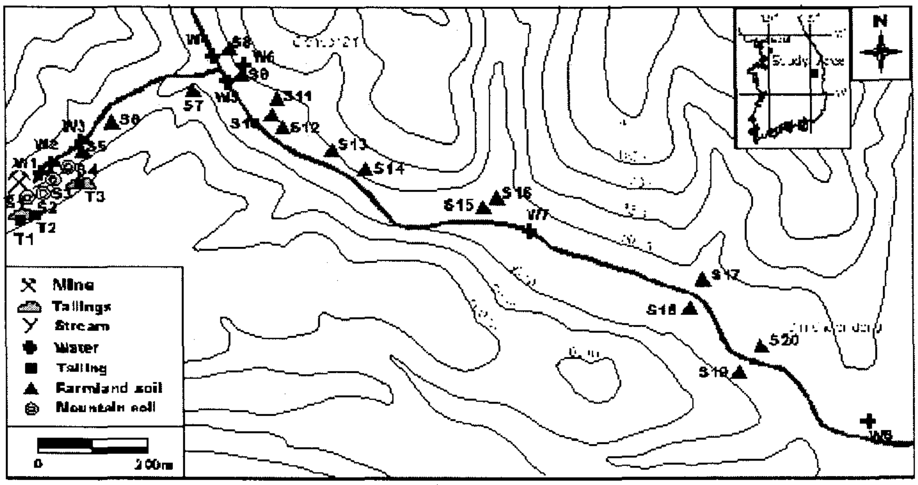

Fig. 1. Sampling location map.

2. Human Health Risk Assessment

For toxic heavy metals, average daily dose(ADD) was calculated by following equation.

$$ADD[mg/kg/day] = \frac{C[mg/kg] * IR[kg/day] * EF[day/yr] * ED[yr]}{BW[kg] * AT[yr]}$$

C: Concentration of metals in soil, plant and water [mg/kg/day]
IR: Ingestion Rate [kg/day]
EF: Exposure Frequency [day/yr]
ED: Exposure Duration [yr]
BW: Body Weight [kg]
AT: Average Time [yr]

For the toxic risk assessment, the Hazard Quotient(HQ) was calculated from ADD dividing by Reference Dose(RfD) for each element, and the Hazard Index(HI) was sum of all HQ. Carcinogenic risk was calculated by multiplying ADD with Slope Factor(SF). HQ indicates whether concentrations of chemicals of concern can make adverse effect on health (HQ>1) or not (HQ<1), and carcinogenic risk means probability of cancer occurrence. Two values - RfD and SF were quoted from IRIS database (U.S. EPA.).

Determination of bioaccessible soil concentration for health risk assessment

The concentrations from aqua regia digestion of soil and total extraction of plant are the levels of soil and plant themselves. However, the proportion of available form is more important than total content. Even though 1st step contents of sequential extraction test can indicate bioaccessible form, it is less proper for health risk assessment than the test to simulate the conditions of stomach and intestine. In this EHS(Extraction of Heavy metals in Stomach and Small intestine) test, simulation of the stomach and the small intestines was performed to determine bioaccessible soil concentration. The simulation consists of 2-step extraction test for 1 g of -80 mesh dried soil; 1 ml pepsin solution was added as enzyme with 19 ml glycine buffer(pH 1.5) at 1st step, and 1 ml pancreatin solution with 19 ml phosphate/borate buffer(pH 8) at 2nd step. Soils were mixed with solution and shaken in waterbath for 100 rpm. For 1st and 2nd steps, the reaction was continued for 2 hours and overnight, respectively. The reactions were done at 37℃ without any light input for both of those two steps.

3. Results

Concentrations of 0.011 As mg/L, 8.4 Mn mg/L, 5.6 Zn mg/L and 258 SO_4^{2-} mg/L were found in stream water collected nearby waste rock piles. Arsenic concentration in groundwater, which has been used for drinking water around the mine area, was 15.4 µg/L, which is higher than the permissible level suggested by WHO. The range and average concentration of heavy metals extracted by aqua regia are presented in Table 1.

Table 1. Range and average concentration of heavy metals in soil and tailings(unit in mg/kg).

Sample Type	As	Cd	Cu	Mn	Pb	Zn	Hg
Tailings	2724 - 6688	1.70 - 5.73	58.5 - 756.2	3124 - 4083	5273 - 32631	528 - 2874	1.01 - 4.37
(n=3)	4570	3.76	404	2044	21535	2044	3.18
Mountain soils	241 - 5262	2.91 - 23.7	34.9 - 224.5	4105 - 42357	542 - 12780	605 - 6685	0.20 - 6.08
(n=3)	2970	12.4	154	21612	7961	3180	3.61
Farmland soils	34.8 - 239	0.69 - 3.23	1.9 - 49.6	754 - 3958	117 - 858	135 - 470	0.05 - 2.15
(n=16)	82.7	1.34	29.4	1786	295	224	0.37

n : number of samples

Mean concentrations of heavy elements in farmland soils were higher than those permitted by domestic regulation. Significant levels of heavy metals in tailings can impact on soils and waters around the mine. The highest level of heavy metals was found in bean leaves from the mine area (1.07 As mg/kg, 2.05 Cd mg/kg, 4.76 Cu mg/kg, 4.97 Pb mg/kg and 138 Zn mg/kg). The biological absorption coefficients (BAC) in most plants were in the order of Cd > Zn > Cu > As > Pb.

There are three pathways of heavy metals to human body; through mouth (oral exposure), through nose (inhalation exposure), and through skin (thermal exposure). In this study, only the oral route was considered among these three pathways. The exposure target was applied to the female resident of the mine area, and the scenario was that she ingests heavy metals through rice, drinking water, and soil during her field farming. The calculated ADD and the result of health risk assessment are shown in Table 2.

Table 2. Health risk through oral exposure.

	Elements	Concentration in soil (mg/kg)	Concentration in water (mg/L)	Concentration in rice (mg/kg)	Oral intake (ADD) (mg/kg/day)	Oral risk
Non - carcinogenic effects	As	2.63	15.4 [ppb]	0.201	6.10E-04	1.53E+00
	Cd	0.75	0.001	0.061	1.36E-04	1.49E-01
	Cu	5.79	0.029	1.89	4.12E-03	2.58E+00
	Mn	443	< d.l.	13.4	2.77E-02	1.98E-01
	Pb	83.7	0.028	0.616	1.84E-03	NA
	Zn	78.1	0.077	28.5	5.76E-02	1.92E-01
	SUM					4.65E+00
Carcinogenic effects	As	2.63	15.4 [ppb]	0.201	6.10E-04	1.24E-03

* NA – Not applicable.
< d.l. – Under detection limit.

As a result of human health risk assessment, there was a potential of cancer to 1,239 persons in million due to As exposure. Toxic heavy metals (As, Cd, Cu, Mn, Pb and Zn) could cause adverse effects on human health for the female residents of the mine area.

4. Conclusion

Mean concentrations of farmland soils of the Dongjung Au-Ag-Cu mines area are elevated to 82.7 As mg/kg, 1.34 Cd mg/kg, 29.4 Cu mg/kg, 1786 Mn mg/kg, 295 Pb mg/kg, 224 Zn mg/kg and 0.37 Hg mg/kg (by aqua regia digestion). These metals were highly accumulated in plants grown at farmland soil near mine site. Especially bean leaves had more 1.6 times of Cd than soil which bean had grown at. High levels of As were shown in stream water and groundwater used as drinking water. The level of heavy metal contents in soils, plants are decreased with the distance from the mine site. With the results from EHS (Extraction of Heavy metals in Stomach and Small intestine) test for determining bioaccessibity contents of heavy metals, there was a potential of cancer to 1,239 persons in million due to As exposure. Adverse effects on human health for the female residents of the mine area can be possible due to the toxic elements (As, Cd, Cu, Mn, Pb and Zn).

References

Höhmann, A., 1994, In-Vitro-Untersuchunhgen zur enzymatischen Abbaubarkeit von Futtermitteln Für Hunde

Kolluru R. V., Bartell S. M., Pitblado R. M. and Stricoff R. S., 1976, Risk assessment and management handbook, McGraw-Hill p.1.3-4.30

US EPA, 1991a. Risk Assessment Guidance for Superfund, vol. I , Human Health Evaluation Manual, Supplemental Guidance: Standard Default Exposure Factors(Interim Final), OSWER Directive 9285.6-03. Office of Emergency and Remedial Response, US Environmental Protection Agency, Washington, DC.

US EPA, 1991b. Risk Assessment Guidance for Superfund, vol. I , Human Health Evaluation Manual. Part B. Development of Risk-based Preliminary Remediation Goal (Interim), PB92-963333. Publication 9285.7-01B. Office of Emergency and Remedial Redponse, US Environmental Protection Agency, Washington, DC.