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Human risk assessment of As, Cd, Cu and Zn in the abandoned metal mine site

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Abstract

The cancer risk and the non-cancer hazard index for inhabitants exposed to As, Cd, Cu and Zn in the soils and stream waters of the abandoned Songcheon Au–Ag mine area were evaluated. Mean concentrations of As, Cd, Cu, Pb and Zn in agricultural soils were 230, 2.5, 120, 160, and 164 mg kg^{-1}, respectively. Mean concentrations of As, Cd and Zn of the water in the stream where drinking water was drawn was 246 μg L^{-1}, 161 μg L^{-1} and 3899 μg L^{-1}, respectively. These levels are significantly higher than the permissible levels for drinking water quality recommended by Korea and WHO. The resulting human health risks to farmers who inhabited the surrounding areas due to drinking water were summarized as follows: (1) the non-cancer health hazard indices showed that the toxic risk due to As and Cd in drinking water were 10 and 4 times, respectively, greater than those induced by the safe average daily dosages of the respective chemicals. (2) the cancer risk of As for exposed individuals through the drinking water pathway was 5 in 1000, exceeded the acceptable risk of 1 in 10,000 set for regulatory purposes.

Introduction

In Korea, most of precious metal mines were closed in the 1970s and large amounts of mine wastes were left behind without proper environmental safeguard and permanent placements. Mining can be significant sources of heavy metal contamination of the environment owing to activities such as mineral excavation, ore transportation, smelting and refining, disposal of the tailings and waste waters around mines (Adriano 2001). In typical metal mine districts, massive stockpiles of sulfide containing refuse and tailings in the inactive mines are weathered and oxidized over long term atmospheric exposures. The acidic mine drainage with elevated levels of heavy metals are discharged to contaminate the downstream water bodies, agricultural soils and food crops. The fugitive metals in the receiving water and soils may pose a potential health risk to the residents in the vicinity of the mines (Davies & Ballinger 1990; Merrington and Alloway 1994). There is a need to accurately quantify the toxicological risk to the resident populations in the contaminated environments. Current assessment models derive the total human exposure (Kolluru *et al.* 1996; Kimmel *et al.* 1999; Akagi *et al.* 2000; Alcock *et al.* 2000; Green *et al.* 2000; Lee *et al.* 2000, 2004; Paustenbach 2002; Sekhar *et al.* 2003) by evaluating the fate and transport of toxic elements through exposure pathways such as drinking water, food intake, dust inhalation and hand-to-mouth soil ingestion. The adverse health effects of human exposure to toxic elements however have not been rigorously appraised.

In this study, to assess the risk of adverse health effects on human exposure to arsenic and other heavy metals by past mining activities, environmental geochemical surveys and risk assessment were undertaken in the abandoned Songcheon Au–Ag mine area in Korea.

Materials and methods

The Songcheon gold-silver mine is located in Samsan-ri, Yeoungok-myun, Gangneung-si, eastern harbor city of South Korea (37°49′4″N, 128°38′1″E). The deposit of this mine was classified as a hydrothermal vein type with Au–Ag minerals in quartz veins and the main geology is Precambrian felsic gneiss. Sulfide containing minerals consist of arsenopyrite, pyrite, galena and sphalerite. It was an active mine from 1939 to 1977. The reported total outputs were 208 kg of gold and 1606 kg of silver. Approximately 50% of the products were recovered during the first 10 years of the operation.

The mining and smelting ceased in 1970s and, upon closure, large amounts of mine wastes were left behind without proper environmental safeguards. The unprotected mining wastes have been dispersed down the slope by wind and water as a point source pollution of the vicinity of this mine. Because there is no facility providing the public water supply around the Songcheon area, the stream waters nearby the mine tailings is the source of drinking water for the inhabitants.

Sampling of tailings, soils and stream waters in the vicinity of the Songcheon mine was carried out in October, 2002 and the sampled locations are marked on Figure 1 which is a geographical sketch of the study area. Surface soil samples (0–15 cm depth) were collected from the agricultural land around the mine area. Each soil comprised a composite of 15–20 subsamples taken across a 1×1 m square. Tailing and soil samples were air-dried, sieved to −10 mesh (<2 mm), quartered and pulverized into −80 mesh (<180 μm) for the chemical analysis. Two grams of soil sample were digested with aqua regia (HNO_3/HCl) and the samples were then heated at 70 °C for 1 h. Concentrations of As, Cd, Cu, Pb, and Zn in soil extracts were determined by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry). Waters used as drinking water were mainly collected along the downstream from the mine tailings. Stream water samples were filtered through 0.45 μm membrane filters and then samples were acidified by conc. HNO_3 for analyses of the cations using the ICP-MS (Inductively Coupled Plasma Mass Spectrometry). Human health risk assessment of exposures to As and potentially hazardous metals was evaluated based the data obtained from the water, soil, and tailing samples.

Results and discussion

Geochemical characteristics of tailings, soils and waters

Ranges and mean concentrations of As, Cd, Cu, Pb and Zn in tailings, soils and stream waters are shown in Table 1. The concentrations of the potentially hazardous elements in the tailings from the Songcheon gold–silver mine were 24,080, 6.6, 130, 3830, and 2410 mg kg^{-1} for As, Cd, Cu, Pb, and Zn, respectively. They represented the contaminant levels at the pollution source that could seriously impact the soils and waters around the tailing piles. As the soils and vegetations in the entire region had been affected by the emissions and fallouts of the mining operation, it would not be possible to establish the background concentration levels for the elements. The mean concentrations of As, Cd, Cu, Pb and Zn in agricultural soils were considerably higher than the typical contents of comparable soils around the world (Bowen 1979) and average concentrations of uncontaminated soils of Korea (Ahn 2000). The As concentrations of the soils are especially alarming as the element in significant quantities would be expected to transfer from soils to rice grains and other crops grown in these agricultural fields.

Arsenic concentrations in stream waters used for drinking water from the Songcheon mine area were significantly higher than the permissible level (0.05 mg L^{-1}) for drinking water quality recommended by Korea (Table 1). Also, concentrations of Cd and Zn in stream waters exceeded the permissible level (0.005 Cd mg L^{-1} and 1.0 Zn mg L^{-1}) for drinking water quality in Korea.

Human risk assessment

The US National Academy of Sciences (NRC 1983) stipulated that risk assessment is the process of estimating the probability of occurrence of an

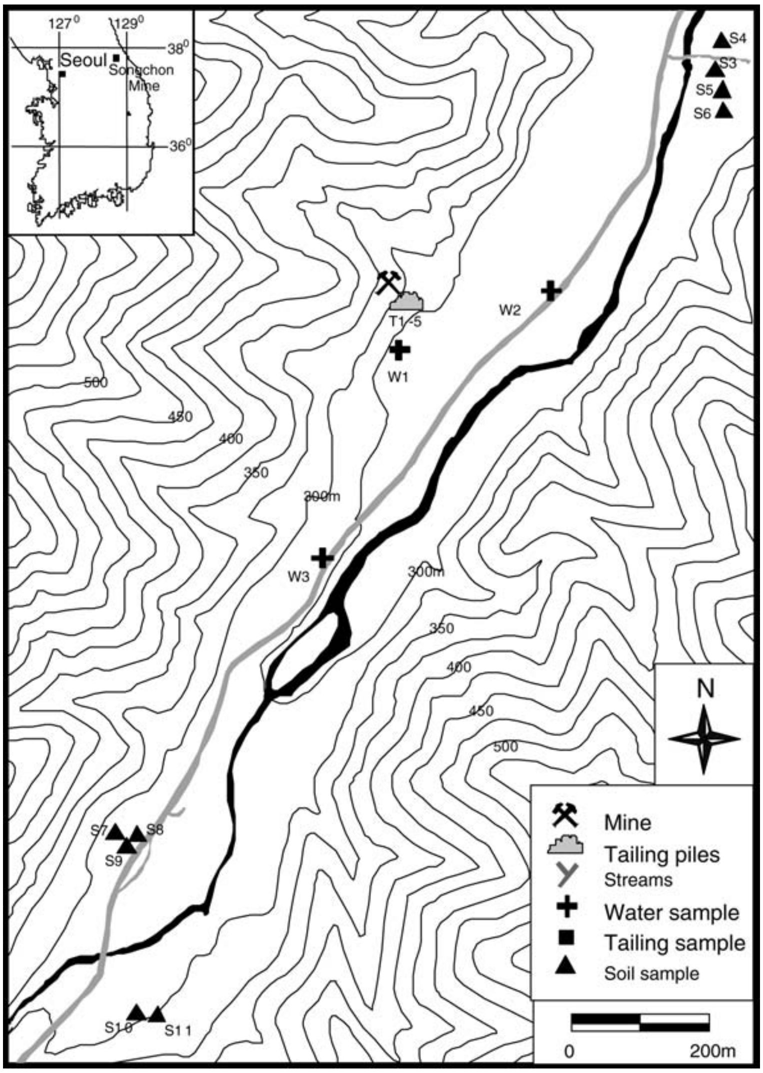

Fig. 1. Sampling location map in the Songcheon Au–Ag mine area.

event and the probable magnitude of adverse health effects on human exposures to environmental hazards (Kolluru *et al.* 1996; Paustenbach 2002). A full fledged risk assessment consists of four interactive and iterative steps, namely the hazard identification, exposure assessment, dose–response (toxicity) assessment and risk characterization. The basic frame work for risk assessment was adopted for assessing the health risk of an adult farmer who resides in the affected area and is exposed to As and other heavy metals in the contaminated soils and water (Figure 2). The hazard identification process was accomplished through field sampling the tailings, soils, and water and the subsequent determinations of the contaminant levels in these samples (Table 1). While all of the elements identified in Table 1 were potentially harmful to human, Pb was not considered as the reference dose concerning its toxic effects was pertaining to young children and not applicable to the adults being considered in our case. The remaining components of the risk assessment depicted in Figure 2 are elaborated in the following sections.

Exposure assessment

The exposure assessment identifies the pathways by which humans are potentially exposed the

Table 1. Ranges and mean concentrations of As, Cd, Cu, Pb and Zn in tailings, soils and stream waters from the Songcheon Au–Ag mine.

Sample type		As	Cd	Cu	Pb	Zn
Tailings (N[a] = 5)	Mean	24070	6.6	130	3830	2410
(mg kg^{-1})	Range	3620–56260	2.8–12.8	30–210	90–12050	480–6040
	SD[b]	22670	4.0	70	4270	2140
Agricultural soils	Mean	230	2.5	120	160	164
(N = 9) (mg kg^{-1})	Range	53–490	2.0–3.2	21–710	45–420	78–340
	SD	153	0.3	210	124	90
Natural soil of Korea (Ahn 2000)		9.6	0.5	19	27	60
World's natural soil (Bowen 1979)		6.0	0.35	30	35	90
Stream waters[c]	Mean	0.246	0.161	0.003	0.001	3.899
(N = 3) (mg L^{-1})	Range	0.003–0.555	0.127–0.191	0.002–0.004	0.001–0.001	2.48–5.40
	SD	0.230	0.026	0.0009	0.0005	1.192

[a] N = No. of samples.
[b] SD = standard deviation.
[c] Stream water used for drinking water in the Songcheon mine area.

toxicants and estimates the magnitude, frequency and duration of these actual and/or potential exposures. Conducting an exposure assessment involves analyzing contaminant releases; identifying exposed populations; identifying all potential pathways of exposure; estimating exposure point concentrations for specific pathways; and estimating contaminant intakes for specific pathways. An exposure assessment starts with the construction of a conceptual model that depicts all possible exposure pathways and narrows them down to one or several realistic scenarios. In this study, the conceptual model was based on the exposures of a typical Korean farmer residing close to the mine. The exposure scenario in this situation was narrowed down to the intake of potentially toxic elements through drinking water and direct ingestion of soil caused by improper personal

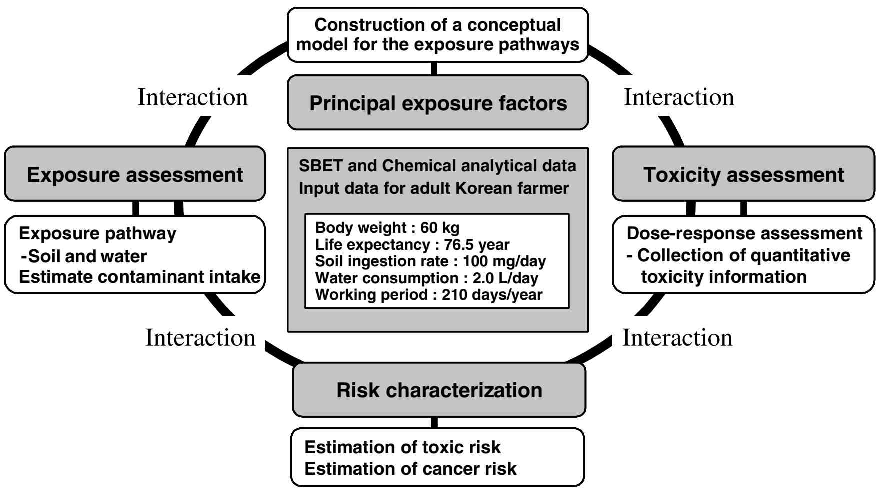

Fig. 2. Risk assessment modeling for the abandoned metal mine site.

hygiene that transferred soils attached on hand to mouth. A major component of the Korean diet is rice, but the food pathway through direct ingestion of rice grain was not considered in our case. Because there were no paddy fields in this area affected by mining, rice samples can not be taken from the mine area. The dosage of the exposures may be estimated by the expected quantities of toxicants in the ingested water and soils.

The average daily dose (ADD) of the contaminant via the identified pathways (i.e. soil ingestion and drinking water pathways) indicates the quantity of chemical substance ingested per kilogram of body weight per day (Kolluru *et al.* 1996; Paustenbach 2002) that:

$$\mathrm{ADD} = \frac{C \times \mathrm{IR} \times \mathrm{ED} \times \mathrm{EF}}{\mathrm{BW} \times \mathrm{AT} \times 365} \qquad (1)$$

Where C is the concentration of the contaminant in the environmental media (mg kg^{-1} or mg L^{-1}), IR is the ingestion rate per unit time (mg day^{-1} or L day^{-1}), ED is the exposure duration (years), EF is the exposure frequency (days year^{-1}), BW is the body weight of the receptor (kg), and AT is the averaging time (years), equal to the life expectancy), and 365 is the conversion factor from year to days. The principal exposure factors that have been taken into account to carry out the risk assessment calculations are shown in Table 2.

Table 3 summarizes the outcomes of the ADD estimations for As, Cd, Cu and Zn with the two exposure pathways. The average daily intakes of As, Cd and Zn via the drinking water pathway were 10^3 to 10^4 times higher than those of the soil ingestion pathway while the ADD of Cu were comparable in the pathways involving soil ingestion and drinking water.

Evaluation of non-cancer (toxic) risk

Toxic risks refer to the non-carcinogenic harms incurred due to the exposures. The extent of the harm is indicated in terms of a hazard quotient (HQ):

$$\mathrm{HQ} = \mathrm{ADD}/\mathrm{RfD} \qquad (2)$$

where the RfD is the reference dose. The reference dose is the daily dosage that enables the exposed individual to sustain this level of exposure over a prolonged time period without experiencing any harmful effect. The toxic risk estimates are based on a comparison of actual exposure to the reference dose for the particular chemical involved. The RfD for chemicals is derived from toxicological data. The US EPA IRIS (Integrated Risk Information System) is by far the most frequently cited RfD database and its values for As, Cd, Cu, and Zn were adopted for this study (Table 4).

When more than one potential toxicant is present, the interactions must be considered. The toxic risks due to potentially hazardous substances present in the same media are assumed to be additive. The HQs may then be summed to arrive at the overall toxic risk, the hazard index (Kolluru *et al.* 1996; Paustenbach 2002) that:

$$\mathrm{HI} = \Sigma \mathrm{HQ}_i; \quad i = 1 \ldots n \qquad (3)$$

where HI is the hazard index for the overall toxic risk. If the calculated HI is less than 1.0, the non-carcinogenic adverse effect due to this exposure pathway or chemical is assumed to be negligible.

The HQ values for As, Cd, Cu, and Zn via the soil exposure pathway were all ≤ 0.1 and their sum was also ≤ 0.1 (Table 5). Therefore, there is mini-

Table 2. Exposure factors for an adult Korean farmer.

Factor/Parameter	Symbol	Units	Residential/ Agricultural	Data source
Exposure Duration	ED	Years	30	US EPA 1997
Exposure Frequency	EF	days year^{-1}	350	US EPA 1997
Averaging Time	AT	Years	76.5	KNSO 2001
Body Weight	BW	Kg	60	ATS 1997
Ingestion rate				
Soil	IR_s	Kg day^{-1}	100×10^{-6}	US EPA 1997
Drinking water	IR_w	L day^{-1}	2.0	KOWACO 2001

Table 3. The ADD values of As, Cd, Cu and Zn with exposure pathways.

Exposure pathway	As	Cd	Cu	Zn
ADD via soil pathway ($mg\ kg^{-1}\ day^{-1}$)	5.9×10^{-6}	1.5×10^{-7}	1.4×10^{-5}	1.5×10^{-5}
ADD via water pathway ($mg\ kg^{-1}\ day^{-1}$)	3.1×10^{-3}	2.0×10^{-3}	3.8×10^{-5}	4.9×10^{-2}

Table 4. Reference doses and slope factors of As, Cd, Cu and Zn.

Element	RfD ($mg\ kg^{-1}\ d^{-1}$)	SF ($(mg\ kg^{-1}\ d^{-1})^{-1}$)
As[a]	3×10^{-4}	1.5
Cd[a]	5×10^{-4}(water) /1×10^{-3}(food)	n.a.
Cu[b]	3.7×10^{-2}	n.a.
Zn[a]	3×10^{-1}	n.a.

[a] US-EPA IRIS database (http://www.epa.gov/iriswebp/iris/index.html).
[b] Decision Support System (DSS) developed in the API (American Petroleum Institute).

mal soil ingestion risk in the Songcheon mine area. However, the HQ values for As and Cd by the drinking water exposure route were 10.3 and 4.0, respectively (Table 5). The resulting HI values for As and Cd are significantly higher than 1.0 and their toxic risks due to drinking water are strong in the Songcheon mine area.

Evaluation of cancer risk

The cancer risks are expressed in terms of the probability one may develop cancer at a given lifetime exposure level. The cancer risk probability is determined from the slope factor (SF) of the dose-response curve in the low-dose region where the relationship between the exposure dose (measured in $mg\ kg^{-1}$ BW day^{-1}) and response (measured in terms of probability of developing cancer) is assumed to be linear. Mathematically, the SF denotes the probability of developing cancer per unit exposure level of $mg\ kg^{-1}\ day^{-1}$ and its values may be obtained from the IRIS database (Table 2). The lifetime exposure level (ADD_{life}) is arrived by prorating the exposure incurred over the exposure duration over the expected life span. According to the IRIS database a slope factor has only been derived for As. Cancer risk is then calculated as follow (Kolluru *et al.* 1996; Paustenbach 2002):

$$\text{Cancer risk} = ADD_{life} \times SF \quad (4)$$

For the Songcheon mine area, only As is a carcinogen. The cancer risks of being exposed to As by the soil ingestion and drinking water routes, according to Equation 4, are 8.8×10^{-6} and 4.6×10^{-3}, respectively. The As cancer risk via the exposure pathway of drinking water exceeded the acceptable risk of 1 in 10,000 for regulatory purposes. Thus, the daily intake of stream water by the local residents can pose a potential health threat due to long-term arsenic exposure.

Table 5. Hazard indices and hazard quotients for As, Cd, Cu and Zn in the Songcheon mine site.

Exposure route	As	Cd	Cu	Zn	HI
Soil ingestion	0.0	0.0	0.0	0.0	0.0
Water ingestion	10.3	4.0	0.0	0.2	14.5
HI	10.3	4.0	0.0	0.2	–

Conclusions

Tailings of the Songcheon mine, closed since the 1970s, contained As, Cd, Cu, Pb, and Zn at concentrations of 24,080, 6.6, 130, 3,830, and 2410 mg kg^{-1}, respectively. These concentrations are considerably elevated above the background levels and can seriously impact the soils and waters of the surrounding areas through surface erosion caused by the elements. Mean concentrations of As, Cd, Cu, Pb and Zn in agricultural soils were 230, 2.5, 120, 160, and 164 mg kg^{-1}, respectively. Mean concentrations of As, Cd and Zn in stream waters used for drinking water in this area were 246 μg L^{-1}, 161 μg L^{-1} and 3899 μg L^{-1}, respectively. These levels are significantly higher than the permissible levels for drinking water quality criteria recommended by the government of Korea and the WHO.

The outcomes of the risk assessment showed that the toxic risk HI (hazard index) of As and Cd for the exposed individuals (adult farmers) in the affected area were significantly greater than one due primarily to exposure from drinking water that is drawn from the metal-contaminated stream. The cancer risk of As for the exposed individuals via the drinking water pathway exceeded the probability of one cancer case in ten thousand threshold set by regulatory purposes. Drinking water posts a significant human health risk to the inhabitants of the abandoned Songcheon mine area.

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