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Distribution of Trace Metals at Two Abandoned Mine Sites in Korea and Arsenic-Associated Health Risk for the Residents

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Abstract

Two abandoned mine sites in Jeongseon, Korea were investigated to determine the distribution of six trace metals such as Cu, Cr, Cd, Pb, Hg, and As in soil, water, and rice, and to assess the health risks for the residents of the mine sites from their exposure to As via possible exposure pathways. Lead and arsenic were found to be the major contaminants. Health risk assessments conducted on As through soil ingestion, water ingestion, rice ingestion, and dermal contact with soil or water showed high non-carcinogenic (HI values of 12.8 and 8.3) and carcinogenic (risks of 22.0 $\times 10^{-4}$ and 14.3 $\times 10^{-4}$) at both mine sites, suggesting that the residents have high chance of developing adverse health effects from their chronic exposures. The ingestion of polished rice grown in the contaminated paddy soils accounted for 90% or higher of the total risk values. Therefore, appropriate measures need to be taken to prevent possible health effects, in particular from the ingestion of crop plants grown in the contaminated soils.

Keywords: Abandoned mine site, Arsenic, Health risk, Rice, Trace metals

Introduction

Mining, milling, and smelting operations are typical sources of soil and water trace metal contaminants such as As, Cd, Zn, and Pb[1-3]. This is because smelting wastes known as tailings have usually been heaped on the neighboring soil surface without any proper measures to prevent their loss caused by wind or rain. These tailings commonly contain above residual metals, which have been reported to leach into nearby environmental media such as soil, surface water, and ground water over a long time[4,5].

Vegetables and grain crops grown in metal-contaminated soils have been found to contain high metal contents through the soil-to-plant transfer process[6-10]. Rice was contaminated with metals when it was raised in abandoned mine paddy soil irrigated with contaminated surface water, suggesting that dietary consumption of such contaminated food can be a significant residential exposure source of trace metals[2,11,12]. Since municipal drinking water is typically not supplied to the residents of abandoned mine areas, ground water is normally used as a drinking water supply, compounding their exposure to trace metals[2,4,5,13]. Residents near abandoned mine sites can be additionally exposed to trace metals by dermal contact with soil followed by percutaneous absorption. Moreover, when contaminated water is used for showering or bathing, dermal exposure can take place though metals, unlike small organic molecules, do not readily penetrate the skin[14].

Approximately 1,000 mine sites have been closed and abandoned in Korea, of which gold and silver mines account for more than 80%. Tailings and mine wastes in these sites have been inappropriately disposed of, becoming pollution sources of trace metals in vicinal soil and water. Some studies were conducted to assess human risk from exposure to trace metals and found that oral intake of rice, ground water, or soil could pose a potential health risk including cancer to the residents due to their exposure to As[2,5,11,13].

In this study, two abandoned mine sites located in Jeongseon, Gangwon-do were selected to assess the health risks of the residents from their exposure to trace metals, by measuring the concentrations of metals in soil, surface water, ground water, and polished rice samples.

Results and Discussion

Concentration Distributions of Trace Metals

Table 3 shows the descriptive summary of the concentrations of the six metals in the samples collected at the Dongmyung and Sewoo mine sites. The Cr, Cd, and Hg concentrations were found to be relatively low in most of the samples, with many of them below their respective MDLs. Exceptions were the concentrations of Cr (15.9-40.0 mg/kg) in the tailings samples at the Dongmyung site, as well as those of Cd (1.84 and 30.7 μg/L) in the surface water samples at the Sewoo site.

Table 1. Types and number of samples collected from each location at two mine sites.

Mine site	Sampling location	Sample type	
		Soil	Water
Dongmyung	D-1	Mountain, farmland	Surface
	D-2	Farmland*	Mine drainage
	D-3	Farmland, tailings*	Mine drainage
	D-4	Farmland	Surface
	D-5	Farmland	Surface, ground
	D-6	Paddy	Ground
Sewoo	S-1	Tailings	Surface
	S-2	Farmland	Surface, ground
	S-3	Farmland, paddy	Ground
	S-4	Farmland	Ground
	S-5	Tailings, paddy	_**

*Two composite samples were collected for this specimen. Otherwise, only a single composite sample per medium was collected from each location.

**No sample was collected.

The three other metals were determined to be above their respective MDLs in most of the samples. In particular, Pb and As were found to be the major constituents in the soil samples at both mine sites. The Pb concentrations in the soil samples ranged from 100 (paddy at Dongmyung) to 4,241 (paddy at Sewoo) mg/kg. Its concentrations were markedly high in both types of agricultural soils, particularly at the Sewoo mine site. The arsenic concentrations ranged from 330 to 3,634 mg/kg in the tailings samples, and from 274 to 757 mg/kg in the farmland and paddy soil samples for both mine sites. Such high soil levels of Pb and As suggested that these metals could be taken up by crops grown in the contaminated soils. Lim *et al.*[5] reported that the As concentrations in farmland soil at an abandoned mine site in Korea were between 7 and 626 mg/kg, with an average of 175 mg/kg, values that are approximately half of those from the two mine sites sampled in this study. In a study conducted for a mining area in Mexico[32], the concentrations of Pb and As in soil samples collected near a mining area were reported to be as high as 3,450 and 17,384 mg/kg, respectively, indicating that mining activities are an important pollution source of nearby soils.

In the present study, the results of water sample analyses indicated that both surface and ground waters as

Table 2. Exposure factors, reference doses, and slope factors used for risk assessment.

Factor	Abbreviation	Unit	Value	Reference
Exposure frequency	EF	day/yr	365	22
Exposure duration	ED	yr	30	22
Body weight	BW	kg	63	23
Averaging time	AT	yr	30	22
Lifetime	LT	yr	78.6	24
Ingestion rate	IR			
Soil	IR_s	kg/day	5.0×10^{-5}	22
Water (drinking)	IR_w	L/day	0.86	24
Rice (polished)	IR_r	kg/day	0.219	24
Skin surface area	SA			
Forearms/hands	SA_s	cm^2	1,845	24
Whole body	SA_w	cm^2	17,084	24
Adherence factor (soil)	ADF	kg/cm^2	4.4×10^{-7}	22
Absorption factor (As)	ABF	_*		
Ingestion of soil	ABF_{is}		0.25	29
Ingestion of rice	ABF_{ir}		0.89	30
Dermal contact with soil	ABF_{ds}		0.032	31
Skin permeability constant	PC	cm/hr	3×10^{-4}	25
Shower duration per day	ET	hr/day	0.29	24
Reference dose	RfD			
Oral	RfD_o	mg/kg/day	3.00×10^{-4}	17
Dermal	RfD_d	mg/kg/day	1.23×10^{-4}	20
Slope factor	SF			
Oral	SF_o	$(mg/kg/day)^{-1}$	1.50	17
Dermal	SF_d	$(mg/kg/day)^{-1}$	3.66	20

*Unitless

Table 3. Concentrations of six trace metals measured for soil, water, and rice samples collected at two mine sites.

Mine site	Medium (unit)	Sample type (*N*)	Cu	Cr	Cd	Pb	Hg	As
Dongmyung	Soil (mg/kg)	Tailings (3)	24.1-47.1 (33.7)*	15.9-40.0 (31.8)	<MDL-2.46 (0.85)	670-3,434 (1,716)	4.01-24.3 (11.3)	330-1,161 (635)
		Mountain (1)	14.9	24.2	<MDL (0.05)***	3,397	1.53	381
		Farmland (4)	15.0-31.8 (21.7)	<MDL-54.7 (17.3)	All<MDL (0.05)	201-1,251 (640)	1.54-4.05 (3.25)	274-353 (327)
		Paddy (1)	18.0	52.2	<MDL (0.05)	100	4.52	323
	Water (μg/L)	Drainage (2)	2.67-8.46 (5.57)	2.93 (2.93)	<MDL-0.75 (0.41)	44.9-47.3 (46.1)	0.13-1.40 (0.77)	7.74-10.6 (9.17)
		Surface (3)	6.44-12.6 (9.17)	<MDL-2.93 (2.19)	All<MDL (0.07)	17.1-37.4 (27.7)	<MDL-0.13 (0.06)	7.09-9.84 (8.09)
		Ground (3)	4.48-13.9 (8.61)	<MDL-2.93 (2.19)	All<MDL (0.07)	21.9-28.3 (26.2)	<MDL (0.03)	8.49-9.88 (9.41)
	Grain** (mg/kg)	Rice (1)	62.6	<MDL (3.40)	<MDL (0.23)	15.3	<MDL (0.15)	3.15
Sewoo	Soil (mg/kg)	Tailings (2)	44.1-84.5 (64.3)	<MDL-12.8 (6.75)	<MDL-39.6 (19.8)	446-2,379 (1,413)	6.01-20.3 (13.2)	2,745-3,634 (3,190)
		Farmland (3)	30.5-59.9 (46.0)	<MDL-23.5 (8.30)	All<MDL (0.05)	1,083-1,355 (1,242)	3.05-4.07 (3.54)	335-430 (395)
		Paddy (2)	27.2-41.8 (34.5)	<MDL-35.2 (18.0)	<MDL-1.15 (0.60)	1,351-4,241 (2,796)	3.02-8.51 (1.77)	679-757 (718)
	Water (μg/L)	Surface (2)	<MDL-2.66 (1.56)	2.93 (2.93)	1.84-30.7 (16.3)	6.05-9.53 (7.79)	<MDL (0.03)	9.24-25.3 (17.3)
		Ground (3)	2.24-9.83 (6.11)	2.93-6.61 (4.94)	All<MDL (0.07)	5.17-14.3 (9.04)	<MDL (0.03)	8.01-13.7 (11.6)
	Grain (mg/kg)	Rice (2)	61.4-66.5 (64.0)	14.2	All<MDL (0.23)	<MDL-1.49 (0.93)	All<MDL (0.15)	<MDL-3.15 (1.95)

*Minimum-maximum (average)

**Concentrations were expressed on a dry weight basis.

***Values below MDLs were assumed to be one half respective MDLs.

well as the mine drainage contained relatively high concentrations of Pb and As. The highest Pb concentrations were found in the mine drainage samples (44.9-47.3 μg/L) obtained from the Dongmyung site, followed by surface water (17.1-37.4 μg/L) and then ground water (21.9-28.3 μg/L). These values met the current Korean Drinking Water Standard (50 μg/L), but did not meet the action level of 15 μg/L in the EPA National Drinking Water Standards. The water Pb concentrations at the Sewoo mine site were all below 15 μg/L. The concentrations of As in the surface water were about two times higher at the Sewoo mine site than those at the Dongmyung site, ranging between 9.24 and 25.3 μg/L. These levels, however, were all below the Korean Drinking Water Standard for As (50 μg/L) but two ground water samples (13.1 and 13.7 μg/L) and one surface water sample (25.3 μg/L) at the Sewoo mine site exceeded the EPA Maximum Contaminant Level of 10 μg/L. A study conducted for the Songcheon mine site in Korea Lee *et al.*[2] showed very high levels of As and Cd in stream waters, 246 and 161 μg/L on average, respectively. By contrast, the Cu and Pb concentrations were as low as 3 and 1 μg/L, respectively. In a study[4] conducted for rural areas in Washington, USA, the concentrations of As and Pb in ground water were very high, ranging from <1 to 298 μg/L and from 10 to 94 μg/L, respectively. In a study conducted for a mining area in Mexico, Razo *et al.*[32] the concentrations of As in water storage pond samples were found to be much higher than those in this study, ranging between 5,894 and 7,165 μg/L.

Some metals such as Cu, Pb, and Pb were found to be accumulated in rice. The accumulation of Cu in the rice was noticeable, with concentrations of 61.4 to 66.5 mg/kg at both sites. These levels are approximately 15 times higher than the average background concentration of ~4 mg/kg for Asian countries such as Japan, Indonesia, China, Philippines, Taiwan, and

Table 4. ADD, HI, LADD, and risk values for As at two mine sites.

Exposure route	Dongmyung				Sewoo			
	ADD	HQ	LADD	Risk ($\times 10^{-4}$)	ADD	HQ	LADD	Risk ($\times 10^{-4}$)
Soil ingestion	6.2E-05	0.21	2.4E-05	0.36	7.5E-05	0.25	2.9E-05	0.43
Water ingestion	1.3E-04	0.42	4.8E-05	0.72	1.6E-04	0.52	5.9E-05	0.89
Rice ingestion	3.7E-03	12.2	1.4E-03	20.9	2.3E-03	7.5	8.6E-04	12.9
Dermal contact with soil	4.1E-06	0.033	1.5E-06	0.057	4.9E-06	0.040	1.9E-06	0.068
Dermal contact with water	2.2E-07	0.0018	8.5E-08	0.0022	2.7E-07	0.0022	1.0E-07	0.0038
		HI=12.8		Total=22.0		HI=8.3		Total=14.3

Bangladeshi[33]. The concentration of Pb in the rice at the Dongmyung mine site and that of Cr in the rice at the Sewoo site were found to be relatively high: 13.1 and 12.1 mg/kg, respectively. The As concentrations in the rice ranged from 0.64 to 2.68 mg/kg at both sites, which were slightly higher than those (0.35-0.76 mg/kg) from previous studies[11,34] measured at other mine sites in Korea. Li *et al.*[3] showed that soils near a lead/zinc mine were contaminated with trace metals, in particular Pb, and that the metals were transferred to plants grown in the soils in inverse proportion to plants' distance from the mine. In the present study, however, such a relationship was not found.

Health Risk Assessment for Residents

Non-carcinogenic and carcinogenic risk assessments were conducted for As and the results are shown in Table 4.

In the non-carcinogenic assessments at both mine sites, the ADDs and HQs were estimated for each exposure pathway, and then the hazard index (HI) for each site was calculated by summing the HQs for the five exposure pathways. At both mine sites, rice ingestion was found to be the major route of exposure to As. The HQs for the ingestion of As from rice consumption at the Dongmyung and Sewoo sites accounted for 95 and 90% of their respective HIs (12.2 vs. 12.8 at the Dongmyung and 7.0 vs. 7.8 at the Sewoo), respectively. Water ingestion was the second contributor to the HI followed by soil ingestion, though the HQs for both routes are less than 1 at both sites. Dermal absorption pathways from water and soil were negligible. Since the HIs exceed 1 at both mine sites, non-carcinogenic toxic effects are expected to occur to both mine residents.

The carcinogenic risk assessments showed that the risk values at both mine sites exceeded 1.0×10^{-4}, amounting to 22.0×10^{-4} for Dongmyung and 14.3×10^{-4} for Sewoo. Like the non-carcinogenic risk assessments, rice ingestion pathway had the highest contribution to total risks at the Dongmyung and Sewoo sites, with the risks from that route accounting for 95 and 90% of the total risks, respectively. However, the other two ingestion pathways were not negligible. Soil and water ingestion pathways at both sites brought about risk values greater than 1.0×10^{-5} (3.6×10^{-5} to 8.9×10^{-5}), while dermal contact with soil resulted in risk values greater than 1.0×10^{-6}. Dermal contact with water was a relatively minor pathway, with risk values less than 1.0×10^{-6} (0.22×10^{-6} for the Dongmyung and 0.38×10^{-6} for the Sewoo). The total cancer risks estimated for both sites suggest that the residents in these areas have a very high probability of developing cancers, particularly due to the consumption of polished rice grown in contaminated soil.

This health risk assessment on As was performed with several limitations such as a small sample size and lots of assumptions in exposure estimation. More detailed studies on metal speciation, bioaccessibility, and bioavailability are needed for reducing uncertainty in the risk assessment. However, the above results based on previous data obtained suggest high health risks for mine site residents due to their exposure some hazardous metals.

Lee *et al.*[34] showed that the HI values through four exposure pathways (soil ingestion, water ingestion, rice ingestion, and dermal contact with soil) at three abandoned mine sites in Korea ranged from 3.1 to 6.7, rice ingestion accounting for 97.3 to 99.4%. Similar results were obtained from a study for another abandoned mine site in Korea, where the non-carcinogenic effect was estimated at a HI of 15 and the carcinogenic risk was estimated at 27×10^{-4}, mainly from the ingestion of contaminated water, vegetables (e.g., red pepper, Chinese cabbage, and green onion) and grain (e.g., soybean) crops[4]. However, inorganic fractions of As in exposure media and bioavailability data via the ingestion route were not considered in the above studies.

In this study, the following conclusions could be drawn. At the two abandoned mine sites investigated, it was found that soils (farmland and paddy soils), waters (surface and ground), and rice grains were heavily contaminated with trace meals such as Cu, As, and Pb. Health risk assessments for As showed that resi-

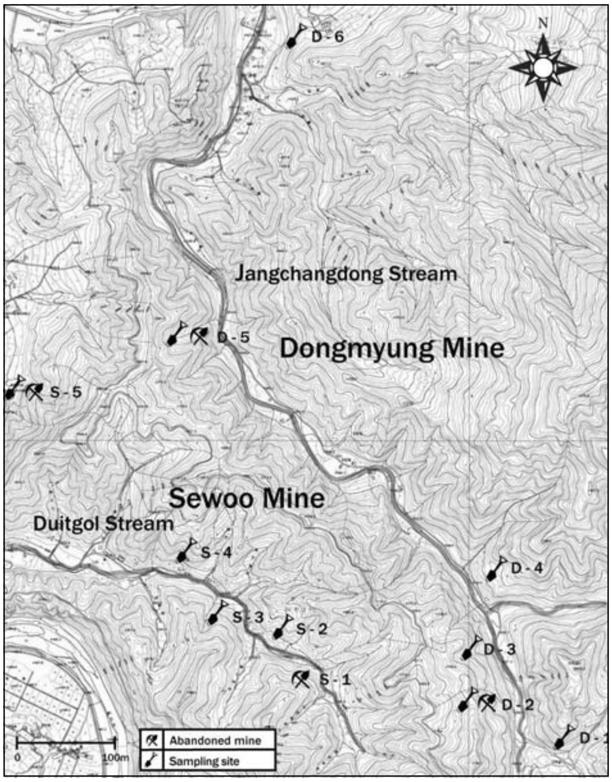

Figure 1. Map of study areas showing the location of the abandoned mines and sampling sites.

dents living near the two abandoned mine sites could have relatively high chance of developing carcinogenic toxic effects from their arsenic exposure through either ingestion of soil, water, and polished rice or dermal contact with soil. The most contributing exposure pathway was the oral ingestion of rice grown in the contaminated paddy soil. Therefore, appropriate measures should be taken to protect the inhabitants in the mine areas from high exposure to hazardous trace pollutants.

Methods

Study Sites

Two abandoned mine sites in Gangwon-do, Dongmyung and Sewoo mine sites, were selected for this study (Figure 1).

The Dongmyung mine site is located at Songgei-5-ri, Imgye-myeon, Jeongseon. The mine was opened in 1934 and closed in 1988. The products of the mine were Cu, Pb, and Zn in addition to Au and Ag. Since no measures had been taken to prevent the loss of tailings and mine wastes, stream water and adjacent agricultural soils were found to be highly contaminated with trace metals[15]. Soil near the mine site was used for agricultural purposes such as farm or paddy soil. Some vegetables such as potatoes, corns, Chinese cabbages, cabbages, and radishes were being cultivated in the soil during site visits, and farmland (D-1 to D-5) and paddy soils (D-6) were supplied with nearby stream water. Residents in this area were mostly provided with municipal water but some used ground water for drinking and household activities.

The Sewoo mine site is located at Nakcheon-2-ri, Imgye-myeon, Jeongseon. The same kinds of metals had been mined from 1934 to 1971. Like the Dongmyung mine site, mine wastes had been heaped around the mine area without proper measures to prevent their loss to near environmental media. Agricultural fields situated along the side of the stream as well as paddy fields (S-5) near the lower reaches of the stream were irrigated by stream water.

Sample Collection

Sampling at the two mine sites was conducted on November 14, 2006 and the sampling locations are shown on the map in Figure 1. The types of samples from each site are summarized in Table 1. Abandoned mines were located at D-2, D-5, S-1, and S-5 sites. All the sampling locations were situated within a distance of 1.5 km from the mineheads of two mine sites.

Soil samples were collected from six locations (D-1 to D-6) at the Dongmyung site, and from five locations (S-1 to S-5) at the Sewoo site. The soil samples were classified into four categories based on where they were collected: mountain, tailings, farmland, and paddy. Approximately 1 kg of composite soil samples were collected at a depth of approximately 15 cm below the ground surface at each site. Three types of water samples (mine drainage, surface, and ground) were collected in 2 L polyethylene bottles, into which concentrated nitric acid was added to adjust the acid concentrations to about 2%. One composite polished rice (*Oryza sativa*) sample was collected from a rice mill for the Dongmyung site and two from S-3 and S-5 at the Sewoo site.

Sample Preparation and Analyses

The soil samples were dried at room temperature for 2 days; particles less than 2 mm were used in trace metal analysis. One gram of dried and sieved soil was digested using concentrated nitric acid (65%) in a microwave system (EnviroPro Q 45, Questron Technology Inc.), according to the procedure previously reported[16]. Rice samples were washed with ultrapure water in the laboratory to eliminate airborne pollutants and soil particles. The water content was determined by drying at 70°C in a drying oven until a constant weight was achieved. The dried samples were ground using a ceramic-coated mortar. Approximately 0.2 g of each rice sample was then digested using 10 mL of concentrated nitric acid in a microwave system, after which the extract was diluted to 25 mL with ultrapure water.

The soil, water, and crop samples were analyzed for total concentrations of Cu, Cr, Cd, Pb, Hg, and As using an atomic absorption spectrometer (AAS, SpectraAA 400, Varian Inc.) in either the flame, graphite furnace, vapor generation (As), or cold vapor (Hg) mode. Metal speciation was not determined. The analytical reproducibility for each metal in each matrix was determined as the relative standard deviation (RSD, %) from seven replicate measurements, ranging from 2.8 to 7.1%. The average matrix spike recoveries ranged from 83.0 to 99.4%. The method detection limits (MDL) for six metals in soil, water, and rice samples were estimated based on the 7 replicate measurements. The MDLs for Cu, Cr, Cd, Pb, Hg, and As in soil samples were estimated at 0.90, 1.4, 0.091, 14.6, 0.17, and 65 mg/kg, respectively, while those in water samples were estimated at 0.89, 1.4, 0.13, 0.12, 0.060, and 0.31 μg/L, respectively. Those in rice samples were estimated at 4.5, 6.8, 0.46, 0.71, 0.30, and 1.5 mg/kg, respectively. In data analysis, the values below MDLs were assumed to be half the respective MDLs.

Risk Assessments

Among the six trace metals, risk assessments were conducted for As only. The reason is as follows. There is a great difference in the toxicity of Cr between its two oxidation states (III and VI), but only total Cr concentrations were measured in this study. The concentrations of Cd and Hg were below their respective MDLs in most of the samples. No risk assessment was conducted for Pb because it is difficult to identify the threshold value necessary to develop a reference dose (RfD) and no value has been suggested for its cancer slope factor (SF), even though Pb is classified as a probable human carcinogen by the USEPA. Long-term exposure to Cu can cause irritation of the nose, mouth, and eyes. Copper is not classifiable as to its human carcinogenicity (class D) by the USEPA due to inadequate data. Due to its low toxicity to humans, however, risk assessment on Cu was not conducted.

Exposure to inorganic As can cause irritation of the stomach and intestines, decreased production of red and white blood cells, skin changes, and lung irritation[17]. In addition, very high exposure to As can cause infertility and miscarriage in women[17]. It also can cause skin disturbances, declined resistance to infections, heart disruptions, and brain damage[17]. Arsenic is classified as a human carcinogen[18], and it is suggested that the uptake of significant amounts of inorganic As can increase the chances of developing skin, lung, liver, or bladder cancer[19].

The reference doses (RfDs) and cancer slope factors (SFs) used in the risk assessment are shown in Table 2. Only oral and dermal exposure pathways were considered because the inhalation data were not available in this study. The values were applied from either the Integrated Risk Information System (IRIS)[17] or the Risk Assessment Information System (RAIS)[20].

The average daily dose (ADD) or lifetime average daily dose (LADD) via each exposure route and medium was estimated in assessing either non-carcinogenic or carcinogenic health risk[21]. Only rice was considered in estimating oral ingestion exposure. The average concentrations of As in the farmland soil, ground water, or rice samples at the two mine sites were used in the exposure assessment. Inorganic As fractions in soil, water, and rice samples were assumed to account for 0.96[26], 0.98[27], and 0.44[28], respectively, based on the previous studies. The following equations were applied for exposure estimations.

For oral ingestion of soil, water, or rice:

$$\mathrm{ADD_{oral}\ or\ LADD_{oral}} = \frac{\mathrm{C \times IR \times ABF \times EF \times ED}}{\mathrm{BW \times AT(LT) \times 365}}.$$

For dermal contact with soil:

$$\mathrm{ADD_{derm\text{-}s}\ or\ LADD_{derm\text{-}s}} = \frac{\mathrm{C \times SA \times ADF \times ABF \times EF \times ED}}{\mathrm{BW \times AT(LT) \times 365}}.$$

For dermal contact with water while showering:

$$\mathrm{ADD_{derm\text{-}w}\ or\ LADD_{derm\text{-}w}} = \frac{\mathrm{C \times SA \times PC \times ET \times EF \times ED}}{\mathrm{BW \times AT(LT) \times 365}}.$$

Table 2 shows exposure factors and their values used in estimating the ADDs and LADDs. When exposure factors were available for the Korean people, they were used.

The non-carcinogenic and carcinogenic risks were estimated following the U.S. EPA guidelines[21]. The non-carcinogenic risks were assessed in terms of hazard quotients (HQs): $\mathrm{HQ} = \frac{\mathrm{ADD}}{\mathrm{RfD}}$. Two or more HQs for multiple exposure pathways were summed to obtain hazard indices (HIs) at both sites. In estimating the carcinogenic risks, the following equations were used: Cancer risk $=$ LADD $\times$ SF.

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References

1. Lee, Y. H. & Stuebing, R. B. Heavy metal contamination in the river toad, *Bufo juxtasper* (inger), near a copper mine in east Malaysia. *Bull Environ Contam Toxicol* **45**, 272-279 (1990).
2. Lee, J.-S., Chon, H.-T. & Kim, K.-W. Human risk assessment of As, Cd, Cu and Zn in the abandoned mine site. *Environ Geochem Health* **27**, 185-191 (2005).
3. Li, Y., Wang, Y.-B., Gou, X., Su, Y.-B. & Wang, G. Risk assessment of heavy metals in soils and vegetables around non-ferrous metals mining and smelting sites, Baiyin, China. *J Environ Sci* **18**, 1124-1134 (2006).
4. Peplow, D. & Edmonds, R. Health risk associated with contamination of groundwater by abandoned mines near Twisp in Okanogan County, Washington, USA. *Environ Geochem Health* **26**, 69-79 (2004).
5. Lim, H.-S., Lee, J.-S., Chon, H.-T. & Sager, M. Heavy metal contamination and health risk assessment in the vicinity of the abandoned Songcheon Au-Ag mine in Korea. *J Geochem Explor* **96**, 223-230 (2008).
6. Dowdy, R. H. & Larson, W. E. The availability of sludge-borne metals to various vegetable crops. *J Environ Qual* **4**, 278-282 (1995).
7. Guttormensen, G., Singh, B. R. & Jeng, A. S. Cadmium concentration in vegetable crops grown in a sandy soil as affected by Cd levels in fertilizer and soil. *Fert Res* **41**, 27-32 (1995).
8. Lăcătuţşu, R., Răuţă, C., Cârstea, S. & Ghelase, I. Soil-plant-man relationships in heavy metal polluted areas in Romania. *Appl Geochem* **11**, 105-107 (1996).
9. Wang, X., Shan, X., Zhang, S. & Wen, B. A model for evaluation of the phytoavailability of trace elements to vegetables under the field conditions. *Chemosphere* **55**, 811-822 (2004).
10. Cui, Y.-J. *et al.* Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China. *Environ Int* **30**, 785-791 (2004).
11. Lee, J.-S., Lee, S.-W., Chon, H.-T. & Kim, K.-W. Evaluation of human exposure to arsenic due to rice ingestion in the vicinity of abandoned Myungbong Au-Ag mine site, Korea. *J Geochem Explor* **96**, 231-235 (2008).
12. Sipter, E., Rózsa, E., Gruiz, K., Tátrai, E. & Morvai, V. Site-specific risk assessment in contaminated vegetable gardens. *Chemosphere* **71**, 1301-1307 (2008).
13. Lee, S.-W., Lee, B.-T., Kim, J.-Y., Kim, K.-W. & Lee, J.-S. Human risk assessment for heavy metals and As contamination in the abandoned metal areas, Korea. *Environ Monit Assess* **11**, 233-244 (2006).
14. Guy, R. H, Hostýnek, J. J., Hinz, R. S. & Lorence, C. R. in *Metals and the Skin*: *Topical Effects and Systemic Absorption* (Marcel Dekker, New York, 1999).
15. Kim, H. J. *et al.* Fraction and geoaccumulation assessment index of heavy metals in abandoned mines wastes. *J Kor Soc Soil Groundwat Environ* **10**, 75-80 (2005).
16. Kim, H., Kim, D.-J., Koo, J.-H., Park, J.-G. & Jang, Y.-C. Distribution and mobility of chromium, copper, and arsenic in soils collected near CCA-treated wood structures in Korea. *Sci Total Environ* **374**, 273-281 (2007).
17. Integrated Risk Information System (IRIS), http://cfpub.epa.gov/ncea/iris/index.cfm (1998).
18. United State Environmental Protection Agency. in *Guidelines for Carcinogen Risk Assessment* (U.S. EPA, Washington, D.C., 2005).
19. Eisler, R. Arsenic hazards to humans, plants, and animals from gold mining. *Rev Environ Contam Toxicol* **180**, 133-165 (2004).
20. Toxicity Profiles-Risk Assessment Guidance for Superfund, http: //rais.ornl.gov (2009).
21. United State Environmental Protection Agency. in *Guidelines for Exposure Assessment* (U.S. EPA, Washington, D.C., 1992).
22. United State Environmental Protection Agency. in *Exposure Factors Handbook* (U.S. EPA, Washington, D.C., 1997).
23. Korean Agency for Technology and Standards. In *Report on Korean Body Size Survey* (KATS, Seoul, 2004).
24. Jang, J. Y., Jo, S. N., Kim, S. Y., Kim, S. J. & Cheong, H. K. in *Korean Exposure Factors Handbook* (Ministry of Environment, Seoul, 2007).
25. United State Environmental Protection Agency. in *CalTOX*: *a Multimedia Total Exposure Model for Hazardous Waste Site* (U.S. EPA, Washington, D.C., 1996).
26. Chappell, J., Chiswell, B. & Olszowy, H. Speciation of arsenic in a contaminated soil by solvent extraction. *Talanta* **42**, 323-329 (1995).
27. Zheng, J., Hintelmann, H., Dimock, B. & Dzurko, M. S. Speciation of arsenic in water, sediment, and plants of the Moira watershed, Canada, using HPLC coupled to high resolution ICP-MS. *Anal Bioanal Chem* **377**, 14-24 (2003).
28. Schoof, R. A. *et al.* A market basket survey of inorganic arsenic in food. *Food Chemical Toxicol* **37**, 839-846 (1999).
29. United State Environmental Protection Agency. in *Preliminary Evaluation of the Non-dietary Hazards and Exposure to Children from Contact with Chromate Copper Arsenate* (*CCA*)*-treated Wood Playground Structures and CCA-contaminated Soil* (U.S. EPA, Washington, D.C., 2001).
30. Albert, L. *et al.* In vivo assessment of arsenic bioavailability in rice and its significance for human health risk assessment. *Environ Health Perspect* **114**, 1826-1831 (2006).
31. Wester, R. C., Maibach, H. I., Sedik, L., Melendres, J. & Wade, M. In vivo and in vitro percutaneous absorption and skin decontamination of arsenic from water and soil. *Toxicol Sci* **20**, 336-340 (1993).

32. Razo, I., Carrizales, L., Castro, J., Díaz-Barriga, F. & Monroy, M. Arsenic and heavy metal pollution of soil, water and sediments in a semi-arid climate mining area in Mexico. *Water Air Soil Pollut* **152**, 129-152 (2004).
33. Herawati, N., Rivai, I. F., Koyama, H., Suzuki, S. & Lee, Y. Copper in rice and in soils according to soil type in Japan, Indonesia, and China: A baseline study. *Bull Environ Contam Toxicol* **60**, 266-272 (1998).
34. Lee, J.-S., Kwon, H.-H., Shim, Y.-S. & Kim, T.-H. Risk assessment of heavy metals in the vicinity of the abandoned metal mine areas. *J Kor Soc Soil Grounwat Environ* **12**, 97-102 (2007).