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Variations in heavy metal contamination of stream water and groundwater affected by an abandoned lead–zinc mine in Korea

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Abstract

This study evaluated variations in heavy metal contamination of stream waters and groundwaters affected by an abandoned lead–zinc mine, where a rockfill dam for water storage will be built 11 km downstream. For these purposes, a total of 10 rounds of stream and groundwater samplings and subsequent chemical analyses were performed during 2002–2003. Results of an exploratory investigation of stream waters in 2000 indicated substantial contamination with heavy metals including zinc (Zn), iron (Fe) and arsenic (As) for at least 6 km downstream from the mine. Stream waters near the mine showed metal contamination as high as arsenic (As) 8,923 $\mu g\ L^{-1}$, copper (Cu) 616 $\mu g\ L^{-1}$, cadmium (Cd) 223 $\mu g\ L^{-1}$ and lead (Pb) 10,590 $\mu g\ L^{-1}$, which greatly exceeded the Korean stream water guidelines. Remediation focused on the mine tailing piles largely improved the stream water qualities. However, there have still been quality problems for the waters containing relatively high concentrations of As (6–174 $\mu g\ L^{-1}$), Cd (1–46 $\mu g\ L^{-1}$) and Pb (2–26 $\mu g\ L^{-1}$). Rainfall infiltration into the mine tailing piles resulted in an increase of heavy metals in the stream waters due to direct discharge of waste effluent, while dilution of the contaminated stream waters improved the water quality due to mixing with metal free rain waters. Levels of As, Cu and chromium (Cr) largely decreased after heavy rain but that of Pb was rather elevated. The stream waters were characterized by high concentrations of calcium (Ca) and sulfate (SO_4), which were derived from dissolution and leaching of carbonate and sulfide minerals. It was observed that the proportions of Ca and SO_4 increased while those of bicarbonate (HCO_3) and sodium and potassium (Na + K) decreased after a light rainfall event. Most interestingly, the reverse was generally detected for the groundwaters. The zinc, being the metal mined, was the most dominant heavy metal in the groundwaters (1758–10,550 $\mu g\ L^{-1}$) near the mine, which far exceeded the Korean standard of 1000 $\mu g\ L^{-1}$ for drinking water. The decreases in the heavy metals contents in the groundwaters associated with reduced rainfall were quite different from the increases observed for the stream waters, which is not clearly understood at this time and warrants further investigation.

Introduction

Instances of soil and groundwater contamination by heavy metals at abandoned metal mines are markedly increasing in Korea (Lee *et al.* 2004a,b). This drew the attention of the environmental community to undertake detailed site investigations and to identify remediation technologies for the mines. Especially, the abandoned mines located within and upstream of a dam construction site have become a public concern. There were a large number of metal mines (over 1500), scattered all over the country, most of which were abandoned because of the lack of ore (Lee *et al.*

2001a,b). These abandoned and non-remediated or not properly treated mines including tailings and gob piles impose a heavy burden on the local government and relevant environmental authorities.

Many excellent studies of heavy metal contamination derived from mining activities have been undertaken for soils, plants, surface waters and stream sediments in Korea (Jung & Thornton 1996; Jung 2001; Lee *et al.* 2001a; Jung *et al.* 2002; Kim *et al.* 2002). However, studies of heavy metal or trace metal concentrations of both groundwaters and stream waters are scarce in Korea (e.g., Lee *et al.* 2001b; Kim & Chon 2001). Thus, a detailed monitoring of heavy metals in both waters would enhance understanding of the state of the overall water contamination in the metal mine areas.

The objectives of this study are (1) to investigate the extent and degree of toxic metal contamination and chemical compositions of both the stream waters and groundwaters and (2) to examine variations in heavy metal contamination of both waters sampled from the area affected by mining activities. The results of this study will provide a basis for appraisal of the environmental costs of remediating the contaminated stream waters and groundwater system.

Geologic, topographic and hydrogeologic settings

The study area, including an abandoned lead–zinc mine, is located in the southeastern part of Korea (Figure 1a). The mine was operated from 1964 to 1972. The mineralogy, classified as a hydrothermal replacement type, contains sphalerite, galena and chalcopyrite with a small amount of arsenopyrite and pyrite. There are no reliable data about the amount of concentrated ore produced. The mine was set in an area of mountainous geomorphology, with rounded rolling hills and narrow valleys that form a dendritic type drainage network.

The closure of the mining activity left about 23,000 tons of waste rocks and tailings. During the period of 1998–1999, to tackle potential environmental problems from the mining wastes, the provincial authority undertook remediation strategies including installation of drainage ditches, surface plant cover, containment/barrier wall and subsequent reclamation mainly focused on the mining dump (Figure 1c). However, the mining wastes had been dispersed downslope by surface runoff mainly during heavy rainfall, wind action and draining effluent, which caused contamination of paddy fields, stream sediments and stream waters. The nearest residential area is located within 1 km downstream of the mine portal. The area of flatland within the valley-bottom is irrigated from nearby stream waters and/or groundwaters. For domestic consumption or commercial sale, cattle are grazed on the surrounding hillsides and the irrigated flatland (paddy fields) is farmed intensively for rice and vegetables.

The study area is an area of relatively high topographic relief, underlain by the Gyeongsang sedimentary formation and the geology in and around the mine is greatly influenced by Cretaceous igneous activity. The sedimentary formation is mainly composed of sandstone, shale, and conglomerate, which were metamorphosed by the igneous rocks. The igneous rocks are Cretaceous quartz porphyry, rhyolite, intermediate dykes and granites. In the stream and lowlands, alluvial and colluvial deposits overlay unconformably the bedrocks.

The main streams and creeks run from northeast to southwest (Figure 1b). A large number of branch streams converge to the main stream. Although the study area is sparsely populated mainly along the streams, there are not a few private and public groundwater wells for drinking and/or living currently in use because there are no service pipes in the area. Most of the groundwater wells are situated in the immediate vicinity of the streams. The depths of the groundwater wells vary from 3 to 270 m and the elevation of the water table closely follows the land surface topography. Mean annual precipitation in this area during 1966–1999 is 1020 mm, which is slightly lower than the mean value of 1270 mm for the whole country. Sixty-four percent of the total precipitation occurs in the wet season (June–September), which is characteristic of monsoon weather in eastern Asia (Lee & Lee 2000). Annual air temperature for past 10 years averages 11.2 °C.

A rockfill dam with a storage volume of $48.7 \times 10^6\ \mathrm{m}^3$ for flow control and public water supply will be built on an area about 11 km downstream of the mine dump site (see Figure 1b), which is located within 6 km upstream from the

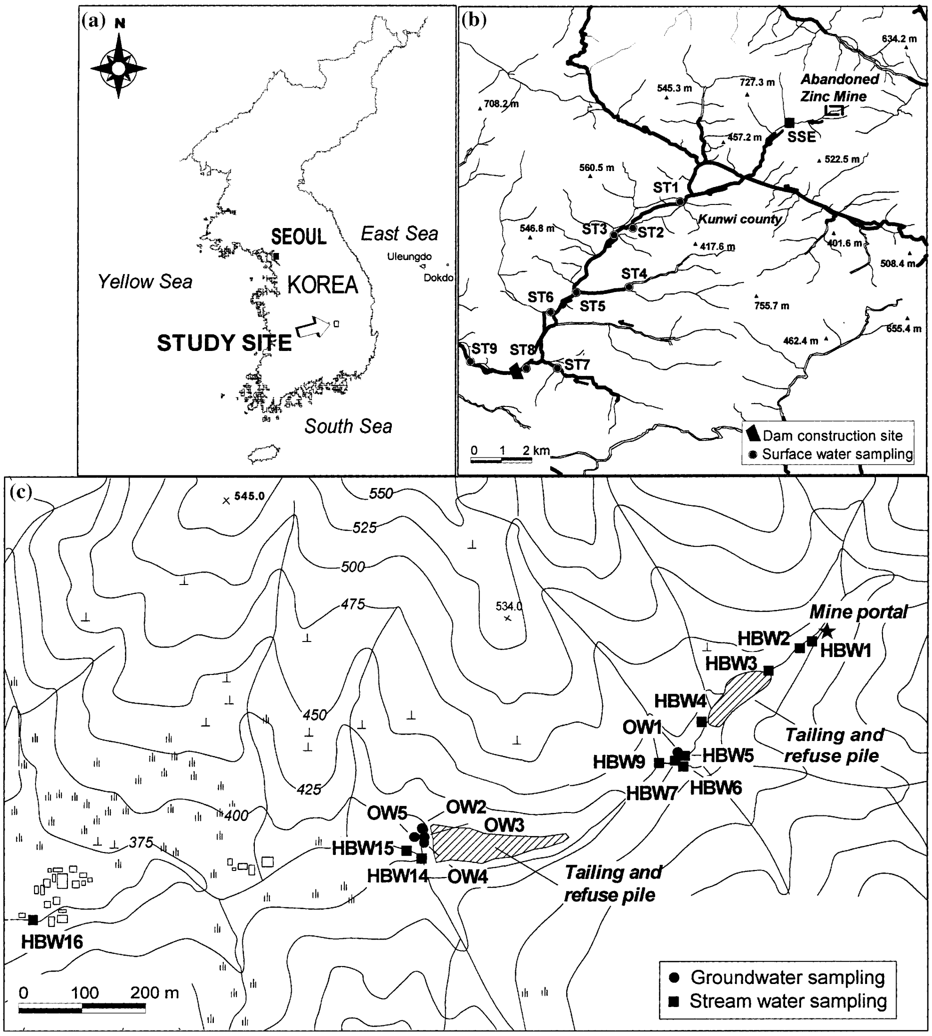

Fig. 1. Locations of the study site and the water sampling locations. The abandoned Pb–Zn mine location is also shown. *Arrows* indicate general flow direction. The bottom figure illustrates layout of the groundwater and stream water sampling points nearby the mine portal. The locations of the reclamated and the non-remediated mining refuse piles are also shown.

uppermost edges of the planned area submersed by the dam construction. Concerns about the potential harmful effect of the abandoned mine on the storage water of the planned dam initiated a comprehensive environmental study including soil, sediment, stream water and groundwater.

The mine portal is located in the mountainous valley (see Figure 1c). The topographic levels range between 400 and 500 m above mean sea level. There is a mining waste dump (tailing/refuse piles) with a volume of 5,000 m^3, which is 500 m downstream from the mine portal where mine effluent discharge still occurs with a rate of 5–10 m^3 day^{-1}. In spite of the remediation efforts undertaken during 1998–1999, some amounts of untreated mining wastes still were piled up in the vicinity of the mine portal and furthermore, some parts of the reclamation area were damaged.

Stratigraphic units underlying the mine area include Cretaceous sedimentary rock intruded by Cretaceous granite, and covered by colluvial soil and/or a local reclamation layer. The surface soil is observed at depths ranging from 0 to 2 m below the ground surface. The weathered rock ranging between 2.5 and 4 m below ground surface has secondary permeability features and is hydraulically connected to the colluvial deposits and/or reclamation layer. The weathered zone is underlain by the soft rock. This unweathered zone extends from 4 to 19 m below the ground surface. A moderate number of fractures with random orientations are observed at depths from 4 to 15 m in this unit, but are not uniformly distributed. Below the soft rock, the hard rock exists. This relatively impervious (not completely) layer serves as a lower confining bed for the upper aquifer. The water levels of the groundwaters at the site occur at an average depth of 5.27 m below the surface.

Methods and materials

Exploratory surface water samples were collected from nine locations within 6 km upstream to 2 km downstream areas of the planned dam construction site (see sampling locations in Figure 1b) in May, July, September and November of 2000 (MOCT & KOWACO 2002). The sampling was intended to investigate overall quality of the surface waters around the dam construction site and to examine the extent of potential heavy metal contamination derived from the abandoned mine. In each sampling round, field parameters, major ions, and heavy or trace metals were analyzed in Kyongbook water analysis branch of Korea Water Resources Corporation according to the Water Quality Conservation Act of Korea.

To closely examine the quality of the stream waters and its seasonal variations immediately around the abandoned metal mine, eight rounds of stream water samplings in May, July, August of 2002 and January, February, July, August of 2003 were conducted (see sampling locations in Figure 1c). In addition, two rounds of groundwater samplings in the vicinity of the mine were also performed in July and August of 2003. Prior to the samplings, water temperature, pH, oxidation–reduction potential (ORP), dissolved oxygen (DO) and electrical conductivity (EC) were measured in the field using standard probes. The stream water samples were filtered through a 0.45 μm filter, collected in polypropylene bottles and those destined for cation analysis were preserved with ultra-pure HNO_3 to $pH < 2$.

For the groundwaters, at least three well volumes of water were purged before sampling, using a low-rate submersible pump attached to a polyethylene (PE) hose, which was connected to a closed flow-through cell (see sampling locations in Figure 1c). Prior to water sampling for laboratory analysis, the temperature, pH, redox potential (ORP), EC and DO were also measured with standard probes in the cell. Samples were collected only when the values stabilized. Water samples for the laboratory analysis were collected directly from the unbroken water stream. Samples for multi-element analysis were syringe-filtered at 0.45 μm and preserved using ultra-pure HNO_3 in 125 mL HDPE bottles. Samples for laboratory analysis of anions were collected in 60 mL HDPE bottles through a 0.45 μm syringe filter. All samples were stored at 4 °C until analysis. At least 10% of the samples were spiked and duplicated.

Ionic constituents (NO_3^-–N, NO_2^-–N, NH_4^+–N, PO_4^{3-}, SO_4^{2-}, F^-, Cl^- and Br^-) were analyzed by ion chromatography (IC, DX-120, DIONEX), and other constituents (Al, Fe, K, Ca, Mn, Si, Mg, Na, Cr, Fe, Cu, Zn, As, Cd and Pb) were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS, Ultramass 700, Varian), atomic absorption (AA, 5100PC, Perkin Elmer) and ICP (ICP-IIIS, Shimadzu) following USEPA standard methods. Bicarbonate (HCO_3^-) concentration was determined by the titration method.

Results and discussion

Surface water quality

The overall quality of the surface waters down and upstream of the planned dam construction site was slightly worse than the Korean guidelines for first grade surface water according to (Surface) Water Quality Conservation Act (Table 1). The water temperature showed a wide range of variation from 4.4 to 24.4 °C, which reflected a seasonal change in atmospheric air temperature. In this country, four seasons are very distinct with air temperatures reaching high in summer (June–August) and very low in winter (Late November–February). The pHs were slightly alkaline or alkaline ranging from 7.2 to 9.4. Some values of pHs were greater than regulation guidelines (6.5–8.5). Interestingly, in most of the sampling locations (6 out of 9), the pHs slightly decreased from May to November. This appeared to be related to low surface water flow (discharge) in the dry season. The high DO concentrations (7.2–

Table 1. Summary of physico-chemical parameters for surface waters.

Parameters	Date	ST1	ST2	ST3	ST4	ST5	ST6	ST7	ST8	ST9	Ref[a]
Temperature (°C)	25 May 2000	16.8	18.2	17.0	16.5	15.3	16.5	16.0	17.0	15.8	–
	31 July 2000	23.2	23.8	23.7	24.3	24.4	23.6	23.0	21.2	22.7	
	21 September 2000	17.6	16.9	18.0	17.7	18.5	19.1	17.7	19.7	18.8	
	22 November 2000	4.4	5.0	7.5	6.2	12.0	12.3	6.6	13.8	8.5	
pH	25 May 2000	8.7	7.9	8.7	8.7	8.0	7.4	9.4	7.5	8.0	6.5—8.5
	31 July 2000	8.2	8.0	7.9	7.9	7.4	7.6	7.9	7.2	7.6	
	21 September 2000	7.9	7.9	7.6	7.6	7.6	7.6	7.7	7.3	7.5	
	22 November 2000	7.8	8.1	7.9	7.9	7.6	7.7	8.0	7.7	7.6	
DO (mg L^{-1})	25 May 2000	7.8	7.4	8.6	8.3	8.8	8.0	9.0	8.1	8.4	>7.5
	31 July 2000	8.0	8.1	8.2	7.5	7.6	7.9	7.6	7.2	8.1	
	21 September 2000	9.3	9.5	9.8	9.4	9.2	9.0	9.3	8.8	8.9	
	22 November 2000	13.5	13.2	11.8	12.0	11.0	10.0	14.7	11.3	11.8	
BOD (mg L^{-1})	25 May 2000	0.7	0.9	1.2	1.1	0.6	0.2	1.5	0.6	0.5	<1
	31 July 2000	0.9	0.8	0.5	0.4	1.1	0.5	1.8	0.8	0.1	
	21 September 2000	1.1	1.5	1.4	1.5	1.3	1.1	0.9	0.8	1.1	
	22 November 2000	0.9	1.6	1.1	0.9	0.8	0.4	1.1	0.5	0.1	
COD (mg L^{-1})	25 May 2000	3.2	3.4	2.5	3.2	2.1	1.2	3.4	1.3	1.7	–
	31 July 2000	2.8	3.0	2.4	3.4	1.9	1.8	4.2	1.2	1.3	
	21 September 2000	2.5	2.6	2.8	2.1	2.4	2.0	1.9	1.6	2.0	
	22 November 2000	1.4	2.5	1.6	0.9	1.2	0.6	1.5	0.6	0.2	
Turbidity (NTU)	25 May 2000	3.0	3.1	3.6	3.4	5.6	5.8	4.3	2.1	2.5	–
	31 July 2000	0.6	0.3	0.2	0.3	0.4	0.4	0.8	0.5	0.3	
	21 September 2000	0.2	0.4	0.3	0.2	0.1	0.2	0.2	0.2	0.2	
	22 November 2000	0.2	0.7	0.2	0.4	6.6	0.7	0.8	0.5	0.2	
Suspended solid (mg L^{-1})	25 May 2000	2.3	2.0	4.8	3.3	6.3	1.9	2.7	0.8	1.5	<25
	31 July 2000	0.7	0.8	0.7	0.1	0.1	0.2	0.8	0.7	0.1	
	21 September 2000	0.8	1.1	0.7	0.1	0.1	0.1	0.2	0.1	0.1	
	22 November 2000	0.1	0.1	0.1	0.1	4.0	0.1	0.1	0.3	0.1	
Hardness (mg L^{-1})	25 May 2000	84.4	59.0	60.6	38.8	57.1	48.0	48.7	49.7	43.3	–
	31 July 2000	84.5	88.0	87.2	38.3	75.0	72.6	36.4	79.4	84.0	
	21 September 2000	76.0	36.1	65.7	23.5	62.2	48.3	29.0	47.7	47.3	
	22 November 2000	65.7	53.6	60.2	33.0	54.8	54.0	30.1	47.2	43.1	
Alkalinity (mg L^{-1})	25 May 2000	57.1	51.1	36.8	33.9	33.7	31.0	31.9	25.8	24.0	–
	31 July 2000	40.7	41.0	40.5	26.9	35.8	33.3	24.3	32.6	31.6	
	21 September 2000	35.5	34.7	34.5	27.3	29.9	30.5	29.5	32.4	32.7	
	22 November 2000	36.5	38.1	38.1	18.4	30.5	28.5	57.7	26.0	24.2	

Table 1. Continued.

Parameters	Date	ST1	ST2	ST3	ST4	ST5	ST6	ST7	ST8	ST9	Ref[a]
Chlorophyll-a (mg m^{-3})	25 May 2000	2.0	0.9	2.5	1.9	1.7	0.1	0.7	0.4	0.2	–
	31 July 2000	1.1	1.4	0.8	0.2	0.5	0.6	1.0	0.3	0.6	
	21 September 2000	0.1	0.2	0.4	0.3	0.1	0.1	0.1	0.1	0.1	
	22 November 2000	1.2	0.6	0.2	0.1	0.2	0.0	1.6	2.7	0.2	

[a] Korean guidelines for first grade surface water according to (Surface) Water Quality Conservation Act.

14.7 mg L^{-1}) indicated the aerobic conditions of the waters. The higher concentrations of DO in the winter season (November in this study) indicated increased solubility of air into the surface water due to lowered air temperature (Hem 1992). The three field measured parameters (i.e., temperature, pH and DO) showed no discernible trend along the main stream flow direction.

Low levels of both biological oxygen demand (BOD) and chemical oxygen demand (COD) indicated a deficiency of organic matter in these surface waters and no significant organic contamination. But some of the BODs were greater than guideline value of 1.0 mg L^{-1} for first grade surface water. Higher values of turbidity in May were associated with turbulent water flow due to heavy rain occurring immediately before the sampling event. Elevated levels of the suspended solids also reflected the same effect in May. Hardness (23.5–88.0 mg L^{-1}) mostly characterized by calcium and magnesium, ranged from soft (0–60 mg L^{-1}) to moderately hard (61–120 mg L^{-1}) (Hem 1992). Alkalinities were relatively low compared with those of petroleum-contaminated groundwaters (Lee *et al.* 2001c,d). Low levels of chlorophyll-a indicated a low activity of plant plankton. In addition, nitrogen and phosphorous, critical factors in the eutrophication of water bodies, were low, which indicated a deficiency of nutrients for aquatic organisms (Table 2). The most dominant components of the surface waters were HCO_3^-, SO_4^{2-} and Ca^{2+}. High values in SO_4^{2-} and Ca^{2+} at ST1 may be a result of the dissolution of sulfide and carbonate minerals in the mining wastes and the bedrocks (Aykol *et al.* 2003; Gemici & Oyman 2003).

Among heavy metals, Zn appeared consistently in surface water during all the sampling period (Table 3). Relatively high concentrations of Zn at remote locations (ST5–ST9) appeared to be associated with mine tailing materials transported downstream from the metal mine. According to Lee *et al.* (2003), paddy soils were severely contaminated with toxic metals for at least 12 km downstream along the main stream from the abandoned metal mine. The detected As concentrations ranged from 6 to 57 μg L^{-1} with the highest concentration at ST1, which is most proximal to the mine. Arsenic occurred at all the main surface waters (ST1, ST3, ST5, ST6, ST8, ST9) while it was not detected at tributary surface waters (ST2, ST4, ST7). This indicated that the arsenic was mainly derived from the metal mine along the main stream flow. Meanwhile, the Korean guideline for As in surface water is 50 μg L^{-1}. In these surface waters, Cd, Pb, Hg and Cr were not detected. Based on these contaminant occurrences, it was inferred that substantial contamination of the surface water with toxic metals was restricted to the area upstream of ST1 although surface waters and paddy soils at greater distances were also contaminated with trace concentrations.

Stream waters nearby the abandoned mine

As previously mentioned, during the period of 1998–1999, the provincial authority initiated remediation strategies including installation of drainage ditch, surface plant cover, containment/barrier wall and subsequent reclamation mainly focused on the mining waste dump (see the refuse piles in Figure 1c). Table 4 shows the qualities of stream waters nearby the mine portal a few months before the remediation action for the refuse pile. The pHs of the waters were acidic, and were not within the regulation ranges of 6.5–8.5. Some concentrations of heavy metals were observed in the effluent of mine water (HBW1). Most interestingly, however, a dramatic increase in heavy metal concentrations at HBW4

Table 2. Summary of chemical analysis results for surface waters.

Ions	Date	ST1	ST2	ST3	ST4	ST5	ST6	ST7	ST8	ST9
T-P[a] (mg L^{-1})	25 May 2000	0.043	0.072	0.021	0.017	0.016	0.016	0.022	0.020	0.005
	31 July 2000	0.066	0.047	0.034	0.014	0.027	0.025	0.069	0.027	0.015
	21 September 2000	0.053	0.038	0.045	0.013	0.028	0.023	0.032	0.023	0.018
	22 November 2000	0.018	0.008	0.013	0.004	0.028	0.013	0.011	0.022	0.017
PO_4–P (mg L^{-1})	25 May 2000	0.038	0.067	0.010	0.016	0.011	0.014	0.015	0.016	0.004
	31 July 2000	0.060	0.042	0.031	0.012	0.024	0.022	0.063	0.025	0.014
	21 September 2000	0.037	0.030	0.034	0.007	0.026	0.025	0.031	0.021	0.018
	22 November 2000	0.010	0.001	0.008	0.002	0.024	0.012	0.003	0.013	0.004
T–N[b] (mg L^{-1})	25 May 2000	2.73	1.69	3.08	0.55	3.51	2.50	2.41	4.27	3.29
	31 July 2000	7.61	7.68	7.31	2.61	7.48	6.00	3.42	6.90	6.51
	21 September 2000	4.76	1.90	4.65	1.44	3.96	3.98	2.34	4.08	3.91
	22 November 2000	3.01	2.22	3.17	2.45	2.77	2.46	2.28	2.83	2.75
NH_4–N (mg L^{-1})	25 May 2000	0.03	0.02	0.03	0.02	nd	nd	0.05	0.01	0.04
	31 July 2000	0.01	0.02	0.02	0.03	0.02	0.02	0.01	0.02	0.01
	21 September 2000	nd[c]	nd	0.01	nd	0.01	nd	0.02	0.02	nd
	22 November 2000	nd	nd	nd	nd	0.01	nd	nd	0.01	nd
NO_2–N (mg L^{-1})	25 May 2000	0.016	0.008	0.004	0.002	0.003	0.000	0.009	0.000	0.011
	31 July 2000	0.010	0.008	0.010	0.002	0.003	0.004	0.010	0.003	0.008
	21 September 2000	0.003	0.002	0.002	0.000	0.002	0.001	0.002	0.001	0.002
	22 November 2000	0.003	0.003	0.002	0.001	0.007	0.002	0.004	0.002	0.004
NO_3–N (mg L^{-1})	25 May 2000	1.75	0.91	1.81	0.36	1.74	1.83	1.24	3.12	2.51
	31 July 2000	3.63	4.64	5.10	0.72	4.24	4.45	1.11	5.07	4.36
	21 September 2000	4.60	1.80	4.57	0.91	3.56	3.51	2.01	3.49	3.45
	22 November 2000	2.88	1.50	2.48	1.90	2.54	2.29	1.69	2.52	2.46
SO_4^{2-} (mg L^{-1})	25 May 2000	28.4	11.5	19.3	9.3	16.8	16.6	14.3	14.9	14.5
	31 July 2000	23.4	21.8	20.9	9.6	19.1	18.9	9.3	17.5	15.9
	21 September 2000	17.3	8.6	16.0	6.6	13.3	13.0	8.3	12.9	12.4
	22 November 2000	27.2	10.0	19.8	11.2	20.7	16.8	8.7	16.1	14.4
Cl^- (mg L^{-1})	25 May 2000	7.3	4.7	5.6	3.4	4.9	5.0	5.5	4.9	5.0
	31 July 2000	5.7	6.4	6.6	2.6	5.8	5.9	3.4	5.8	5.5
	21 September 2000	4.4	1.8	4.5	1.5	3.6	3.6	2.7	3.2	3.5
	22 November 2000	6.7	5.1	6.7	4.8	7.7	5.9	4.2	5.9	5.0
Ca^{2+} (mg L^{-1})	25 May 2000	24.13	15.59	14.50	9.59	13.70	11.95	11.16	11.87	10.99
	31 July 2000	21.57	22.65	22.90	9.13	19.72	18.83	8.96	18.89	17.64
	21 September 2000	17.35	11.87	14.45	7.47	12.30	11.78	7.15	24.24	10.17

Table 2. Continued.

Ions	Date	ST1	ST2	ST3	ST4	ST5	ST6	ST7	ST8	ST9
	22 November 2000	18.03	22.01	17.42	8.26	14.07	15.81	9.91	11.87	11.44
Mg^{2+} (mg L^{-1})	25 May 2000	5.14	3.78	3.76	2.23	2.66	3.17	2.75	3.11	2.87
	31 July 2000	5.32	5.75	5.81	1.97	5.64	4.82	2.49	4.91	4.57
	21 September 2000	4.15	2.72	3.71	1.55	3.13	3.03	1.77	3.99	2.81
	22 November 2000	4.70	4.70	4.38	1.97	3.87	3.73	2.57	3.06	2.96

[a] Total phosphorous.
[b] Total nitrogen.
[c] Not detected.

was detected together with depressed pH. The HBW4 was located immediately downstream of the non-remediated tailing and refuse pile. This indicated that the high concentrations of the heavy metals at HBW4 were directly derived from the metal-bearing sulfide minerals in the waste pile. At this location, the heavy metals in the stream waters exceeded the Korean guideline values by factors of 178, 22 and 106 for As, Cd and Pb, respectively.

Table 3. Trace metals[a] for surface waters.

Metals	Date	ST1	ST2	ST3	ST4	ST5	ST6	ST7	ST8	ST9
Zn (μg L^{-1})	25 May 2000	3	11	3	2	110	72	4	24	6
	31 July 2000	9	5	4	22	10	15	4	23	10
	21 September 2000	9	3	4	2	3	5	4	5	4
	22 November 2000	24	9	7	9	21	15	15	13	4
Cu (μg L^{-1})	25 May 2000	nd[b]	9	nd	nd	nd	nd	nd	nd	nd
	31 July 2000	nd	nd	nd	nd	nd	nd	nd	nd	nd
	21 September 2000	8	nd	nd	nd	8	nd	8	8	14
	22 November 2000	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fe (μg L^{-1})	25 May 2000	60	nd	nd	nd	nd	nd	nd	nd	nd
	31 July 2000	50	nd	nd	nd	nd	nd	nd	nd	nd
	21 September 2000	nd	50	nd	nd	nd	50	50	60	50
	22 November 2000	nd	nd	nd	nd	150	nd	50	nd	nd
Mn (μg L^{-1})	25 May 2000	nd	nd	15	nd	nd	nd	nd	nd	nd
	31 July 2000	nd	nd	nd	3	nd	nd	nd	nd	nd
	21 September 2000	nd	nd	nd	nd	nd	nd	nd	11	nd
	22 November 2000	nd	nd	nd	nd	34	nd	nd	nd	nd
As (μg L^{-1})	25 May 2000	57	nd	17	nd	16	10	nd	13	13
	31 July 2000	31	nd	16	nd	14	12	nd	9	10
	21 September 2000	8	nd	8	nd	7	7	nd	6	10
	22 November 2000	23	nd	15	nd	11	10	nd	9	9

[a] Cd, Pb, Hg and Cr were not detected.
[b] Not detected.

Table 4. Water quality for stream waters prior to waste remediation action during December 1998–August 1999 (KOWACO 2003).

Parameters	HBW1	HBW2	HBW4	Ref[a]
PH	6.4	6.7	6.1	6.5-8.5
As (μ g L^{-1})	18	11	8923	50
Cu (μ g L^{-1})	nd[b]	nd	616	na[c]
Cd (μ g L^{-1})	5	nd	223	10
Pb (μ g L^{-1})	120	nd	10590	100

[a] Guideline values regulated by relevant laws in Korea.
[b] Not detected.
[c] Not available.

Table 5 shows qualities for stream waters nearby the metal mine after the rock waste pile remediation during 1998–1999. Comparing pHs and heavy metal concentrations prior to the remediation with those after the waste treatment, it was concluded that the stream water qualities were largely improved. Except for HBW4, pHs of HBW1 and HBW3 changed from acidic to neutral or slightly alkaline, which may be derived from partial filling of calcite into the mine portal. However, stream waters at HBW4 were still acidic. Levels of arsenic at HBW1 steadily and slowly decreased from 18 to 11 μg L^{-1} for the monitoring period. At HBW4, arsenic concentrations dramatically decreased after the remediation (see Tables 4 and 5). However, they appeared to have rebounded, reaching 174 μg L^{-1} in January 2003 and 99 μg L^{-1} in February, which was much greater than the stream water guideline of 50 μg L^{-1} for As. The increase in arsenic concentrations may be due to the surface erosion and damage by reclamated vegetation on the refuse pile from heavy rain storms during the last summer. Unlike arsenic, cadmium (Cd) concentrations at the three sampling locations steadily decreased and reached below detection limit level. Lead concentrations also dramatically decreased compared with those prior to the remediation. But the concentration of Pb also again slightly increased starting in 2003. Concentrations of Hg and Cr were mostly below detection limits throughout the monitoring period. Although the remediation action for 1998–1999 largely improved the stream water quality, there have still been some quality problems for the waters, resulting from the reemergence of heavy metal concentrations.

Variation of metal concentrations measured on 10 July 2002 along the main stream flow direction is presented in Figure 2. Concentrations of Zn, As and Cd decreased from mine water (HBW1) to HBW3 mainly due to mixing with waters of low metal abundance. However, at HBW4 (immediately downstream from the gob pile), their concentrations (especially As and Zn) again greatly increased. But beyond that location, they steadily decreased. For Cd, its concentration reached non-detect level at about 1.3 km away (HBW16) from the mine portal. Most interestingly, arsenic concentrations rather increased beyond the HBW4. The levels of As at HBW4, HBW16 and SSE (1.8 km away from the mine portal, Figure 1b) were much higher than that of mine water by factors of 3, 2.7 and 4.9, respectively. The increase of As at downstream locations was generally unexpected. This may be caused by further leaching of As from waste tailings transported downstream by storm waters prior to the remediation. As previously mentioned, the paddy soils and stream sediments were extensively contaminated with these mining wastes for at least 12 km from the mine portal along the main stream, which meant the paddy fields received contaminated sediments during flooding (Miller *et al.* in press). The zinc concentrations were much higher, ranging from 397 to 3879 μg L^{-1}. The highest concentration was observed in the mine water (HBW1). Although zinc is not regulated by the (Stream) Water Quality Conservation Act of the country for the present, excess Zn concentration is still considered toxic to plant and human health (Calderon 2000; Watt *et al.* 2000).

Effects of rainfall on the quality of stream waters

Effects of rainfall on stream water quality (mainly heavy metal concentrations) were investigated for both wet and dry seasons. For the wet season, heavy metal concentrations measured at 150 m downstream (HBW3) from the mine portal are

Table 5. Water quality for stream waters after rock waste pile reclamation.

Parameters	Date	HBW1	HBW3	HBW4	Ref[a]
pH	30 May 2002	7.5	7.1	6.7	6.5-8.5
	10 July 2002	7.6	7.0	7.1	
	26 July 2002	na[b]	7.3	na	
	12 August. 2002	na	7.4	na	
	21 January 2003	na	na	6.3	
	28 February. 2003	7.6	na	6.6	
As (μg L^{-1})	30 May 2002	18	11	8	50
	10 July 2002	15	11	45	
	26 July 2002	na	24	na	
	12 August. 2002	na	6	na	
	21 January 2003	na	na	174	
	28 February. 2003	11	na	99	
Cd (μg L^{-1})	30 May 2002	44	17	70	10
	10 July 2002	46	10	17	
	26 July 2002	na	8	na	
	12 August. 2002	na	1	na	
	21 January 2003	na	na	nd	
	28 February. 2003	nd[c]	na	nd	
Pb (μg L^{-1})	30 May 2002	nd	nd	nd	100
	10 July 2002	na	nd	nd	
	26 July 2002	na	2	na	
	12 August. 2002	na	5	na	
	21 January 2003	na	na	na	
	28 February. 2003	18	na	26	
Hg (μg L^{-1})	30 May 2002	nd	nd	nd	0
	10 July 2002	nd	nd	nd	
	26 July 2002	na	3	na	
	12 August. 2002	na	nd	na	
	21 January 2003	na	na	na	
	28 February. 2003	na	na	na	
Cr (μg L^{-1})	30 May 2002	nd	nd	nd	50
	10 July 2002	nd	nd	nd	
	26 July 2002	na	2	na	
	12 August. 2002	na	1	na	
	21 January 2003	na	na	nd	
	28 February. 2003	nd	na	nd	

[a] Guideline values regulated by relevant laws in Korea.

[b] Not available.

[c] Not detected.

presented in Figure 3(a). There was no rain for the sampling on 26 July 2002 while there were heavy rains during the sampling on 12 August 2002 (Figure 3b). When the rainfall occurred, it would affect stream water quality in two ways. First, the infiltration of rainwater into the refuse pile and subsequent leaching of soluble metals from the waste is likely to aggravate stream water quality. In contrast, dilution of contaminated stream water thorough direct mixing with metal-free rain waters would improve water quality. For this site, concentrations of As, Cu, Cd and Cr decreased after

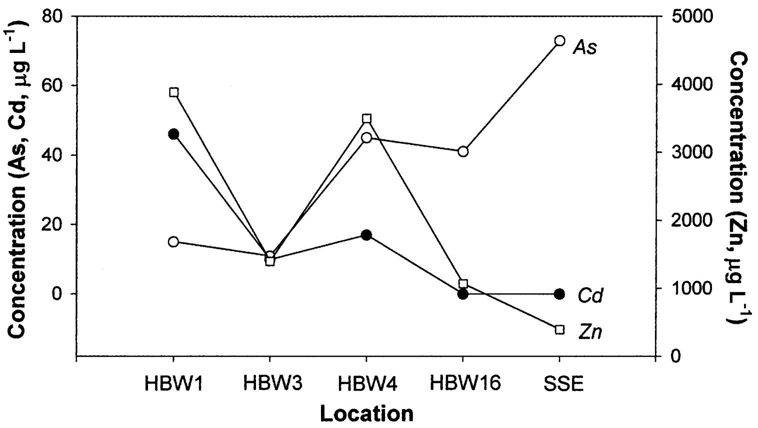

Fig. 2. Concentrations of heavy metals, As, Cd and Zn in the stream waters near the metal mine (10 July 2002).

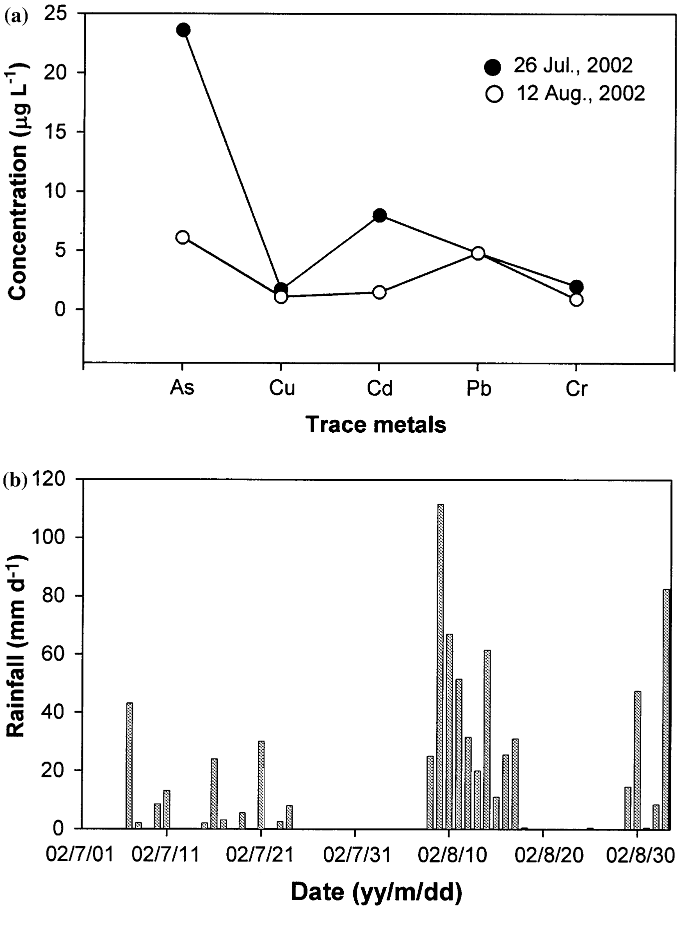

Fig. 3. Variations of heavy metal concentrations in the stream waters collected at HBW3 on 26 July and 12 August of 2002 and rainfall occurring for the sampling period.

heavy rain by factors of 3.9, 1.5, 5.3 and 2.2, respectively. Concentrations of lead, however, were rather elevated.

Levels of heavy metals at HBW4 measured on 21 January and 28 February of 2003 (dry season) and rainfall for the same period are presented in Figure 4(a) and (b), respectively. Stream flow increased by a factor of 20 on 28 February compared with that measured on 21 January. Although As concentration decreased by about a half after rainfall, the total mass of As discharged increased ten-fold. However, Pb concentrations rather increased after rain. This phenomenon was exactly the same for the wet season (see Figure 3a). The reason for this is not exactly known for the present. Concentrations of Cd and Cu were still low (not detected) for both before and after rainfall.

Overall chemical compositions and heavy metals of stream waters nearby the mine

To examine chemical composition and heavy metal concentrations of stream waters near the mine, two more samplings and field measurements were performed in July and August of 2003. The redox potential (ORP), EC and DO were measured in the field and major anions and cations including heavy metals were analyzed in the laboratory. Prior to the sampling on 15 July 2003, 232.5 mm of rainfall occurred from 9 July to 13 July while before the sampling on 13 August, rainfall amounted to 13.5 mm from 8 August to 11 August (Figure 5). Consequently, the stream flow rate was greatly reduced in August compared with that in July.

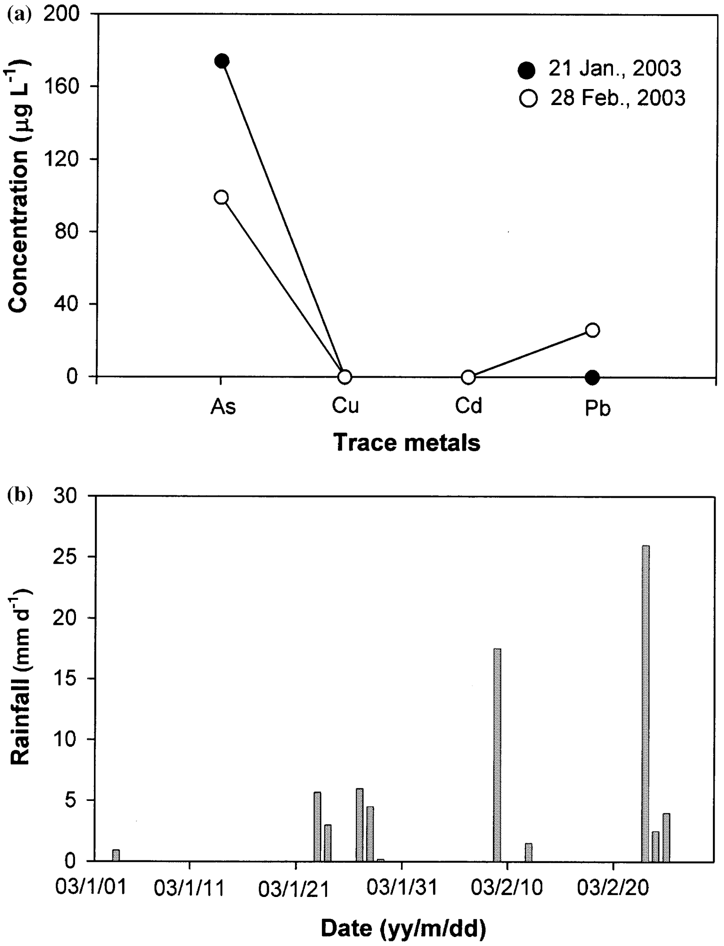

Fig. 4. Changes in heavy metal concentrations of the stream waters collected at HBW3 on 21 January and February of 2003 and rainfall occurring for the sampling period.

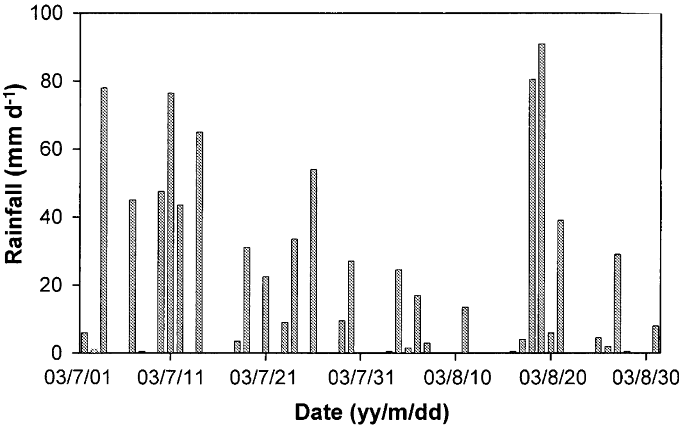

Fig. 5. Rainfall occurred from 1 July to 30 August of 2003. Stream and groundwater samplings were performed on 15 July and 13 August.

Qualities for the stream waters near the mine are presented in Table 6. The pHs were nearly neutral, ranging from 6.8 to 7.2 and from 6.5 to 7.1 with means of 7.1 and 6.9 for both sampling events, respectively. Paired *t*-test indicated a slight decrease in the pH values at $p = 0.05$ level during the sampling interval. Water temperatures slightly increased from July to August, which was consistent with the increase in atmospheric air temperature during the summer season. All the positive values of redox potentials (92–177 mV) and high values of DO (3.6–6.3 mg L^{-1}) indicated aerobic conditions of the stream water environments. The EC of the stream waters were relatively low even though the highest value was observed at HBW1. Interestingly, the EC values at all the measurement locations except for HBW1, increased by 13–79 μS cm^{-1}, which was mostly associated with the increases in concentrations of Ca, Mg, HCO_3 and SO_4 (Table 7). The four constituents account for 99% of the variance of EC. The high abundances of the Ca, Mg and SO_4 ions appeared to be derived from dissolution and leaching of carbonate and sulfide minerals in the exposed rock tailing materials, respectively (Lee *et al.* 2001b) and increases in their concentrations during the period appeared to be related to relatively low stream flow due to reduced rainfall in the period. Interestingly, the proportion of the variance of the EC explained by the constituents was generally low for 13 August 2003. The reduced proportion of the variance appeared to be explained by the increases in contents of other constituents, including heavy metals.

When comparing total concentrations, SO_4 was generally the most abundant ion, followed by HCO_3, Si, Ca, Na, Cl, Mg and K. The Si and Cl were replaced by Ca and Mg, respectively, for the August sampling. Concentrations of NH_4–N, NO_3–N and Br were nearly below the detection limits. A piper diagram of the stream water chemistry is presented in Figure 6. A relatively wide distribution of water types was observed in the plot although Ca–SO_4 type was most dominant, which is typical of mine drainage waters. For cations, Ca and Na were more abundant but Mg was less abundant. For anions, SO_4 and HCO_3 were more abundant but Cl was less abundant. Comparing water compositions of both sampling events, it was generally observed that proportions of Ca and SO_4 contents increased while those of HCO_3 and Na + K decreased in August. It meant an upward movement of the data points on the Piper plot (see Figure 6). The increase in the relative proportions of Ca and SO_4 appeared to be due to reduced rainfall water directly entering the stream, which also meant that heavy metals were less diluted or relatively more enriched.

Heavy metal concentrations in the stream waters are also shown in Table 6. The Zn was the most abundant heavy metal because this was the metal mined and its maximum concentration was 3298 μg L^{-1} in July 2003. Concentrations of Al dramatically decreased during the sampling interval. Copper and lead were below the detection limits for the two sampling rounds. Although it was expected that the low rainfall would enrich heavy metal concentrations in stream waters, the

Table 6. Qualities for stream waters near the mine collected at 15 July and 13 August of 2003.

Parameters	HBW1	HBW2	HBW3	HBW4	HBW5	HBW6	HBW7	HBW9	HBW14	HBW15	HBW16
pH	6.9 [a]; 6.8[b]	6.9; 6.5	7.0; 6.7	6.8; 6.9	7.2; 6.9	7.1; 6.9	6.9; 7.0	7.2; 7.1	7.3; 7.0	7.2; 7.0	7.2; 7.1
Temperature (°C)	11.3; 10.7	14.6; 16.7	14.8; 17.4	15.8; 19.0	16.5; 18.9	15.9; 17.0	15.6; 17.8	16.3; 18.8	17.2; 19.9	16.0; 17.8	18.1; 20.5
ORP (mV)[c]	176; 143	140; 130	153; 136	167; 126	146; 112	142; 153	159; 168	154; 99	177; 92	134; 104	167; 144
DO (mg L^{-1})	6.2; 6.3	5.7; 5.2	6.2; 5.0	4.8; 4.7	5.6; 5.1	5.9; 5.5	6.1; 4.7	4.9; 4.8	5.4; 5.2	4.9; 3.6	5.7; 4.4
EC (µs cm^{-1})	346; 339	36; 56	46; 99	53; 102	52; 104	47; 60	46; 77	45; 73	69; 148	182; 259	79; 143
Ca (mg L^{-1})	15.1; 18.7	2.4; 2.8	3.5; 6.3	2.9; 6.4	2.8; 6.2	1.8; 3.0	2.4; 6.3	2.1; 2.3	4.7; 10.6	3.3; 7.5	5.3; 9.5
Mg (mg L^{-1})	7.7; 7.0	0.9; 1.1	1.0; 1.9	1.0; 2.0	0.9; 2.0	0.7; 1.1	0.9; 2.1	1.0; 1.8	1.4; 2.7	2.8; 3.9	1.6; 2.9
Na (mg L^{-1})	6.4; 5.5	3.4; 3.9	3.5; 4.2	3.8; 4.3	3.0; 4.3	3.1; 4.0	3.4; 4.3	5.2; 6.4	3.7; 4.7	4.4; 4.9	3.9; 5.0
K (mg L^{-1})	1.1; 1.1	0.4; 0.4	0.4; 0.5	0.5; 0.5	0.4; 0.5	0.4; 0.3	0.4; 0.5	0.3; 0.5	0.4; 0.6	1.1; 1.1	0.7; 1.3
Si (mg L^{-1})	4.8; 3.9	6.7; 6.4	6.7; 7.2	6.9; 6.7	6.7; 6.7	6.7; 7.1	6.4; 6.2	10.6; 10.0	6.8; 6.3	7.0; 6.7	7.0; 6.6
NH_4–N (mg L^{-1})	< 0.1; < 0.1	< 0.1; < 0.1	< 0.1; nd[d]	nd; < 0.1	nd; < 0.1	nd; < 0.1	nd; nd	nd; < 0.1	nd; < 0.1	nd; nd	nd; nd
NO_3—N (mg L^{-1})	0.2; 0.2	< 0.1; 0.1	< 0.1; 0.1	nd; 0.1	< 0.1; 0.1	0.2; 0.3	0.1; 0.1	nd; 0.1	0.1; 0.1	nd; 0.1	0.7; 0.6
HCO_3 (mg L^{-1})	59.9; 48.8	7.0; 12.2	12.2; 19.5	9.8; 19.5	9.8; 17.1	8.9; 12.2	10.2; 17.1	9.8; 24.4	12.2; 22.0	24.4; 36.6	9.8; 19.5
Br (mg L^{-1})	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd
Cl (mg L^{-1})	2.0; 2.4	2.1; 2.2	2.3; 2.1	2.2; 2.3	2.3; 2.1	2.4; 2.2	2.0; 2.3	2.4; 3.2	2.1; 2.2	2.0; 2.3	2.1; 2.2
SO_4 (mg L^{-1})	125.1; 122.2	8.0; 9.2	13.0; 23.2	10.0; 23.4	10.1; 22.2	6.3; 10.3	8.2; 22.4	6.2; 4.3	17.3; 40.3	64.2; 81.3	19.1; 34.2
Al (µg L^{-1})	nd; nd	450; 250	410; 140	600; 70	700; 40	390; 30	570; 20	1870; 150	380; nd	90; nd	480; nd
Cr (µg L^{-1})	21; 22	72; 32	31; 23	33; 21	52; 21	34; 22	62; 21	72; 21	44; 22	31; 23	52; 21
Mn (µg L^{-1})	275; 28	nd; nd	7; 6	5; nd	5; nd	nd; nd	nd; nd	5; nd	19; 71	635; 934	17; nd
Fe (µg L^{-1})	52; 100	161; 103	144; 72	212; nd	241; nd	122; nd	181; nd	615; 151	121; nd	63; 52	164; 22
Cu (µg L^{-1})	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd
Zn (µg L^{-1})	2982; 3298	362; 450	403; 819	390; 789	416; 757	134; 154	227; 712	5; 7	397; 899	470; 630	244; 253
As (µg L^{-1})	9; 23	nd; 6	nd; 7	6; 9	8; 15	nd; nd	5; 16	nd; nd	7; 32	93; 109	15; 38
Cd (µg L^{-1})	36; 41	3; 4	4; 8	3; 8	4; 7	nd; 2	2; 7	nd; nd	3; 5	4; 4	2; 2
Pb (µg L^{-1})	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd	nd; nd

[a] Value for 15 July 2003.

[b] Value for 13 August 2003.

[c] Oxidation-reduction potential.

[d] Not detected.

measured change in each heavy metal content showed quite a different behavior. The levels of Al and Cr decreased while those of Zn, As, and Cd increased during the sampling interval. The changes in the levels of Mn and Fe were not consistent. It was naturally expected that heavy metal levels were relatively higher at HBW1 (immediately adjacent to the mine portal). But the level of Al at HBW1 was lowest (below detection limit) although that at downstream locations was very high. The highest levels of Al were observed at HBW9 and HBW2 for July and August samplings, respectively. The concentration of Fe increased only at the mine portal (HBW1). The general decreases of Fe and Mn contents may be partly explained by preferential re-precipitation forming metal oxides (Kim & Chon 2001; Kelly *et al.* 2003). The very different behaviors or changes of the heavy metals resulting from reduced rainfall appeared to be related to some different physical or geochemical reactions of each metal, which can not be readily explained for the present.

Variations of the heavy-metal concentrations along the stream flow direction are presented in Figure 7. The levels of Zn and Cd were the highest at the mine portal (HBW1), and they markedly decreased downstream. However, Mn and As concentrations showed somewhat different behaviors. The highest levels of Mn and As were observed at HBW15 (765 m downstream from the mine portal) although relatively high concentrations of them were still present at HBW1. The highest concentrations of the heavy metals at HBW15 were appeared to be derived

Table 7. Linear regression coefficient (r^2) among physical and chemical parameters.

	pH	Temperature	ORP	DO	EC	Ca	Mg	Na	K	Si	HCO_3	Cl	SO_4
pH	-	0.40[a]; 0.22[b]	0.01; 0.04	0.07; 0.19	0.02; 0.01	0.04; 0.00	0.04; 0.01	0.01; 0.29	0.00; 0.12	0.17; 0.11	0.04; 0.02	0.05; 0.16	0.02; 0.00
Temperature		–	0.01; 0.12	0.20; 0.43	0.47; 0.35	0.47; 0.31	0.55; 0.46	0.34; 0.02	0.18; 0.03	0.25; 0.36	0.61; 0.41	0.07; 0.00	0.49; 0.44
ORP			–	0.02; 0.07	0.09; 0.01	0.34; 0.01	0.15; 0.00	0.16; 0.15	0.01; 0.00	0.05; 0.15	0.12; 0.03	0.08; 0.10	0.07; 0.00
DO				–	0.03; 0.01	0.14; 0.15	0.07; 0.08	0.01; 0.00	0.00; 0.06	0.37; 0.18	0.07; 0.02	0.02; 0.00	0.04; 0.04
EC					–	**0.82**; **0.74**	**0.97**; **0.93**	0.65; 0.16	0.79; 0.60	0.25; 0.39	**0.97**; **0.90**	0.28; 0.00	**0.99**; **0.98**
Ca						–	**0.91**; **0.85**	0.59; 0.08	0.47; 0.46	0.31; 0.60	**0.87**; **0.61**	0.22; 0.03	**0.80**; **0.78**
Mg							–	0.70; 0.22	0.66; 0.55	0.26; 0.43	**0.98**; **0.90**	0.25; 0.00	**0.96**; **0.94**
Na								–	0.39; 0.19	0.00; 0.09	0.68; 0.36	0.08; 0.71	0.64; 0.10
K									–	0.21; 0.16	0.63; 0.45	0.40; 0.00	0.79; 0.52
Si										–	0.26; 0.19	0.32; 0.38	0.26; 0.49
HCO_3											–	0.22; 0.06	**0.96**; **0.87**
Cl												–	0.30; 0.01
SO_4													–

Higher values (>0.6) are in bold.

[a] Value for 15 July 2003.

[b] Value for 13 August 2003.

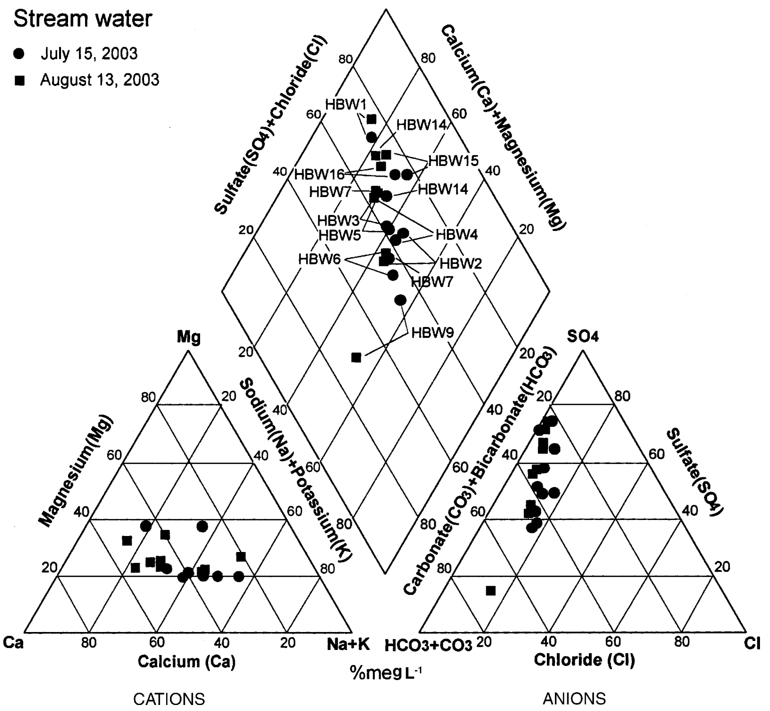

Fig. 6. Piper diagram for the stream waters near the mine collected on 15 July and 12 August of 2003.

from the upper mining waste pile. In spite of the remediation measures during 1998–1999, mining effluents have still occurred from the refuse pile. As previously mentioned, the vegetation cover on the pile was partially damaged and the infiltrated rain water would make more acidic drainage having heavy metals. After the HBW15, the concentrations again largely decreased. The different behavior of the heavy metals (Zn, Cd and Mn, As) along the stream flow is not clearly explained at this time. Most interestingly, the concentrations of most of the heavy metals increased after reduced rainfall (13 August 2003) compared to those on 15 July 2003. Consequently, it was inferred that the reduced rainfall resulting in decreased stream flow aggravated water qualities. The magnitude of these effects appeared to be larger than that of dilution or mixing effects due to metal-free rain waters entering directly into the stream waters. Stream water qualities were mostly aggravated when stream flows were at their low levels in this case like Miller *et al.* (in press). This was quite consistent with the results obtained in July and August of 2002 (see "Effects of rainfall on quality of stream water" section 4.3).

Overall chemical compositions and heavy metals of groundwaters nearby the mine

Qualities of the groundwaters near the mine are shown in Table 8. The pHs were slightly acidic or near neutral (6.4–7.1). The pH values slightly increased in August compared to those in July. Water temperature, ranging from 12.8–22.7 °C, also increased during the summer season mainly due to the increase in air temperature. The positive values of ORP and high DO concentrations indicated the aerobic conditions of the groundwaters. Amounts of dissolved solids of the groundwater were much greater than those of stream waters at the same site. The EC ranged from 116 to 648 $\mu s\ cm^{-1}$ and higher values were observed at OW2 and OW3 wells. The OW1 well most proximal to the mine portal showed the smallest EC value.

Relative ionic abundance in the groundwaters at the mine area showed the trend: $SO_4^{2-} > HCO_3^- > Cl^- > NO_3^- > Br^-$ for the anions and $Ca^{2+} > Mg^{2+} > Na^+ > K^+ > NH_4^+$ for the cations. However, the relative ionic abundances for the OW1 well were: $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^- > Br^-$ for the anions and $Ca^{2+} > Na^+ > Mg^{2+} > K^+ > NH_4^+$ for the cations. Chemical compositions of the

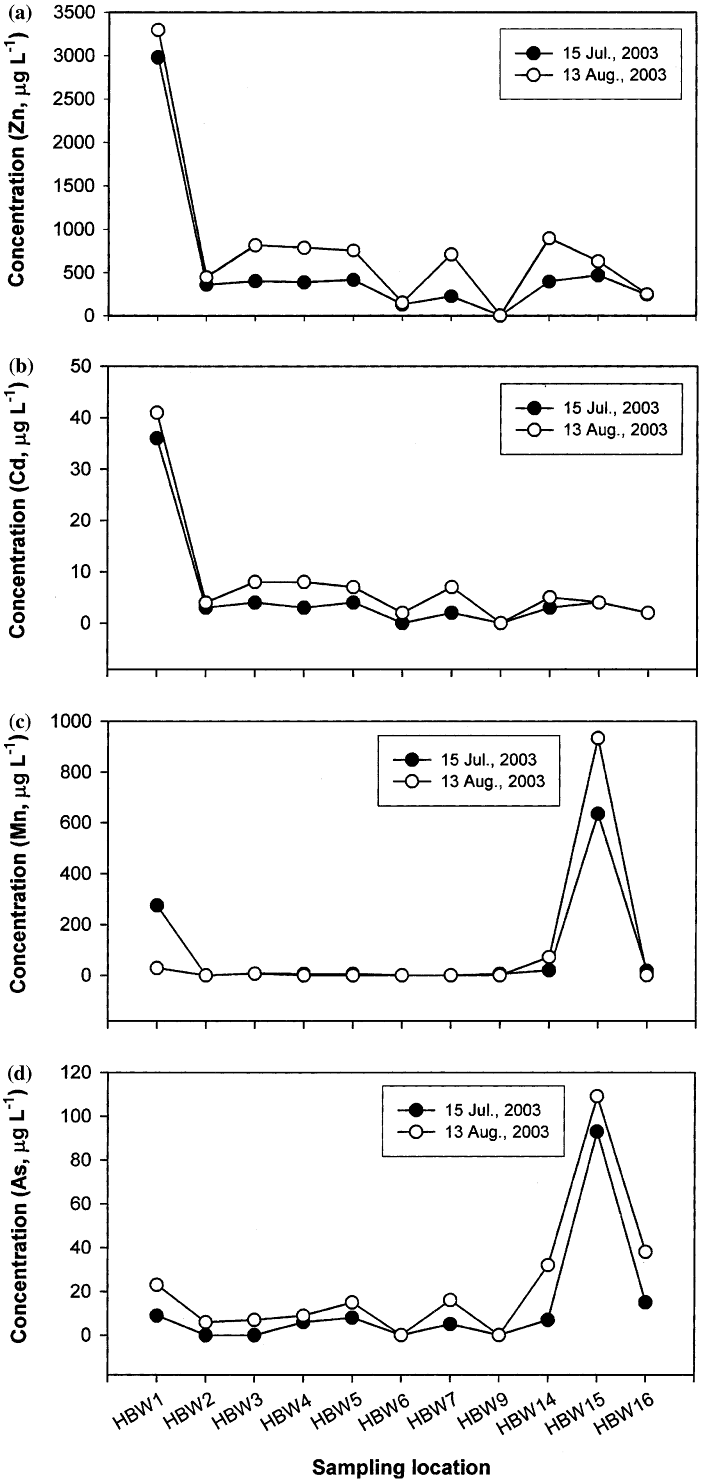

Fig. 7. Changes in heavy metal contents along the flow direction of the main stream.

Table 8. Water quality for groundwaters near the mine collected on 15 July and 13 August of 2003.

Parameters	OW1		OW2		OW3		OW4		OW5		Ref[a]
	July	August	July	August	July	August	July	August	July	August	
pH	6.9	7.0	6.8	6.9	6.9	7.1	6.8	7.0	6.4	6.8	5.8–8.5
Temperature (°C)	14.9	22.7	13.6	13.6	12.8	13.8	14.5	16.3	15.1	15.9	–
ORP (mV)[c]	179	110	212	230	41	46	87	83	250	225	–
DO (mg L^{-1})	3.2	3.6	4.9	4.9	4.4	4.6	2.4	2.3	4.1	3.5	–
EC (μs cm^{-1})	116	128	448	573	648	548	380	434	370	398	–
Ca (mg L^{-1})	5.5	5.2	55.9	27.8	86.9	51.6	22.7	30.1	43.7	31.3	–
Mg (mg L^{-1})	2.4	2.3	13.6	18.3	20.9	16.6	6.7	6.6	7.8	8.5	–
Na (mg L^{-1})	5.1	4.4	8.4	9.5	9.6	8.4	5.3	5.4	5.3	5.5	–
K (mg L^{-1})	0.8	0.7	1.5	1.5	1.8	1.4	2.4	2.4	2.1	2.4	–
Si (mg L^{-1})	2.2	5.0	9.8	59.8	12.3	11.3	8.0	9.9	12.7	14.3	–
NH_4–N (mg L^{-1})	0.8	< 0.1	nd[c]	< 0.1	nd	< 0.1	nd	< 0.1	< 0.1	nd	0.5
NO_3–N (mg L^{-1})	0.1	0.1	0.2	0.3	0.3	0.2	nd	0.1	nd	0.1	10
HCO_3 (mg L^{-1})	22.0	34.2	26.8	34.2	61.0	58.6	51.2	70.8	9.8	36.6	–
Br (mg L^{-1})	nd	nd	nd	nd	< 0.1	nd	nd	nd	nd	nd	–
Cl (mg L^{-1})	4.3	3.0	4.3	4.2	4.1	3.3	3.0	2.3	2.1	3.2	250
SO_4 (mg L^{-1})	17.1	16.2	262.4	306.3	382.5	271.1	146.4	169.3	207.2	176.1	200
Al (μg L^{-1})	20	nd	nd	nd	nd	nd	nd	nd	nd	nd	200
Cr (μg L^{-1})	50	20	22	21	23	22	24	21	41	24	50
Mn (μg L^{-1})	19	25	963	902	1310	839	490	3421	897	331	300
Fe (μg L^{-1})	nd	nd	81	132	133	142	61	103	53	nd	300
Cu (μg L^{-1})	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1000
Zn (μg L^{-1})	2617	10550	2313	1468	3660	1758	7522	3880	3374	1763	1000
As (μg L^{-1})	nd	nd	nd	7	187	148	16	51	nd	15	50
Cd (μg L^{-1})	nd	nd	12	8	4	2	nd	nd	21	9	5
Pb (μg L^{-1})	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	50

[a] Drinking water standards of Korea.
[b] Oxidation–reduction potential.
[c] Not detected.

groundwaters of the four wells, excepting for OW1, were much similar. The piper diagram of the groundwater chemical compositions revealed that the waters were dominantly Ca–SO_4 type (Figure 8). Only OW1 well showed quite a different water type. Comparison of water compositions for the July and August sampling rounds gave the most interesting result. It was generally observed that proportions of Ca and SO_4 decreased while those of HCO_3 and Na + K increased in August (see Figure 8). It meant a downward movement of the data points on the plot. This behavior is completely opposite to that of the stream water, which was also reflected in the changes of concentrations of the heavy metals.

Trace concentrations of Al were observed only at OW1 well (see Table 8). Concentrations of Cr ranged from 21 to 50 μg L^{-1} with a mean of 27 μg L^{-1}. Levels of Cr did not exceed the Korean guideline of 50 μg L^{-1} Cr for drinking water. Mn was the second dominant heavy metal in the groundwaters. It ranged from 19 to 3421 μg L^{-1} with a mean of 920 μg L^{-1}. Contents of Mn much exceeded the Korean drinking water standard of 300 μg L^{-1} by up to 3000 μg L^{-1}. Excess contents of trace elements were known to be toxic to plant and human health (Calderon 2000; Watt *et al.* 2000; Jarup, 2002; Álvarez *et al.* 2003). The level of Mn at OW1 well only was below the standard. Iron was not observed at OW1 well while some levels between 53 and 142 μg L^{-1} were detected at the other wells. Cu

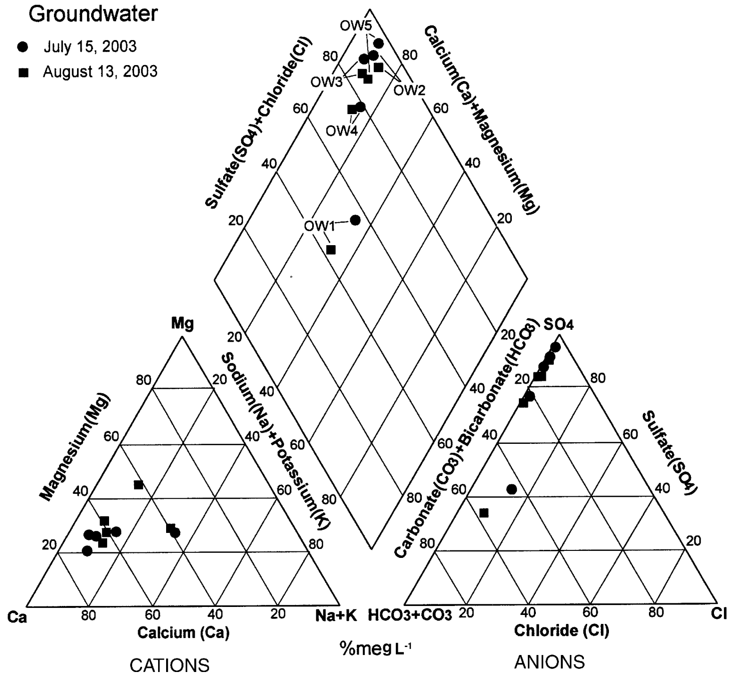

Fig. 8. Piper diagram for the groundwaters near the mine collected on 15 July and 12 August of 2003.

and Pb were below the detection limits in these groundwaters. The Zn was the most dominant heavy metal and ranged from 1758 to 10550 µg L^{-1} with a mean of 3891 µg L^{-1}. Concentrations of Zn exceeded the standard of 1000 µg L^{-1} at all the wells by factors of between 1.5 and 38.9. Concentrations of As were detected as high as 187 µg L^{-1} at OW3, which was much greater than the drinking water standard of 50 µg L^{-1} but it was not detected at OW1 well. The Cd was not observed at OW1 but concentrations of 2–21 µg l^{-1} were observed at the other wells. This heavy metal also exceeded the guideline value, 5 µg L^{-1}, at OW2 and OW5 wells. The very different occurrence and low levels of the heavy metals at OW1 well indicated that the heavy metals occurring in the groundwaters were not mainly derived from the percolated mining effluents at the mine portal but rather from the mining waste piles downstream.

Compared to the concentrations of heavy metals in July, those of Al, Cr and Cd decreased in August. Concentrations of Mn, Fe, Zn and As showed some mixed changes. Levels of Mn increased at OW1 and OW4 wells while those at OW2 and OW3 wells decreased. Contents of Fe increased at OW2, OW3 and OW5 wells but it decreased at OW5 well only. Concentrations of Zn greatly decreased at all the wells except for OW1. Interestingly, the level of Zn at OW1 well dramatically increased by a factor of 4. Arsenic concentrations increased at OW2, OW4 and OW5 but it decreased at OW3 well. Decreases in the heavy metal contents in the groundwaters at the site were unexpected. We expected that general variations in the heavy metal contents of the groundwaters associated with reduced rainfall were similar to those of the stream waters (general increases in the heavy metal contents during low stream water). The different occurrence of the heavy metals at the groundwater wells, which were located within a small area, indicated that the groundwaters were differently fed by various local pathways. Despite this simple explanation, different changes in the heavy metals at a single well can not be clearly interpreted and warrants further investigation.

Summary and conclusions

This study evaluated distribution and seasonal changes in the heavy metal contamination of surface/stream waters and groundwaters around an abandoned metal mine, where a rockfill dam with a storage volume of 48.7 × 10^6 m^3 will be built about 11 km downstream. For the evaluation, eight and two rounds of samplings for the surface/stream water and groundwater were performed, respectively, during May 2002–August 2003.

Results of exploratory analyses of surface/stream waters during 2000 indicated that substantial contamination with heavy metals including Zn, Fe and As was restricted within the area about 6 km downstream from the mine. But the levels of Zn, which was the metal mined, were highest for at least 14 km downstream of the mine. Stream waters near the abandoned mine prior to the remediation action for the waste rock pile during 1998–1999 were acidic (pH 6.1–6.7) and showed metal concentrations as high as, As 8923 $\mu g\ L^{-1}$, Cu 616 $\mu g\ L^{-1}$, Cd 223 $\mu g\ L^{-1}$ and Pb 10,590 $\mu g\ L^{-1}$, which greatly exceeded the Korean guidelines for stream water. After the remediation countermeasures, mainly focused on the mine tailing piles, the stream water qualities were largely improved. However, there have still been some quality problems for the waters. For the same sampling locations, As between 6 and 174 $\mu g\ L^{-1}$, Cd between 1 and 46 $\mu g\ L^{-1}$ and Pb between 2 and 26 $\mu g\ L^{-1}$ were detected. Especially levels of As were much elevated.

Rainfall at this site influenced the heavy metal concentrations in two ways. The rainfall infiltrated into the refuse piles and subsequently it leached more soluble metals from the waste, resulting in an increase of heavy metal concentrations in the stream waters while dilution of contaminated stream waters due to direct mixing with metal free rain waters improved the water quality. For the stream waters near the metal mine, concentrations of As, Cu, Cd and Cr largely decreased after heavy rainfall. Only levels of Pb were rather elevated.

The stream waters were characterized by high concentrations of Ca and SO_4. It was generally observed that proportions of Ca and SO_4 contents increased while those of HCO_3 and $Na+K$ decreased with reduced rainfall. High concentrations of Ca and SO_4 appeared to be from dissolution and leaching of carbonate and sulfide minerals. Lessened rainfall resulted in low stream flow and the heavy metals were relatively enriched. Variations of the heavy metal along the stream flow direction revealed that Zn and Cd concentrations dramatically decreased away from the mine portal although some levels of them still were observed downstream. Very high levels of Mn and As at 765 m downstream from the mine portal partly explained by effects of the upper mining waste piles.

The positive values of redox potential and high DO concentrations indicated aerobic conditions of the groundwaters, which appeared to enhance heavy metal precipitation. Relative ionic abundance in the groundwaters at the mine area showed the trend: $SO_4^{2-} > HCO_3^- > Cl^- > NO_3^- > Br^-$ for the anions and $Ca^{2+} > Mg^{2+} > Na^+ > K^+ > NH_4^+$ for the cations. It was generally observed that proportions of Ca and SO_4 decreased while those of HCO_3 and $Na+K$ increased for reduced rainfall in August of 2003, which was completely opposite to the response of the stream water. Concentrations of Cr ranged from 21 to 50 $\mu g\ L^{-1}$ with a mean of 27 $\mu g\ L^{-1}$, which did not exceed the Korean guideline of 50 Cr $\mu g\ L^{-1}$ for drinking water. Mn was the secondary dominant metal ranging from 19 to 3421 $\mu g\ L^{-1}$ with a mean of 920 $\mu g\ L^{-1}$ exceeding the standard of 300 $\mu g\ L^{-1}$. The Zn was the most dominant heavy metal in the groundwaters because it was the metal mined and it ranged between 1758 and 10,550 $\mu g\ L^{-1}$ with a mean of 3891 $\mu g\ L^{-1}$, which much exceeded the standard of 1000 $\mu g\ L^{-1}$ for drinking water.

Compared to the concentrations of the heavy metals in July, those of Al, Cr and Cd decreased after lessened rainfall in August of 2003. The decreases in the heavy metals contents in the groundwaters were quite different from the increases them for the stream waters associated with the reduced rainfall. Different behaviors of each heavy metal and differences in groundwater and stream water concentration changes associated with the lessened rainfall are not clearly understood at this time and warrant further investigation.

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