



Hydrochemical assessment of environmental status of surface and ground water in mine areas in South Korea: Emphasis on geochemical behaviors of metals and sulfate in ground water



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ABSTRACT

In this study, hydrochemistry of ground and surface water collected around six metalliferous mines and one coal mine in South Korea was investigated to evaluate the status of mining-related impact and pollution. Groundwater system under the mine impact shows varying degrees of immobilization and retardation of heavy metals during the flow. SO_4^{2-} is shown to be the most reliable indicator of the mining impact on groundwater, as it reflects the degree of initial sulfide oxidation even after subsequent removal of metals; SO_4^{2-} is also less prone to sorption, precipitation, and geochemical reduction. A good correlation between the concentrations of SO_4^{2-} and the sum of Ca and Mg is observed, indicating that SO_4^{2-} represents the degree of dissolution of Ca- and Mg-bearing carbonates and silicates (i.e., neutralization of acidic water to circumneutral pH) by generated H^+ that is proportional to SO_4^{2-} . The higher Zn/Cd ratios of ores and water than those of tailings and precipitates indicate a more preferential immobilization of Cd, and this ratio also reflects the inherent composition of each ore. The modified HPI (Heavy Metal Pollution Index) consisting of the measured concentrations and respective environmental standards of Fe, Mn, Al, Zn, Pb, Cd, Cu, As, and SO_4^{2-} is suggested as MPI (Mine Pollution Index) to overall reliably evaluate the status of mining-related water pollution. The plot of SO_4^{2-} versus MPI is very effective to identify the contaminated mine water and its evolution, including the source and the pathways consisting of immobilization (precipitation, sorption) and dilution of contaminants in groundwater system. This study shows that a careful examination of the relationship between MPI and SO_4^{2-} can be very useful to identify diverse geochemical processes occurring in groundwater affected by mine drainage.

1. Introduction

Mining activity causes the exposure of sulfide minerals to oxidative environment; therefore, the mine wastes from metalliferous and coal mines act as the source of metalliferous leachate and subsequent contamination of surface and ground water systems (Yun et al. 2001; Herbert 2006; Cidu et al. 2009; García-Lorenzo et al. 2012; Lghoul et al. 2014; Resongles et al. 2015; Shim et al. 2015). The oxidation of sulfides in mine areas is also one of major anthropogenic contributions to biogeochemical sulfur cycle (Berner and Berner 1987; Stüeken et al. 2012). There have been numerous studies on water geochemistry in mine areas over the world. For instance, Toran (1987) investigated the oxidation of sulfide minerals and subsequent neutralization of acidic water by carbonates at the Pb-Zn mine area in carbonate aquifer near Shullsburg, Wisconsin, USA. Fuge et al. (1993) presented the geochemical behavior

of Zn and Cd in water and solid samples in abandoned metalliferous mines in Wales, UK. Plumlee and Nash (1995) investigated the geo-environmental model according to the types of mineral deposits. In addition, there have been investigations about the behaviors of metal species and arsenic in mine drainage (e.g., Smith et al. 1994). There have also been several comprehensive studies of mine tailings as a major contamination source (Nordstrom and Southam 1997; Holmström et al. 2001; Blowes et al. 2003, 2014; Jambor 2003; Johnson and Hallberg 2003; Huang et al. 2010; Lindsay et al. 2015). However, most studies on the geochemistry of mine water have been restricted to surface water in a specific area or ore deposit; therefore, understanding the immobilization of pollutants in groundwater is still poor.

Several indices have been suggested for the overall evaluation of water quality influenced by municipal or agricultural pollutants (SDD

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Fig. 1. Locations of the studied seven mines in Korean peninsula.

1976; Mano 1989; Cude 2001; Bordalo et al. 2006; Nikolaidis et al. 2007) or metal species (Mohan et al. 1996; Lee et al. 2009; Milijašević et al. 2011; Amadi et al. 2012; Brankov et al. 2012; Prasad et al. 2014). Some of those indices have used the combination of the weighting of individual parameter (Mohan et al. 1996; Prasad et al. 2014). Most of such studies using pollution indices have also focused on a specific watershed, river, or mine area. Therefore, for a better evaluation of the overall water quality in mine area, the suggestion and use of a more

versatile index are still needed.

The objectives of this study are as follows: 1) to understand the behavior of heavy metals and major ions (especially, Ca, Mg, and SO_4^{2-}) in ground and surface water around several mines, and 2) to verify and use geochemical indicators to better assess the overall impact and environmental contamination in mine areas. Especially, the relationships among several hydrochemical parameters and suggested indicators are investigated to evaluate diverse processes such as precipitation, sorption, and dilution occurring in groundwater affected by mine drainage. In addition, removal of heavy metals and arsenic in groundwater system is also evaluated.

2. Studied mines

Five abandoned metallic ore mines and one coal mine under operation in South Korea (Fig. 1) were selected for the overall evaluation of the status of contamination of ground and surface water by mining activities. The climate of South Korea is monsoonal temperate with daily average temperatures ranging between -6 and 27 °C (annual average: 10 – 16 °C; KMA, 2015). Annual average amount of precipitation was about 1000 – 1900 mm during 1981–2010, of which $\sim 70\%$ occurred between June and September (KMA 2015). Ore types, contamination sources, and major species of contamination in the studied mines are summarized in Table 1.

In the abandoned Sambo Pb-Zn-Ba mine, Pb and Zn were major products, with minor amounts of Ba and Ag. Ore minerals occur in fissure-filling hydrothermal quartz veins in metamorphic rocks and consist mainly of sphalerite, galena, and barite with minor amounts of chalcopyrite and pyrite; gangue minerals include quartz, rhodochrosite, calcite, fluorite, dolomite, and sericite (So et al. 1984; Kim and Chon 1993). In the Sambo mine area, there are two huge dumps of tailings in different catchment areas (Fig. 2a): tailing dumps #1 and #2 have the horizontal extent of $51,345$ m² and $18,249$ m², and the depth of 6.9 – 17.5 m and 5.5 – 9.9 m, respectively, with the total volume of $722,000$ m³. Leachates are generated from each dump. In particular, the leachate from tailing dump #1 is flowing out to the land surface with the average flow rate of 131 m³ day⁻¹ (period of measurements: Nov. 2008–Sep. 2009, $n = 46$), contaminating downstream paddy fields where water table is higher than the ground surface. The paddy fields are prohibited to be cultivated because of soil contamination by Cd, Pb and Zn (KME 2003). A drainage with the average flow rate of 230 m³ day⁻¹ (period of measurements: Nov. 2008–Sep. 2009, $n = 46$) is flowing out through an abandoned mine adit near the tailing dump #2 and then joins the leachate from dump #2 (MIRECO 2009a).

The abandoned Buddeun Au-Ag-Cu mine consists of hydrothermal quartz veins in granitic rocks. Major ore minerals are chalcopyrite, sphalerite, pyrite, arsenopyrite, galena, electrum, argentite and native silver; gangue minerals include quartz, rhodochrosite, ankerite, and calcite (Park et al. 1988). Major sources of water contamination are two large tailing dumps (#1 and #2) with the area of $14,779$ m² and

Table 1
Mining history, major ore types, and contamination sources of studied mines.

Name	Province	Operation period	Ore type	Water contamination	
				Sources	Contaminants
Buddeun	Gyeongbuk	1915–1989	Hydrothermal; Au-Ag-Cu	Tailings and adit water	Al, Cd, Cu, Mn, Pb, Zn
Dangdu	Chungbuk	1937–1992	Skarn; Au-Ag-Pb-Zn	Adit water	Cd
Gomyeong and Dongbo	Gangwon	1978–1993	Hydrothermal; Au-Ag	Tailings and adit water	As, Mn
Sambo	Gyeonggi	1956–1991	Hydrothermal; Pb-Zn-Ba	Tailings and adit water	Al, Cd, Mn, Pb, Zn
Samgwang	Chungnam	1928–1996	Hydrothermal; Au-Ag-Pb-Zn	Tailings and adit water	As, Mn
Sangdeok	Gangwon	Under operation	Anthracite coal	Waste rock	Al, Cd, Fe, Mn, Pb, Zn

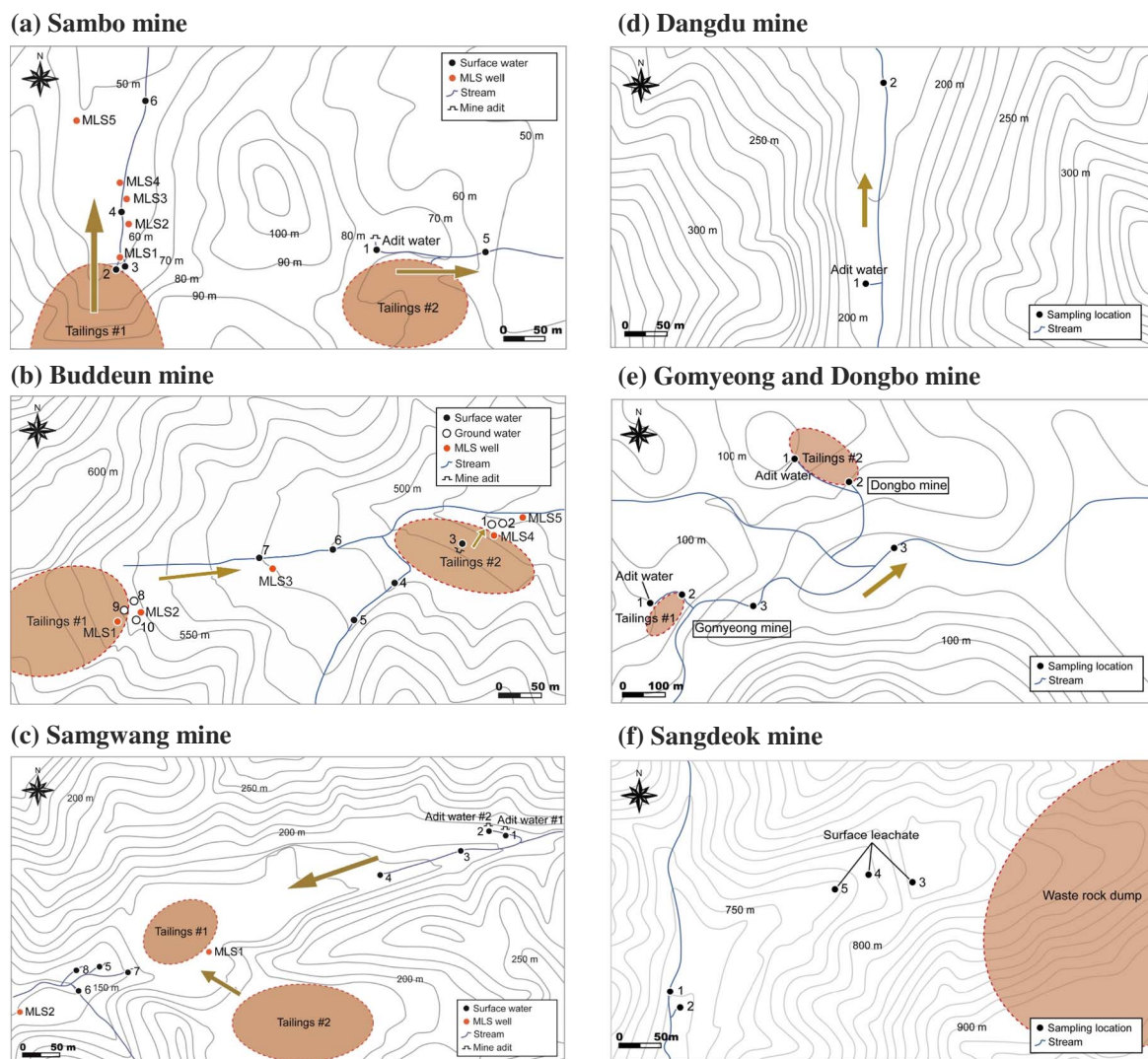


Fig. 2. Topography map, sampling locations, and contamination sources (tailings) in the studied mine areas: (a) Sambo, (b) Buddeun, (c) Samgwang, (d) Dangdu, (e) Gomyeong and Dongbo, and (f) Sangdeok mines. Arrows denote the water flow direction.

10,746 m², respectively (Fig. 2b).

Ores of the abandoned Samgwang Au–Ag mine occur as massive hydrothermal quartz veins in Precambrian gneiss (Lee and Hueley 1973; Jeong et al. 1995). Major ore minerals occupy < 5 vol% of the vein and consist of arsenopyrite, pyrite, sphalerite, chalcopyrite, galena with subordinate pyrrhotite, marcasite, electrum, and argentite; gangue minerals include quartz, K-feldspar, and calcite (Lee et al. 1998; Yoo et al. 2002). There are two tailing dumps and two mine adits (Fig. 2c). The drainages from the adits join a small stream, while leachate from tailing dump #2 does not appear on the land surface and possibly contaminates groundwater at downgradient sites.

The abandoned Dangdu mine was the producer of Au, Ag, Pb, and Zn from massive skarn deposits formed by hydrothermal replacement of limestones near a granitic pluton. The ore minerals are chalcopyrite, galena, sphalerite, magnetite, and pyrrhotite and skarn minerals are calcite, quartz, pyroxene, and chlorite (Lim et al. 2013). Mine drainage is discharging from a vertical shaft to an adjacent stream (Fig. 2d).

The abandoned Gomyeong and Dongbo mines are located in Goseong at the northeastern part of South Korea (Fig. 1) and were the producers of Au and Ag from hydrothermal quartz veins in Precambrian gneiss. Major ore minerals include pyrite, sphalerite, galena, chalcopyrite, and arsenopyrite; gangue minerals include quartz and calcite (Kim et al. 1994). Both the subsurface leachate from the tailing dump

and the mine adit water (flow rate: 36.0–86.4 m³ day^{−1}) affect a stream near the Gomyeong mine (Fig. 2e; MIRECO 2009b). The Dongbo mine also shows a small amount of discharge (< 3 m³ day^{−1}) from the adit and the tailing dump (Fig. 2e).

In the Sangdeok coal mine, pyrite-bearing anthracite seams and metasedimentary rocks of Permian age are the sources of acid mine drainage (AMD). A huge waste rock dump with the horizontal extent of ~100,000 m² discharges acid leachates, which infiltrate into underground and seeps out again at a small stream ca. 200 m away from the waste rock dump (Fig. 2f). Immediately after the discharge into the stream, white precipitates of aluminum hydroxides are formed.

3. Sampling and analysis

3.1. Water sampling

A reconnaissance regional survey was conducted in March 2013 for surface water in all seven mine areas with additional groundwater samples in the Buddeun mine area (Fig. 2). An adit water sample (No. 1), two leachate samples (No. 2 and 3) and three downstream samples (No. 4, 5 and 6) were collected at the Sambo mine (Fig. 2a). Groundwater samples affected by leachates from tailings were collected at 5 boreholes (No. 1, 2, 8, 9 and 10; Fig. 2b) installed for groundwater

monitoring in front of two dumps at the Buddeun mine. Two surface water samples downstream of the tailing dump #1 (No. 6 and 7), one adit water sample (No. 3), and three surface and groundwater samples in a downstream village (No. 11, 12 and 13) were also collected. In the Samgwang mine, two adit waters (No. 1 and 2), their downstream samples (No. 3 and 4), leachates from the tailing dump #1 (No. 5, 7 and 8) possibly affected by the adit waters, and one surface water sample in a downstream village (No. 9) were collected (Fig. 2c). An adit water sample (No. 1) and a surface water sample at downstream (No. 2) were collected in the Dangdu mine. In the Gomyeong mine, an adit water (No. 1), its downstream water (No. 2), and one river water at downstream (No. 3) were sampled. An adit water (No. 1), a leachate from the tailing dump (No. 2) and a river water at downstream (No. 3) were also sampled in the nearby Dongbo mine. Three leachate samples from a waste rock dump (No. 3, 4 and 5) and a surface water at downstream (No. 2) possibly affected by the leachate was collected in the Sangdeok mine. Several surface water samples were also collected from nearby catchment areas or upstream as non-contaminated “background” water (No. 4 and 5 in the Buddeun, No. 6 in the Samgwang, and No. 1 in the Sangdeok). A total of 42 locations were chosen for water sampling for the regional survey distributed by the seven mine areas selected in this study.

To examine the vertical and horizontal variations of groundwater chemistry, 12 multilevel samplers (MLSs) were installed in the Sambo, Buddeun, and Samgwang mine areas (five at Sambo, five at Buddeun, and two at Samgwang) between late May and early June of 2013 (Fig. 2). Boreholes for MLS were installed by rotary drilling down to ca. 20–30 m from the land surface. Immediately after the drilling, tubes and pipes for groundwater monitoring and sampling were inserted into each borehole; then, sand was used as a backfill material (cf. Kim et al. 2014). The lithology of the recovered core from each borehole was described. The uppermost silt or silty sand layer was restricted to the depths below 2 mbgl (meter below ground level) for all three mines, and the depth intervals of fine to coarse sand to bedrock were 8–13 mbgl, 10–16 mbgl, and 10–13 mbgl for the Sambo, Buddeun, and Samgwang mines, respectively.

The MLS bundle consisted of 2.5 cm diameter polyvinyl chloride (PVC) pipes and 0.5 cm diameter polyethylene (PE) tubes of various lengths. Eight PE tubes and two PVC pipes were inserted at each borehole. Each pipe or tube had a 10 cm-long slotted tip wrapped with a stainless steel screen for water inflow (cf. Kim et al. 2014). The potential cross-connection between lithologic layers through the back-filled sand was minimized by maintaining sufficient intervals (≥ 1.5 m) between sampling depths, i.e. ca. 15 times of the radius of borehole (0.1 m), and by maintaining the pumping flow rate below 0.1 L min^{-1} . The cross-connection effect was also carefully checked by examining the changes of physicochemical characteristics of water at each sampling depth.

After the one-month stabilization period, groundwater sampling from MLS wells was conducted in July (the rainy season) and October (the dry season) of 2013. A total of 85 and 93 groundwater samples were collected in July and October, respectively, from twelve MLS wells using a peristaltic pump (Cole-Parmer Inc., USA).

3.2. Analytical methods

3.2.1. Water samples

Collected water samples were filtered through a $0.45 \mu\text{m}$ pore size membrane and then immediately transferred into pre-cleaned 60 ml high density polyethylene (HDPE) bottles. The samples for the analysis of cations were preserved by adding a few drops of concentrated HNO_3 to keep the $\text{pH} < 2$. Sample bottles for the analysis of cations, anions, and dissolved organic carbon (DOC) were completely filled with water and capped with an elastic laboratory film to avoid air contact and then stored in an ice box or refrigerator at 4°C until further analysis.

Field parameters of water samples were measured using portable

meters: electric conductivity (EC) and temperature using Orion model 130A, pH using Orion model 290A, and dissolved oxygen (DO) using Orion model 835A. The portable meters were calibrated in situ once a day. Alkalinity (as HCO_3^-) was also determined in the field by volumetric titration using 0.05 N HNO_3 . Dissolved sulfide ($\Sigma\text{H}_2\text{S} = \text{H}_2\text{S}^\circ + \text{HS}^- + \text{S}^{2-}$) was also determined in the field using a portable colorimeter (model HACH DR-890) following the methylene blue method (Cline 1969).

Concentrations of dissolved major cations (Na, K, Mg, Ca) were analyzed by an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES; Optima 3000XL, Perkin Elmer) at the Center for Mineral Resources Research (CMR), Korea University. Concentrations of trace metals and As were analyzed by Inductively Coupled Plasma Mass Spectrometer (ICP-MS; Elan DRC II, Perkin Elmer) at the Korea Basic Science Institute (KBSI) at Seoul. Anions were measured by ion chromatography (IC; DX-120, Dionex) at CMR. Relative standard deviations were generally below 5% of the measured value for ICP-AES, ICP-MS, and ion chromatography. DOC was determined by Total Organic Carbon analyzer (Sievers 5310C, General Electric) at the National Instrumentation Center for Environmental Management (NICEM) at Seoul National University. Relative standard deviation was below 1% of the measured value for the DOC analysis. Blank samples of deionized water were used and calibration curves were made using standard samples to provide QA/QC for the ICP-AES, ICP-MS, IC, and DOC analyses.

3.2.2. Solid samples

Sulfide minerals were physically separated from the collected ores and rock samples for chemical analysis, while tailings were processed in the bulk form. The rocks/tailings and ore samples were crushed and then pulverized using a ball mill and an agate mortar, respectively. Then, the dried powder samples were combusted for 2 h at 550°C in a muffle furnace to remove organic carbon and volatiles. Each sample of 0.1–1.0 g was reacted and evaporated with 5 ml of mixed acid (HF: aqua regia = 1: 1) in a teflon container on a heating plate at 170°C ; this process was repeated 2–5 times. After the metals were eluted using 10 ml of 0.5 N HNO_3 , supernatant liquid was obtained using a centrifugal separator at 12000 rpm for 20 min; this process was also repeated until the liquid sample of ca. 30 ml was acquired. The liquid sample was evaporated and dried on a heating plate and dissolved organic matter was completely decomposed using 1 ml of HNO_3 and 0.1 ml of HClO_4 and then dried. Afterwards, sequential evaporation and re-dissolution were conducted. First, the sample was reacted with 1 ml of concentrated HCl and then dried again. Second, the sample was reacted with > 1 ml of 2 N HCl ; this process was repeated two times to completely dissolve precipitates.

Metal (As, Cd, Fe, Mn and Zn) concentrations in the solution were finally analyzed using Multicollector (MC) ICP-MS (NU Instruments) at National Institute of Environmental Research (NIER). Calibration curves were made using standard samples to provide QA/QC for the MC ICP-MS. Relative standard deviations were generally below 5% of the measured value for a certified reference material (marine sediment, MESS-3) from National Research Council of Canada.

3.3. Data analysis

Several methods have been suggested to evaluate the degree of water pollution. The Water Quality Index (WQI) was composed of sub-indices regarding parameters such as DO, total nitrogen, and total phosphorous; each sub-index was calculated (e.g., SDD 1976; Mano 1989; Cude 2001; Bordalo et al. 2006) or categorized according to the specified range of each parameter (e.g., Sánchez et al. 2007). Burton et al. (2003) also used several sub-indices regarding population, sewage advancement, and other parameters. However, those criteria and resulting index generally reflected the pollution by municipal, agricultural, and industrial wastewater; therefore, they are not applicable

Table 2
Field measurements and lab analytical data of water samples collected during reconnaissance regional survey.

Mine	Sample no.	Samples ^a	pH	Ca (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	As (μg L ⁻¹)	Cd (μg L ⁻¹)	Cu (μg L ⁻¹)	Mn (μg L ⁻¹)	Pb (μg L ⁻¹)	Zn (μg L ⁻¹)
Buddeun	1	GW	7.3	64	158	1	12	1	3	0	2687
	2	GW	7.0	70	171	1	24	3	4	0	4343
	3	Adit water	7.4	42	70	5	0	0	734	0	566
	4	SW	7.6	4	5	1	1	1	6	0	249
	5	SW	5.8	3	6	1	1	1	1	0	298
	6	SW	5.7	73	278	1	138	785	3131	4	22,220
	7	SW	4.8	84	353	1	192	1230	5484	5	37,774
	8	GW	6.4	222	586	4	219	346	4757	1	39,390
	9	GW	4.6	136	564	3	336	2720	10,605	20	60,903
	10	GW	6.3	173	451	1	260	414	8242	4	51,308
	11	SW	6.1	35	120	1	45	113	896	1	9171
	12	GW	6.3	22	11	0	0	14	12	0	90
	13	GW	8.3	21	17	0	0	1	57	8	25
Dangdu	1	Adit water	7.6	60	44	5	11	1	16	2	707
	2	SW	7.4	20	15	2	1	1	5	0	65
Dongbo	1	Adit water	8.0	15	4	4	0	0	24	3	5
	2	Leachate	6.9	62	5	1	0	1	9890	0	8
	3	SW	8.2	3	5	1	0	1	2	0	28
Gomyeong	1	Adit water	7.4	14	40	82	0	2	5	0	27
	2	SW	7.9	15	34	70	0	1	2	0	13
	3	SW	7.9	4	5	1	0	0	3	0	11
Sambo	1	Adit water	6.7	47	107	5	5	5	1919	107	3889
	2	Leachate	5.9	113	368	0	7	2	13,029	5	12,322
	3	Leachate	6.0	169	711	1	14	6	69,589	74	50,399
	4	SW	6.1	144	542	0	11	2	40,703	1	31,411
	5	SW	6.3	47	169	0	17	26	5333	5	16,463
	6	SW	5.6	75	256	0	0	1	1141	0	2091
Samgwang	1	Adit water	8.2	44	113	753	0	1	4	0	22
	2	Adit water	7.7	59	84	5210	0	0	429	0	12
	3	SW	7.8	22	33	1320	0	0	12	0	10
	4	SW	7.3	25	39	1360	0	1	2	0	11
	5	SW	7.9	29	55	615	0	1	5	0	10
	6	SW	7.6	4	6	7	0	0	1	0	7
	7-1	Leachate	7.3	39	79	928	1	4	24	0	38
	7-2	Leachate	7.2	38	78	901	1	2	31	0	83
	8	Leachate	7.4	46	99	1220	0	1	1	0	11
Sangdeok	1	SW	7.1	13	21	142	0	1	1	0	6
	2	SW	6.4	3	4	0	0	0	1	0	3
	3	SW	5.3	23	186	0	0	9	2060	0	1818
	4	Leachate	5.5	325	1310	-	-	-	-	-	-
	5	Leachate	5.2	506	1974	2	7	145	11,110	6	4202
	5	Leachate	3.8	362	6182	8	14	169	99,081	43	27,775

^a Leachate = leachate from tailings or waste rock dump; SW = surface water; GW = ground water.

for the mine drainage-affected water system. Other indices such as the WPI (Water Pollution Index), MPI (Metal Pollution Index), and HPI (Heavy metal Pollution Index) have adopted the ratio of sample concentration to the water quality standard. The HPI model was proposed by Mohan et al. (1996) and Prasad et al. (2014) to evaluate ground-water quality near mining areas in India (see Eq. (1)).

$$HPI = \frac{\sum_{i=1}^n W_i Q_i}{\sum_{i=1}^n W_i} \quad (1)$$

where Q_i is the subindex of i th parameter, W_i is the unit weightage of i th parameter that can be assessed by making values inversely proportional to the recommended standard, and n is the number of parameters considered (Mohan et al. 1996). Here, sub-index (Q_i) is calculated using Eq. (2).

$$Q_i = \sum_{i=1}^n \frac{\{M_i(-)I_i\}}{(S_i - I_i)} \quad (2)$$

where M_i is the sample concentration of i th parameter, I_i is the ideal value of i th parameter, S_i is the environmental standard of i th parameter. The sign (-) indicates the difference between two values, ignoring the algebraic sign.

In addition, there have been several studies using an index without the unit weightage to evaluate river water quality polluted by domestic

and/or mining wastewater (Nikolaidis et al. 2007; Lee et al. 2009; Milijašević et al. 2011; Amadi et al. 2012; Brankov et al. 2012). In this study, the indicator is named the MPI (Mine Pollution Index), which is made by rearranging the Eqs. (1) and (2) as follows (see Eq. (3)):

$$MPI = \frac{\sum_{i=1}^n \frac{C_i}{S_i}}{n} \quad (3)$$

4. Results and discussion

4.1. General hydrochemical characteristics and behavior of contaminants

Results of reconnaissance regional and detailed (using MLSs) surveys are presented in Table 2 and Fig. 3, respectively. Major contaminants in the Sambo and Buddeun mine areas are Zn and Mn. Maximum Zn concentrations are 50.4 mg L⁻¹ and 60.9 mg L⁻¹ at the Sambo and Buddeun mine areas, respectively, and the maximum Mn concentrations are 69.6 mg L⁻¹ and 29.3 mg L⁻¹ (MLS1), respectively. The abundance of Zn agrees well with the fact that sphalerite is major constituent of ore minerals in the two mines. Previous studies (e.g., Smith et al. 1994) have reported that Zn was highly mobile in mine drainage with the circumneutral pH range. Significant concentrations of Mn might originate from carbonates (e.g., rhodochrosite).

Manganese appears to persist in mine drainage-affected water, while the concentrations of Zn are locally reduced at some locations. While Mn and Zn behave similarly in MLS2 and MLS3 at Sambo, Zn concentration is significantly reduced before MLS4; Mn also decreases in MLS5 (Fig. 3 b to e). MLS1 at Sambo is located in front of an outlet of the underdrain (No. 2) from tailings (Fig. 2a); in contrast to the concentration (~13 mg L⁻¹) of the underdrain leachate, Zn concentration also diminishes in MLS1 (< 0.1 mg L⁻¹; Fig. 3a). On the other hand, Mn maintains high concentrations (5.9–24.6 mg L⁻¹ in July and 0.7–9.6 mg L⁻¹ in October; Fig. 3a). Mn also exhibits higher concentrations at shallow depths in MLS1 (≤ 11 mbgl) at Sambo in July than in October. As SO₄²⁻ is also high in July (616–668 mg L⁻¹) as compared to that in October (530–629 mg L⁻¹) at those depths, an increase in the oxidation of sulfides in the rainy season (July) might

enhance the subsequent release of Mn.

Because the susceptibility of sorption of metal ions is generally known to follow the order of Pb²⁺ > Cu²⁺ > Cd²⁺ ≈ Zn²⁺ (e.g. Schindler et al. 1976; Spark et al. 1995), Pb and Cu are expected to be efficiently sorbed. The concentrations of Pb are < 7 μg L⁻¹ in groundwater samples from the MLS wells, suggesting the immobile characteristics of Pb in groundwater, possibly due to sorption and/or precipitation, although the tailing leachate (No. 3) at Sambo shows high Pb concentration, up to 74 μg L⁻¹ (Table 2). In addition, the high Pb concentration (107 μg L⁻¹) in an adit drainage (No. 1) quickly decreases to 5 μg L⁻¹ (No. 5) after joining the leachate from tailing dump #2, while the concentrations of Cd, Cu, Mn and Zn increase from 5 μg L⁻¹ to 17 μg L⁻¹, from 5 μg L⁻¹ to 26 μg L⁻¹, from 1.9 mg L⁻¹ to 5.3 mg L⁻¹, and from 3.9 mg L⁻¹ to 16.5 mg L⁻¹, respectively (see

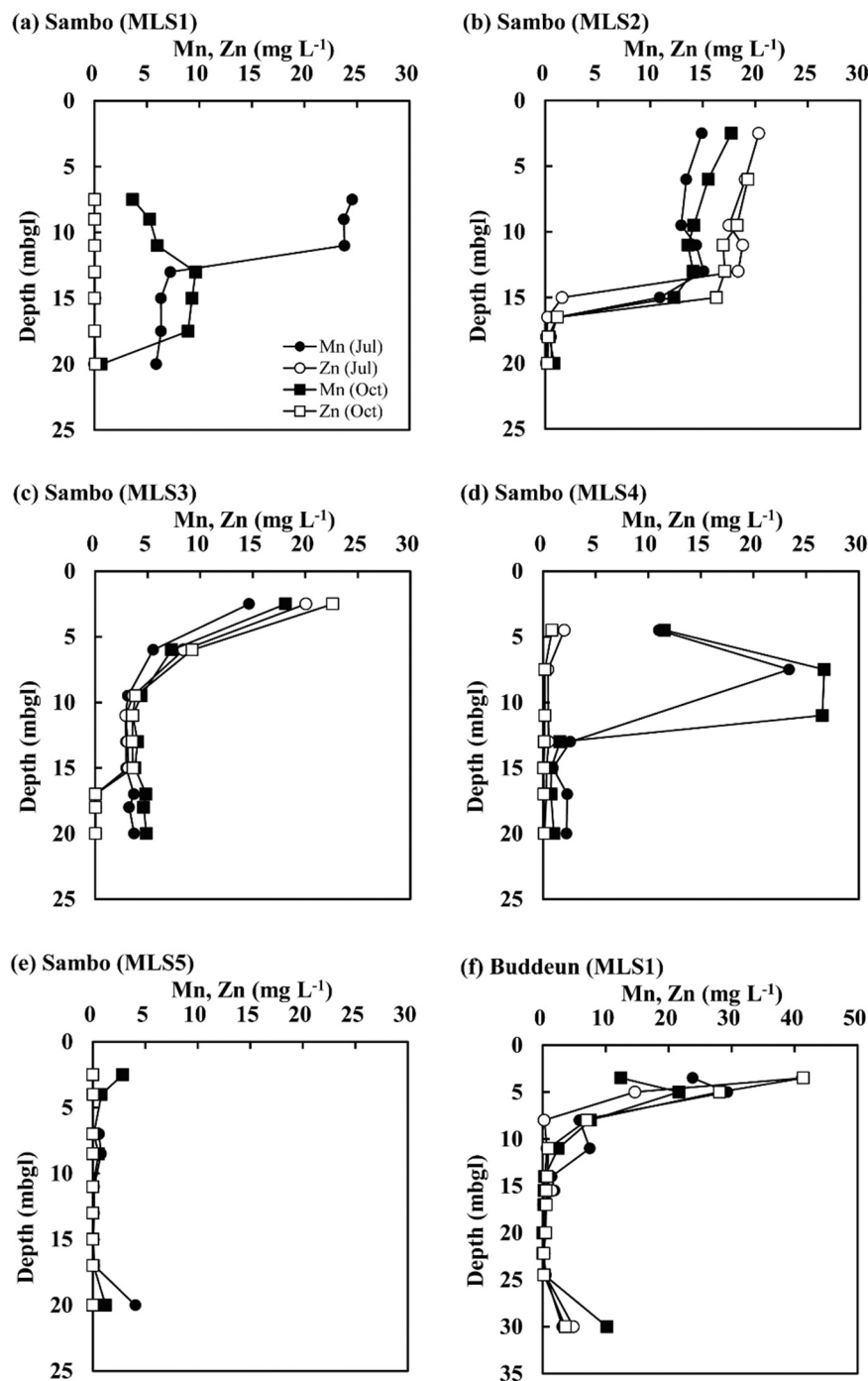


Fig. 3. Vertical profiles of metal concentrations in groundwater from multilevel samplers (MLSs). (a) to (j) = Mn and Zn in the Sambo (a to e) and Buddeun (f to j) mines; (k) and (l) = Mn and As in the Sangwang mine.

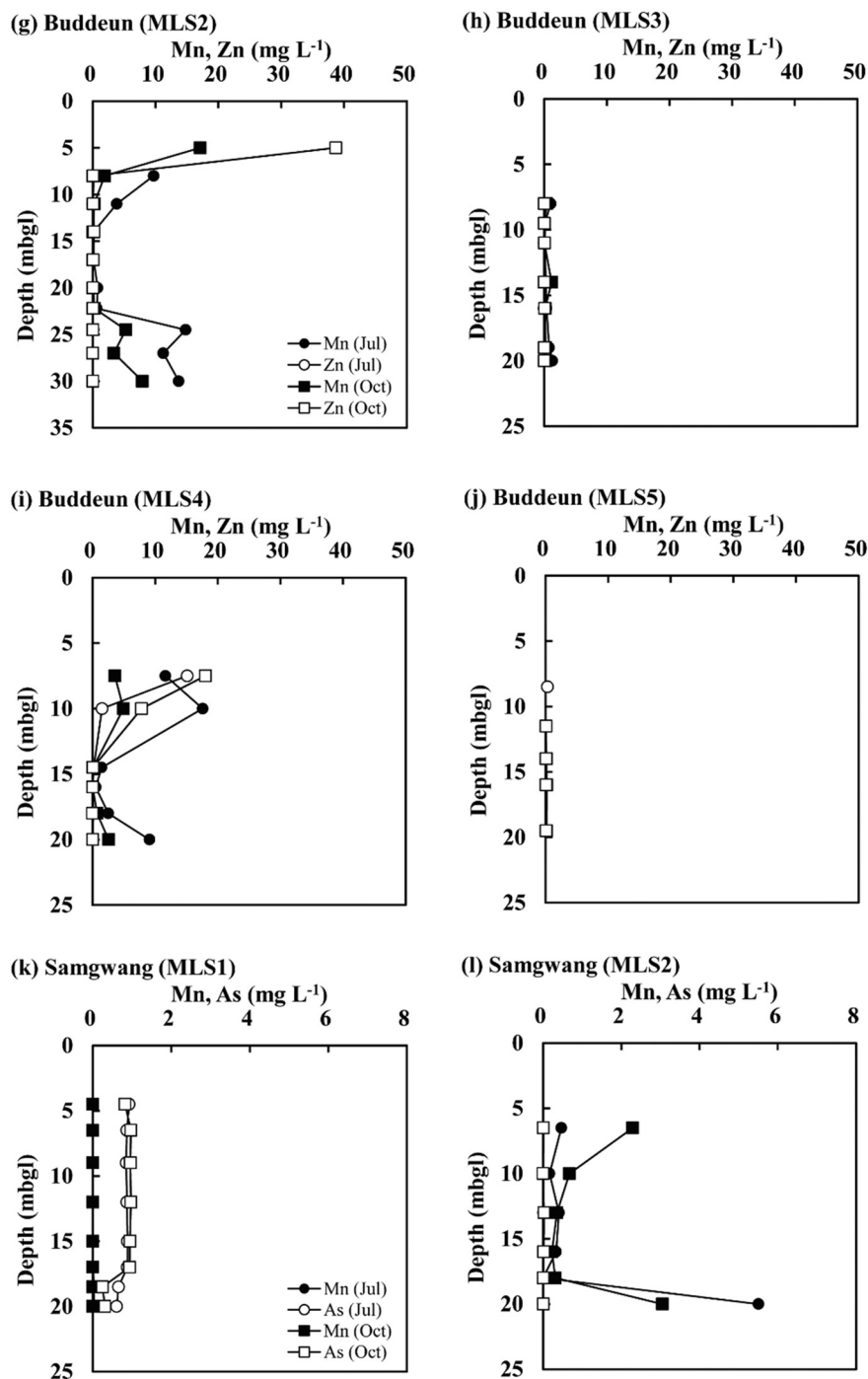


Fig. 3. (continued)

Table 2). Thus, the diminution is significant for Pb along the pathways of surface and ground water. At Buddeun, the Cu concentrations are mostly below 1 mg L⁻¹ at all sampling points of regional and MLS surveys, except for those from the monitoring well adjacent to a tailing dump (No. 9; 2.7 mg L⁻¹) and at the tributary affected by leachate (No. 7; 1.2 mg L⁻¹) during the regional survey (Table 2). The distribution of Cd is similar to that of Cu in general.

The concentration of As reaches as high as 5.2 mg L⁻¹ at the adit water (No. 2) of the Samgwang mine (Table 2) where arsenopyrite is a dominant ore mineral. Iron is sensitive to oxidation and Fe³⁺ is effectively removed by precipitation at pH > 3.5 (Kelly 1988). The maximum Fe concentrations at the Sambo and Buddeun mines were 6.1 mg L⁻¹ and 5.4 mg L⁻¹, respectively. In addition, the lowest pH (3.8) is observed at the leachate of the waste rock dump in the

Sangdeok coal mine (Table 2). Caruccio (1975) pointed out that framboidal pyrite, which usually consists of micron- or submicron-sized crystals with very high specific surface areas, produces acid at much higher rates than larger pyrite grains. Thus, framboidal pyrite of sedimentary origin in the coal mine might effectively generate AMD with a very high SO₄²⁻ concentration (6182 mg L⁻¹) and a low pH (Table 2). A high concentration of H⁺ could elute Al from aluminosilicates to accumulate at concentration up to ~376 mg L⁻¹. On the other hand, contamination levels of trace metals are low for the most of limited samples from the Dangdu, Gomyeong, and Dongbo mines (Table 2).

4.2. Geochemical behavior of Zn and Cd

The Zn/Cd ratios of ores from the Sambo mine are higher

Table 3
Analytical results of ore, tailings, and ochre precipitates.

Samples	Mine	As	Cd	Fe	Mn	Zn	Zn/Cd ratio	
		(mg/kg)	(mg/kg)	(%)	(mg/kg)	(mg/kg)	Weight	Molar
Ore	Buddeun	0.04	0.27	0.88	146	69	258	444
	Gomyeong	0.76	0.09	1.53	208	29	310	534
	Sambo #2	0.02	0.31	0.58	931	281	919	1580
	Sambo #2	0.46	0.09	4.59	731	99	1087	1868
	Samgwang	801.4	7.99	3.04	196	61	4363	7500
Tailings	Dongbo	4.27	1.43	4.35	1777	942	118	203
	Sambo #2	791.7	12.79	0.59	1954	729	511	879
	Samgwang #1	5126.8	16.74	2.35	498	415	32	56
	Samgwang #2	84.0	16.71	1.56	211	499	30	51
	Downstream ochre precipitates	Sambo #1			32.81	1021	7256	434
	Sambo #2			37.67	3604	3243	67	115

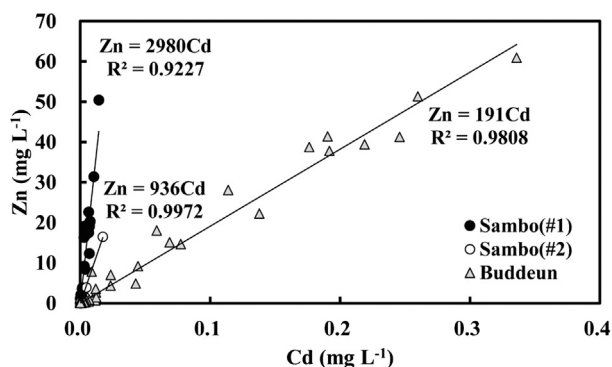


Fig. 4. Relationship between dissolved Cd and Zn in water samples from the Buddeun and Sambo mines.

(919–1087; Table 3) than those from the Buddeun mine (258; Table 3). Tailings of the Sambo mine show a lower Zn/Cd ratio (511) than those of ore sulfides. In addition, tailings of the Dongbo mine also have a lower Zn/Cd ratio (118) than that of ore sulfide at the Gomyeong mine (310); these two adjacent mines show very similar mineralogical characteristics of ores. These possibly indicate that weathering of tailings by rainwater infiltration may leach Zn more effectively than Cd. Cadmium is known as more chalcophilic and thus tends to remain as sulfide, while Zn is easily weathered out. Similarly, Fuge et al. (1993) reported the decreased Zn/Cd ratio of tailings (92) as compared to that of sphalerite (310 and 450) in the Fan mine and the sphalerite from the mid Wales ore field (120–665 with the average of 306; Kakar 1971).

The relationship between dissolved Cd and Zn in the Sambo and Buddeun mines is shown in Fig. 4. The samples from other mines are not shown, as they are mostly negligible in the Cd concentration (below

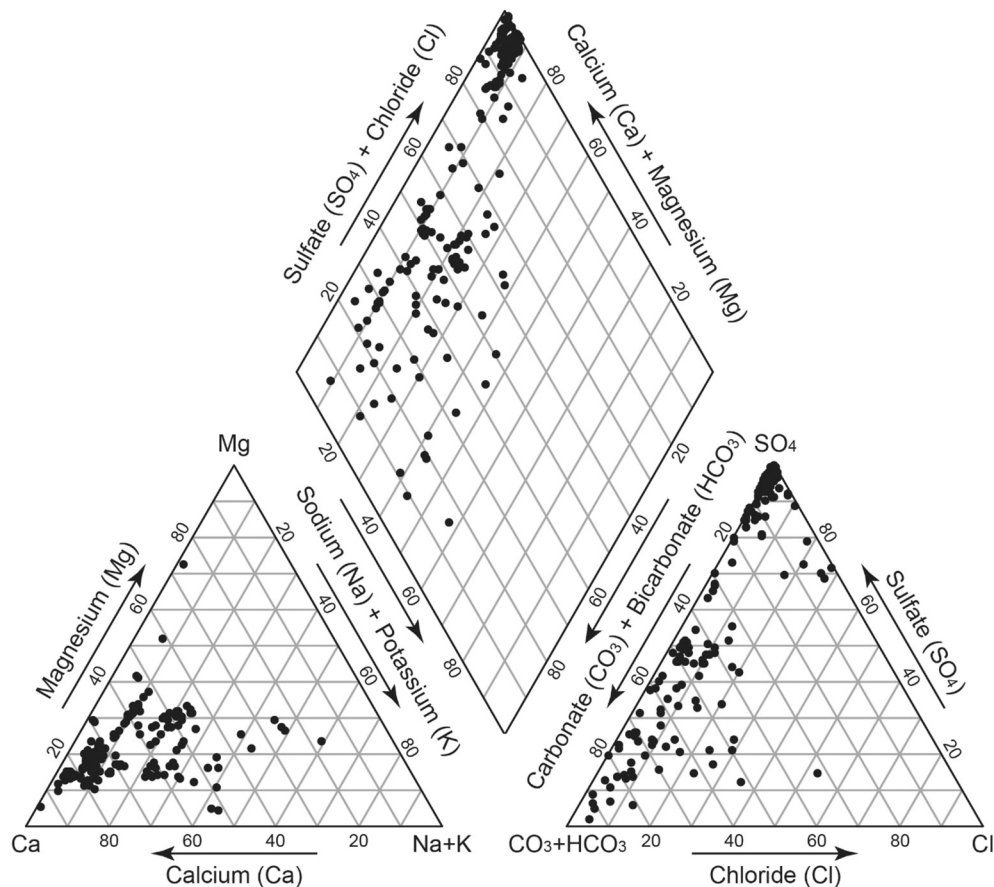


Fig. 5. Piper diagram for water samples collected at the seven mines in this study.

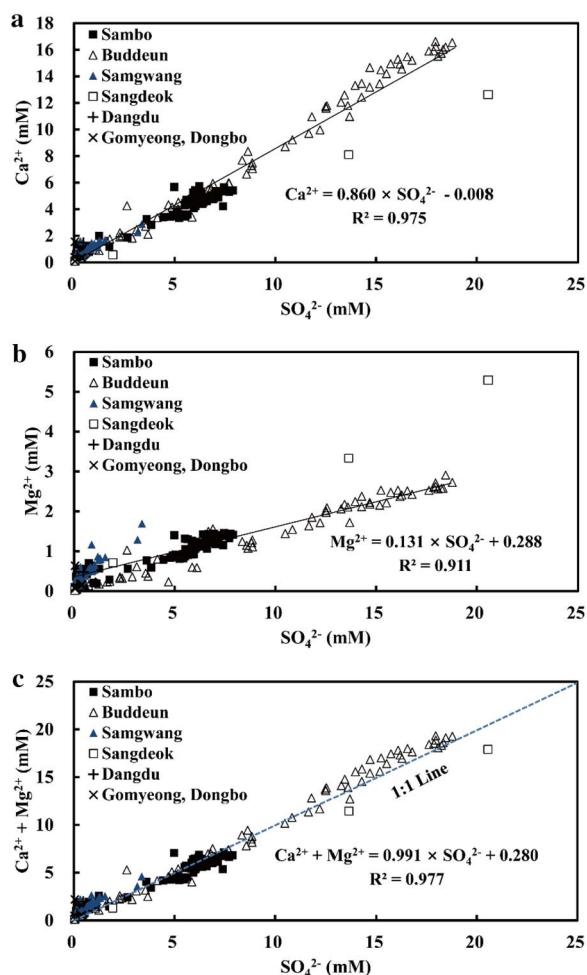


Fig. 6. Relationships among dissolved ions in water collected during a regional reconnaissance and detailed (using MLSs) surveys: (a) SO_4^{2-} versus Ca, (b) SO_4^{2-} versus Mg, and (c) SO_4^{2-} versus the sum of Ca and Mg.

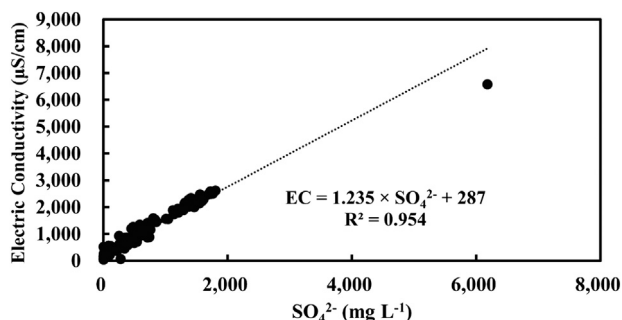


Fig. 7. Relationship between SO_4^{2-} concentration and EC (electrical conductivity) of water samples collected during a regional reconnaissance and detailed (using MLSs) surveys.

Table 4

Ratio of sulfate concentrations between samples and “background” samples from Sambo, Buddeun, Samgwang, and Sangdeok mines.

	Buddeun	Samgwang	Sangdeok
Average	151	13.1	472
Median	141	12.3	320
Max.	329	54.7	1510
Min.	1.00	0.92	1.00

0.01 mg L⁻¹). The linear relationship between Cd and Zn likely suggests the main source of Cd from sphalerite (cf. Wakita and Schmitt 1970; Levinson 1980; Kabata-Pendias and Pendias 1984). Fuge et al. (1993) reported the ratio of Zn to Cd in water from mid Wales ore field to fall between ~12 and 1381; Similarly, Hubbard et al. (2009) reported the ratio of 264 in Rio Tinto, Spain. In surface and ground water samples from Sambo, Zn is significantly higher than Cd, while the Zn/Cd ratios are 191:1 and 67:1 at Buddeun and Dangdu, respectively (Fig. 4, Table 2). At Sambo, the relatively low Zn/Cd ratios are observed for drainage from an adit adjacent to tailing dump #2 (810) and the downstream leachate of the same dump of tailings (946), while higher ratios (1758–5014) are observed for surface water at downstream sites of tailing dump #1. Such differences of Zn/Cd ratio may reflect the inherently different chemical composition of each dump of tailings generated from nearby ore shoots and adits.

The regression line of surface and ground waters near tailing dump #2 at the Sambo mine area shows the higher Zn/Cd ratios (936) than that of tailings (511; Table 3) (Fig. 4). Cadmium has been reported to be effectively scavenged during the precipitation of Fe (Fuge et al. 1993); therefore, Zn/Cd ratio can be significantly higher in water than in precipitates. Actually, precipitates on the streambed sediments at Sambo show very high concentrations of Fe (32.8–37.7%) together with lower Zn/Cd ratios (67–434) (Table 3). Kim and Chon (1993) also reported an average Zn/Cd ratio of 256 for stream sediments at Sambo, which is similar to the range obtained in the present study. Likewise, Jung et al. (2012) reported the Zn/Cd ratios between 149 and 539 for a total of 12 streambed sediment samples, except for the highest and lowest values. Overall, the Zn/Cd ratios of sediments at Sambo are lower than those of surface water. Therefore, it is likely that Cd is more preferentially scavenged by Fe precipitation than Zn in mine drainage.

Similarly, in the Samgwang mine, tailings show low Zn/Cd ratios (30–32; Table 3), as compared to the very high ratio (4363) for arsenopyrite (the predominant sulfide mineral in ores). Surface water samples affected by mine drainage at Samgwang show Zn/Cd ratios between 39 and 160 (average = 77) that as in tailings are lower than in ores. Lee et al. (1998) reported Zn/Cd ratios of streambed sediment samples to be 39–53 (average = 45), which is slightly lower than the range for a drainage obtained in the present study. The small difference between the ratios of sediment and water may be due to the lower contents of Fe in the sediment at the Samgwang mine (3.8–6.7%; Lee et al. 1998) than in the precipitates at the Sambo mine (32.8–37.7%; Table 3).

4.3. Sulfate concentrations as an indicator of mine impact

The ground and surface water samples collected in this study have a major-ion chemistry dominated by Ca-Mg-SO₄-HCO₃ (Fig. 5). The samples are concentrated near Ca-Mg-SO₄ type and diffuse toward Ca-Mg-HCO₃ type. There is little evidence of SO₄²⁻ reduction in all of the mine areas in this study, because this seldom occurs with the presence of ferric iron, which is common in mine areas. The concentration of dissolved sulfide (H₂S and HS⁻) is below 0.1 mg L⁻¹, except in the sample from 20 m depth of MLS3 at Buddeun, collected in July.

The relationship between SO₄²⁻ and Ca or Mg exhibits a linear positive relationship (Fig. 6). The regression line between the molar Ca + Mg and the concentrations of SO₄²⁻ exhibits a slope approaching 1.0 (R² = 0.977; Fig. 6c). As is generally known, H⁺ generated during sulfide oxidation reacts with rocks to effectively release Ca and Mg. In addition, pH was above 5.3 for ca. 95% of the collected water samples (above 4.6 for all samples) and the Fe concentration was below 6.1 mg L⁻¹ for all samples. Thus, the observed relationship can be explained by the following reaction Eq. (4):

Table 5
Calculated HPI and MPI for water samples from a regional reconnaissance and detailed (using MLS) surveys.

Pollution index	Statistics	Buddeun	Dangdu	Dongbo and Gomyeong	Sambo	Samgwang	Sangdeok
HPI	Average	2.79	0.65	0.71	0.49	15.1	6.03
	Median	0.38	0.65	0.24	0.22	15.0	0.36
	Max.	34.2	1.18	2.00	5.28	127	28.3
	Min.	9.10×10^{-3}	0.13	2.53×10^{-2}	5.44×10^{-3}	7.74×10^{-3}	8.00×10^{-5}
MPI	Average	2.90	0.23	1.04	3.72	7.52	59.3
	Median	1.08	0.23	0.51	2.10	7.53	3.57
	Max.	21.6	0.41	4.14	34.5	65.4	283
	Min.	2.36×10^{-2}	6.20×10^{-2}	2.00×10^{-2}	2.98×10^{-2}	8.13×10^{-2}	8.44×10^{-3}

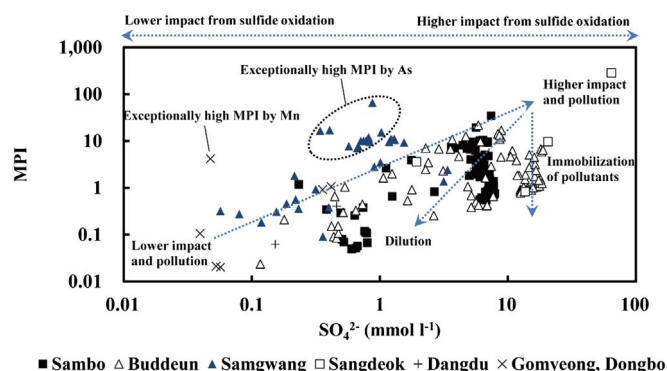
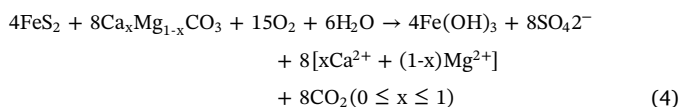


Fig. 8. Plots of SO_4^{2-} concentration versus MPI (Mine Pollution Index) value for water samples from a regional reconnaissance and detailed (using MLS) surveys.



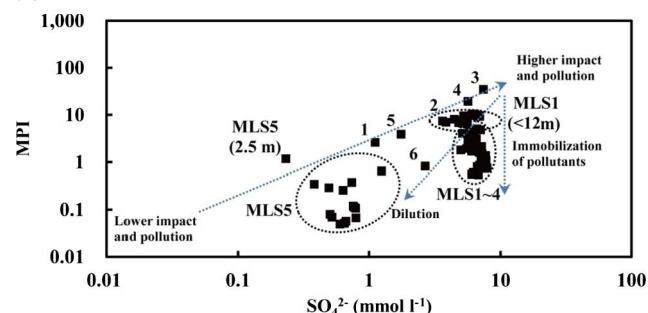
where Fe species generated from pyrite are precipitated as Fe-(hydr) oxides, and calcite with some content of Mg reacts with H^+ to produce Ca^{2+} and Mg^{2+} . Some H^+ may also promote dissolution of Ca- and Mg-silicates in addition to carbonates, producing Ca^{2+} and Mg^{2+} in a similar fashion. Consequently, the molar sum of Ca and Mg can be similar to that of produced SO_4^{2-} . Toran (1987) also reported a very good correlation ($R = 0.99$) between SO_4^{2-} and Ca plus Mg as a consequence of dissolution of dolomite in a specific carbonate aquifer near Shullsburg, Wisconsin, USA.

Samples from the Sangdeok coal mine area deviate from the 1:1 line and show the deficient Ca + Mg, while the concentration of Mg is higher than the regression line for the other metalliferous mines (Fig. 6b and c). Furthermore, a leachate sample with the highest SO_4^{2-} concentration (64.36 mM) showed the Ca + Mg of 34.34 mM and pH of 3.8 (not indicated in Fig. 6c), which can plot near the regression line for other samples from the Sangdeok mine. This indicates that, in the Sangdeok coal mine area, CaCO_3 is possibly lacking during the course of groundwater movement, resulting in insufficient buffering of the acid leachate from waste rock pile.

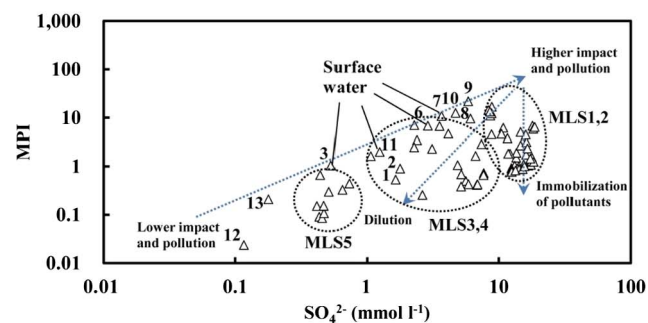
Several geochemical indicators, such as SO_4^{2-} , pH, Fe, and other metal ions, are used to quantitatively evaluate the environmental impact of mines. Among them, Fe and other heavy metals in mine drainage are prone to precipitation or adsorption, while Ca, Mg, and H^+ are susceptible to secondary reactions with carbonate or silicate minerals (Drever 1997). The concentration of SO_4^{2-} directly reflects the degree of sulfide oxidation, though it can also be changed by subsequent mixing with non- or less-contaminated water.

In the mine drainages examined in the present study, increasing concentration of SO_4^{2-} effectively results in the increase of EC (Fig. 7), together with the increase of Ca and Mg (Fig. 6). Since, in the studied mines, both sulfate reduction and the presence of gypsum are not evident, SO_4^{2-} can be effectively used as an indicator of mine impact. The

(a) Sambo mine



(b) Buddeun mine



(c) Samgwang mine

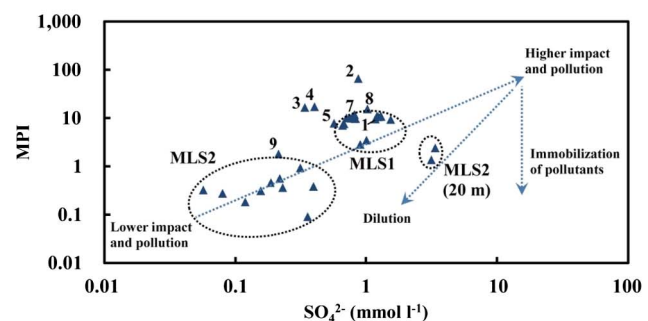


Fig. 9. Plots of SO_4^{2-} concentration versus MPI (Mine Pollution Index) value for water samples from a regional reconnaissance and detailed (using MLS) surveys: (a) Sambo, (b) Buddeun, and (c) Samgwang mines.

ratios of the SO_4^{2-} concentrations between a sample and the non-contaminated “background” sample were calculated for water samples from the Buddeun, Samgwang, and Sangdeok mines where background water could be sampled from upstream sites of surface water (Table 4); the SO_4^{2-} concentrations of background samples were 5 mg L^{-1} for Buddeun (sample #4), 6 mg L^{-1} for Samgwang (sample #6), and 4 mg L^{-1} for Sangdeok (sample #1). The calculated SO_4^{2-} concentration ratio is the highest for Sangdeok (1.00–1510, average = 472; Table 4), because the mine drainage from Sangdeok

had very high SO_4^{2-} concentrations (6182 mg L^{-1}) and aluminum (376 mg L^{-1}) under low pH (3.8). On the other hand, the drainage from Samgwang has the range of 0.92–54.7 (average = 13.1; Table 4), reflecting low degrees of sulfide oxidation and consequent dissolution of metal ions, even though the samples have the high level of As contamination. Therefore, the ratio of the observed SO_4^{2-} concentration to the “background” concentration can be used as an indicator of the impact of mine; in this study, this indicator is named the Mine Impact Index (MII). Even so, the degree of water pollution can be better evaluated in an alternative way.

4.4. Mine pollution index (MPI)

To evaluate the degree of water pollution considering the environmental standards, HPI values were calculated for the samples from regional and detailed (using MLSs) surveys (Table 5). The ideal value (I_i) of each parameter was set to zero for two reasons: 1) the ideal beneficial concentration for each metal is different for human and ecosystem health and 2) the precipitates of Fe and other metals common in mine areas may pose secondary environmental hazards (Bowell and Bruce 1995; Younger et al. 2002). In addition to common heavy metals (Cd, Cu, Fe, Mn, Pb and Zn) and As, Al may also cause an adverse effect on health (WHO, 2011). Similarly, SO_4^{2-} is common in mine areas and is regulated as the drinking water quality standards in the U.S. and Korea. Using the drinking water quality standards in South Korea as the environmental standard (S_i), the HPI values for the studied mines were calculated.

The results of HPI calculation show that the drainages from Samgwang, Sangdeok, and Buddeun have very high HPI values (average > 2.79), while those from Sambo has the low average HPI value (average 0.49; Table 5), even though the Sambo mine exhibits a significant contamination by Cd, Fe, Mn and Zn. A sample from Dangdu (sample #1) exceeded only the environmental limit of Cd ($5 \mu\text{g L}^{-1}$), but had a similar HPI value (1.18) to a sample from Sambo (1.23; sample #2) whose concentrations of Mn, Al, Zn, and SO_4^{2-} are 43 times, 4.1 times, 1.4 times, and 1.8 times higher than the respective environmental limits. Such unreasonable results of evaluation stem from the fact that the metal species with very low levels of environmental standard (e.g., Cd) may have a very high unit weightage, as the HPI value uses the reciprocal value of an environmental standard for unit weightage. Thus, the application of HPI values without unit weightage can be more reasonable. Therefore, we suggest the use of a modified indicator named the MPI.

Our samples from regional and detailed (using MLSs) surveys were evaluated using the MPI (Table 5). The Sangdeok mine shows the highest maximum (283) and average (59.3) values, because the highly acidic condition leaches high concentrations of various metals (especially, aluminum with the maximum MPI(Al) value of 1882; sample #5). The Samgwang mine also exhibits the high maximum (65.4) and average (7.52) MPI values, especially due to the pollution by As. At Samgwang, the MPI values for As ranged between 14.2 and 521 for the samples from the regional survey, except for one background sample. The MPI values for Sambo and Buddeun are 2.98×10^{-2} to 34.5 (avg. 3.72) and 2.36×10^{-2} to 21.6 (avg. 2.90), respectively. On the other hand, most samples from Gomyeong, Dongbo, and Dangdu have relatively low MPI values (Table 5).

4.5. Sulfate versus MPI plots: Evaluation of the evolution of mine drainage

The plots of dissolved SO_4^{2-} versus MPI values for the samples from regional and detailed (using MLSs) surveys are shown in Fig. 8. As described above, the environmental impact from sulfide oxidation can be indicated by the SO_4^{2-} concentration. Both MPI value and SO_4^{2-} concentration are low for Gomyeong, Dongbo, and Dangdu, while the values are higher for Sambo, Buddeun, and Sangdeok. In the diagram, the decrease of MPI can result from the mitigation of pollutants through

immobilization processes, such as sorption onto geologic media including (hydr)oxides. Therefore, such immobilization process can be indicated by a downward arrow in Fig. 8 and can also occur through artificial immobilization of pollutants during mine water treatment. If mixing and dilution by ambient water occur, the evolution of water may follow the diagonal direction (toward the lower left in the figure). However, there are some exceptional samples from Samgwang and Dongbo with a lower SO_4^{2-} concentration, but higher MPI values. The samples with a high MPI at Samgwang have high As concentrations. This is certainly because the environmental criteria for As (0.01 mg L^{-1}) is the lowest among the constituents of the MPI and, therefore, the individual MPI(As) values are very high. A leachate sample from mine tailings of Dongbo has the high MPI value due to the high Mn concentration (9.9 mg L^{-1}) even with the low concentration of SO_4^{2-} (5 mg L^{-1}) and other metal ions. For the sample, HCO_3^- is as high as 313 mg L^{-1} ; therefore, carbonate such as rhodochrosite (MnCO_3) is considered as the source of Mn contamination at Dongbo.

The surface water samples (plots 1 to 5) from Sambo, except for sample #6, plot along the line of “initial” impact and pollution (i.e., from the lower left to the upper right in Fig. 9a). The groundwater samples from multilevel samplers 1 to 4 plot below the adjacent surface water samples (#2, #3, and #4), while groundwater samples collected at the depth of < 12 m below ground surface in MLS1 plot between the surface and groundwater samples (Fig. 9a). This suggests that metals are effectively immobilized in groundwater. Plots of the groundwater samples from MLS5 and a surface water sample (#6) collected at downstream sites from mine tailings indicate the effect of dilution with ambient less-contaminated water. The chemistry of surface water (sample #6) might be changed by the interaction between surface water and groundwater, because the groundwater level near the site is higher than the ground level.

At Buddeun, the samples with the highest MPI and SO_4^{2-} concentrations are groundwater from MLS1, MLS2, and preexisting monitoring wells (#8, #9, #10) near tailing dump #1 (Fig. 9b). For surface water samples, decreasing of MPI and SO_4^{2-} are observed with the increasing distance from the tailings (i.e., from samples #7 and #6 to #11; see Fig. 2 for localities except #11 at 1.2 km downstream), indicating a remarkable dilution effect. Meanwhile, groundwater samples from MLS1 and MLS2 to MLS5 and samples #12 and #13 (ca. 1.2 km downstream) shows lower MPI than contaminated surface water samples. This also indicates a more effective reduction of MPI in groundwater system. Similarly, most groundwater samples at Samgwang have lower MPI values than surface water samples (Fig. 9c). Downstream surface water (sample #9) and groundwater (MLS2) also show the significant dilution effect.

Therefore, the SO_4^{2-} versus MPI plot can be effectively used to characterize and evaluate the evolution of mine-drainage affected water. Immobilization process can be discerned by the vertical decrease of MPI in the diagram and is more distinct in groundwater than surface water. Dilution process by mixing is also revealed by the relatively large decreases of MPI and SO_4^{2-} in the diagram.

5. Conclusions and implications

In the present study, we investigated geochemical characteristics and evolution of surface and ground water influenced by mine drainage from six metallic mines and one coal mine in South Korea. The order of the mitigation of metal species in mine drainages of metalliferous mine areas was found to be generally $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$, i.e. in accordance with the general order of the susceptibility of sorption. Among the metal species, Zn and Cd exhibit similar but slightly different behavior during the generation and evolution of mine drainage. The Zn/Cd ratios of tailings are lower than those of ores, and the ratios of leachate are higher than those of tailings and ochre precipitates. This reflects more chalcophile characteristic and/or preferred scavenge (esp., sorption onto ferric hydroxides) of Cd than Zn.

The approximate 1:1 relationship (0.99:1, $r^2 = 0.98$) was observed between dissolved SO_4^{2-} and the molar sum of Ca^{2+} and Mg^{2+} in the water samples from metallic mines, which indicates that dissolution (i.e., neutralization) of $(\text{Ca},\text{Mg})\text{CO}_3$ and silicates following pyrite oxidation is the major geochemical control of mine drainage. Accordingly, dissolved SO_4^{2-} compared to metal species can be used as a more useful indicator of the impact of mining, because 1) it is less prone to precipitation and/or adsorption and 2) it shows a good relationship with the sum of Ca and Mg as an indicator of the pH buffering of mine drainage (i.e., SO_4^{2-} can maintain the conservative nature even after substantial buffering reactions). Therefore, the concentrations of Ca + Mg and EC can also be used to evaluate the degree of the mine impact for mine drainages under circumneutral pH condition.

We have verified the use of the heavy metal pollution index and suggest the modified pollution index consisting of Al, As, Cd, Cu, Fe, Mn, Pb, SO_4^{2-} and Zn as the mine pollution index (MPI) to overall quantify the degree of pollution (esp., risk) relative to the water quality standards. A diagram showing the SO_4^{2-} versus MPI plots is very beneficial in terms of characterizing and evaluating the pollution status. The degree of impact and pollution can be effectively evaluated in terms of the “initial” condition (i.e., formation of mine drainage) and pathways accompanying immobilization (precipitation/sorption) and dilution in mine drainage-affected surface and ground water. Immobilization of pollutants was especially obvious in the groundwater systems, suggesting appropriate utilization of groundwater in mine-impacted area.

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