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Effect of mining and geology on the chemistry of stream water and sediment in a small watershed

Jae Gon Kim*, Kyung-Seok Ko — *Korea Institute of Geoscience and Mineral Resources, 30 Gajeong-dong Yuseong-gu, Daejeon 305-350 Korea*
Tack Hyun Kim — *Mine Reclamation Corporation, 79-4 Hwangji-dong, Taeback, Gangwon-do 300-090 Korea*
Gyoo Ho Lee — *Korea Gas Corporation, 215 Jeongja-dong Bundang-gu, Seongnam, Gyeonggi-do 463-754 Korea*
Yungoo Song — *Dept. of Earth System Sciences, Yonsei University, 134 Shinchon-dong Seodaemun-gu, Seoul 120-749 Korea*
Chul-Min Chon, Jin-Soo Lee — *Korea Institute of Geoscience and Mineral Resources, 30 Gajeong-dong Yuseong-gu, Daejeon 305-350 Korea*

ABSTRACT: Chemical characteristics of the stream water and sediment in the small watershed with two distinctive mineralization zones (Cu and Pb-Zn), 7 abandoned mines and an active quarry were investigated to examine the effects of mining activity and regional geology on the chemistry. The stream water affected by the abandoned mines had Ca-SO_4 type but the other had Ca-HCO_3 type. The mine affected stream water and sediment showed relatively high concentrations of metals (Cu, Pb, Zn, Cd, Co, Ni, Mn, Al and Fe). The concentrations of Al, Mn, Fe and Cu of the stream water collected near an abandoned mine (Guryong) exceeded the EPA surface water quality standards (Al: 5.52 mg L^{-1}, Mn: 1.58 mg L^{-1}, Fe: 1.49 mg L^{-1}, Cu: 0.63 mg L^{-1}). The effect of mining activity on the stream water chemistry was attenuated in a relatively short distance from the source (< 200 m) along the watercourse but the signature in the sediment showed a longer lasting effect (about 2 km) than that in the stream water. The residual and reducible forms were the dominant fractions of the heavy metals in the stream sediment. The particulate transportation was the major cause of the dispersion of heavy metals in the watershed. There was a contrasting spatial distribution of background metal concentration in the stream sediment: a relatively higher concentration of Cu in the Cu mineralization zone and a relatively higher concentration of Pb, Zn and Mn in the Pb-Zn mineralization zone.

Key words: abandoned mine, active quarry, heavy metals, mineralization zones

1. INTRODUCTION

Chemistry of the stream water and sediment in a watershed is depending on the physical, chemical and biological processes involving regional geology, biological characteristics, climate and human activity (Pinol et al., 1992; Fukushima et al., 2000; Holloway and Dahlgren, 2001; Garcia-Sanchez and Alvarez-Ayuso 2003; Ohta et al., 2005). The major ion chemistry of natural water can be explained by the reaction of water with rock and sediment along the watercourse. In addition to the natural processes, agricultural activity, urbanization and mining in the watershed modify the chemistry of stream water and sediment (Gurrieri 1998; Wenchuan and Kelderman, 2001; Ohta et al., 2005). The agricultural activity and the urbanization in a watershed increase the electrical conductivity (EC) and the concentrations of Cl^-, base cations and nutrients of the stream water and sediment.

Mining activities have left the contamination of river and stream with toxic heavy metals around world (Gurrieri 1998). Metals released from mining sites have often obscured the natural loading of metals to the stream water and sediment (Prusty et al., 1994; Wenchuan and Kelderman, 2001; Wilson et al., 2005). The heavy metals disturb or severely damage the ecosystem of the mine waste affected streams (Gurrieri, 1998). It has been known that heavy metals enter into stream by the discharge of acid mine drainage (AMD) and/or by the direct loading of heavy metal containing mine tailings. Even though long after mining has been ceased, heavy metals from mine wastes may enter into the stream via physical erosion and geochemical input (Helgen and Moore 1996; Pirrie et al., 1997; Pirrie et al., 2002). For many cases, the sediments retain the geochemical and mineralogical record of the mining history within the fluvial catchment although the mine waste is not chemically mobile or physically reworked (Leblanc et al., 2000).

Discrimination between the sources of mining impacts on the stream water and sediment in a watershed is often complicated due to mixing of the original chemical and mineralogical signatures along the watercourse (Helgen and Moore 1996; Helgen and Davis, 2000). It makes difficult to discriminate the relative impact of each source on downstream resources. The natural background and the discrimination of the relative impact of multisources are important for the prediction and management of downstream dispersion of heavy metals and for the identification of ownership for the contamination.

Most metal mines in Korea have been abandoned since 1970s. Heavy metal dispersion from the abandoned mines

*Corresponding author: jgkim@kigam.re.kr

and the resulting contamination of surrounding area are current environmental concerns. In order to manage the old mines without present owner or property rights, Korean government took the responsibility to carry out the inventory, characterization and remediation. The objectives of this study were to examine the impacts of mining activities and regional geology on the chemistry of stream water and sediment and to allocate the responsibility of contamination among multiple sources in a small watershed.

2. MATERIAL AND METHODS

2.1. Characteristics of the Study Site

The study site is a typical agricultural area and is located in the southern part of Korea. The surface area of the studied watershed is about 300 km^2 draining from south to north and the regional geology consists of Cretaceous sedimentary rock (chert, conglomerate, sandstone and shale), andesitic volcanic rock and granite (Fig. 1). There are two distinctive mineralization zones in the watershed: Pb-Zn mineralization zone in the northern part and Cu mineralization zone in the southern part. The ore deposits are typically polymetallic sulfide type occurring as veins in the andestic volcanic rock. The andestic volcanic rock in the Cu mineralization zone had been undergone an intensive hydrothermal alteration producing pyrophyllite deposits with an extensive disseminated sulfides in the host rock. However, an intensive hydrothermal alteration was not observed in the bedrocks in the Pb-Zn mineralization zone.

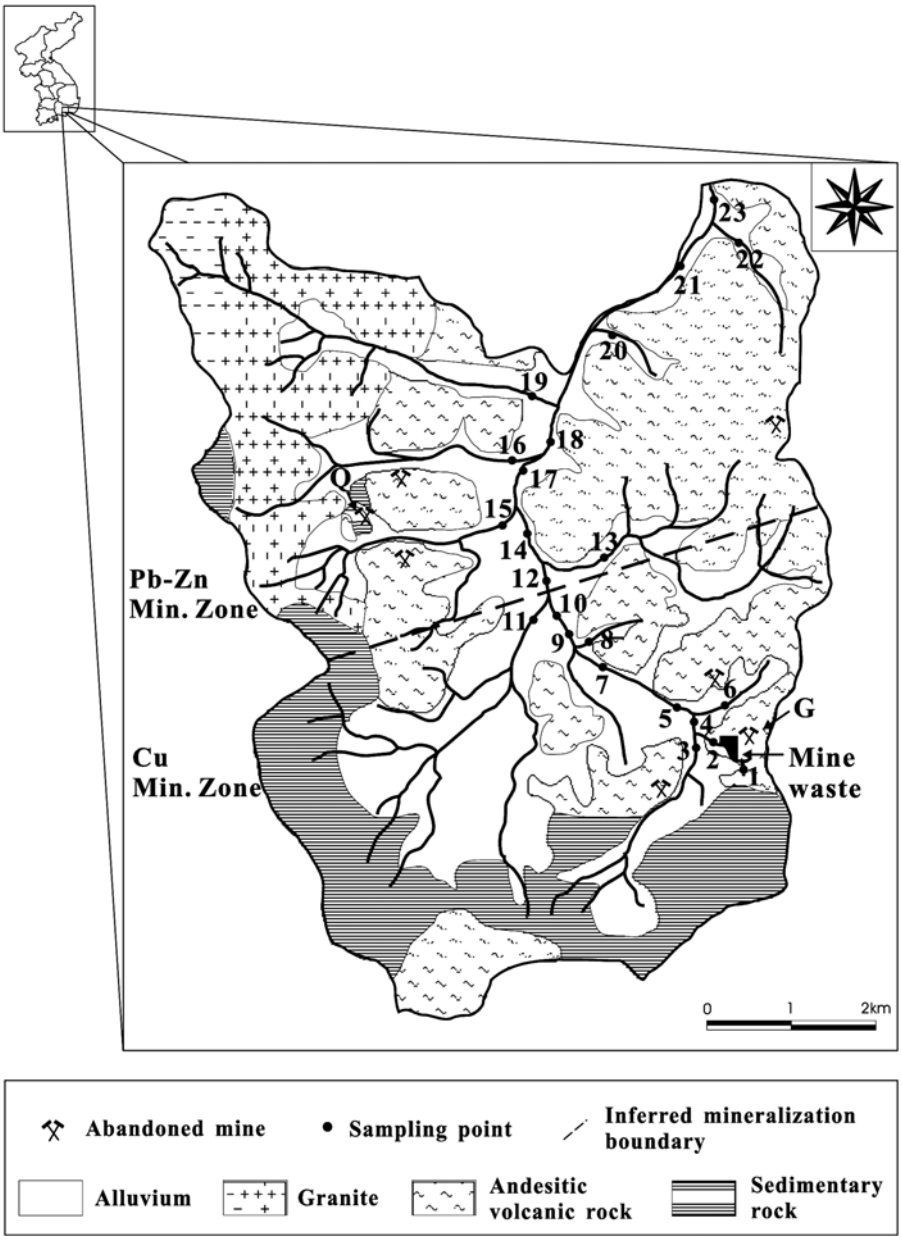

Fig. 1. Location, regional geology and sampling points for the stream water and sediment of the study site.

There are 7 abandon metal mines and one active quarry in the studied watershed: 3 abandoned mines in the Cu mineralization zone, and 4 abandoned mines and an active quarry in the Pb-Zn mineralization zone. Most mines in the watershed were abandoned since 1960s and there are no significant amounts of mine waste and no AMD discharge from mining sites except the last mine, Guryong mine. Guryong mine located in the Cu mineralization zone was operated until 1974. There are large amounts of waste rock and mine tailings in the surrounding area. Red and white colored precipitates were also observed on the streambed nearby Guryong mine indicating the discharge of AMD from the mine wastes. One aggregate quarry is operating in the Pb-Zn mineralization zone and a white colored sediment was observed on the nearby streambed indicating the discharge of rock fragments from the quarry into the stream.

2.2. Sampling and Analysis

Twenty three stream water samples were collected from the main stream and tributaries during a dry season, July of 2003 (Fig. 1). The stream water samples were filtered with a 0.45 μm membrane filter and the alkalinity, electrical conductivity (EC) and pH of the filtered samples were determined within 30 minutes after the sampling in the field. The filtered water samples were stored in polyethylene bottles at 4 °C for the analysis of anions (Cl^-, F^-, NO_3^- and SO_4^{2-}). A portion of the filtered water sample was acidified to be pH < 2 using a concentrated HNO_3 and was stored in a polyethylene bottle for the analysis of major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and heavy metals (Al, As, Mn, Fe, Cu, Cd, Zn, Pb, Co and Ni).

Stream sediment samples were collected at the same sampling points for the stream waters. The sediment was wet-sieved in situ with a 63 μm sieve using the ambient stream water (Helgen and Moore, 1996). The collected sediment samples (< 63 μm) were stored in polyethylene zip bags at 4 °C and dried at 105 °C when we returned to the laboratory. The dried samples were gently ground with a rubber stopper for the chemical and mineralogical analysis.

Mineralogical composition of the sediments was determined with an X-ray diffractometer (XRD, MAC Science MXP 18A Rint-2500) and a scanning electron microscope equipped with an energy dispersive X-ray fluorescence spectroscopy (SEM-EDX, JEOL JSM-6400). Heavy metals in the stream sediments were fractionated into exchangeable, carbonate, reducible, oxidizable and residual forms using a sequential extraction method (Ahn et al., 2003). The detailed sequential extraction procedure is shown in Table 1. The total concentration of each heavy metal in the stream sediment was calculated by the summation of the fractions.

The concentrations of anions in the stream water samples were determined with an ion chromatography (IC, Dionex DX-120). The concentrations of major cations and metals in the stream waters and the extracts were determined with an induced coupled plasma atomic emission spectrometer (ICP-AES, Jobin Yvon Plus-70). Chemical data were processed using a statistics computer program XLSTAT® (Andinsoft Co., NY, USA) to examine the relationship between the samples. The multivariate analysis is a group of statistical techniques (Meglen, 1992). It enables us to calculate multivariables and allows us to consider co-variations in several properties simultaneously. Correlation coefficients are indices that measure the strength of a relationship between variables. Principal component analysis (PCA) carried out on the correlation matrix can find the latent variables that can explain the variance in the correlation matrix and can simultaneously reduce the dimensionality of the problem.

3. RESULTS AND DISCUSSION

3.1. Stream Water

The chemical characteristics of the stream water are shown in Table 2. The stream water sample 2 collected nearby Guryong mine was highly acidic (pH 3.9) and the others except the stream water sample 15 were near neutral. It had the highest concentrations of SO_4^{2-}, major cations and heavy metals. The stream water sample 15 collected at the tributary draining from the active quarry had pH 8.0 and the highest concentration (72.8 mg L^{-1}) of HCO_3^-. The quarry was located on the geologic boundary of sedimentary rock and andesitic volcanic rock.

Calcium was the dominant major cation of the stream waters and HCO_3^- and SO_4^{-2} were the dominant major anions (Table 2 and Fig. 2). The stream water sample 2, 5, 6, 7, 9, 10 and 12 were plotted in the region of $Ca–SO_4$ type in the piper diagram but the others were plotted in the region of

Table 1. Procedure of the sequential extraction method (Ahn et al. 2003) for Cu, Pb, Zn, Cd, Mn and Fe of the stream sediment samples

Fraction	Procedure	Target forms of metals
Exchangeable	pH 7 1.0M $MgCl_2$, reaction at room temperature for overnight	Nonspecifically adsorbed
Carbonate	0.16M HOAc, reaction at room temperature for overnight	Carbonate
Reducible	pH 2.0 $NH_2OH·HCl$, reaction at room temperature for overnight	Fe and Mn oxides
Oxidizable	30% H_2O_2 reaction at 85 °C for 1 hr and to near dry; then pH 2.0 1M NH_4OAc reaction at room temperature for overnight	Organic and sulfide
Residual	36% HCl(3) + 62% HNO_3(1), reaction at 70 °C for 1.5hr	Recalcitrant residual

Table 2. Chemical characteristics of the stream water samples.

ID	pH	EC	HCO_3^-	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na	K	Ca	Mg	Al	Mn	Fe	Cu	Zn	Pb	Co	Ni
		$\mu S\ cm^{-1}$	----------				mg L^{-1}	----------				----------			$\mu g\ L^{-1}$	----------			
1	7.6	93	17.7	ND	5.5	14.2	9.3	5.7	1.1	6.1	2.0	37.7	25.8	24.3	4.5	6.8	0.7	1.1	10.9
2	3.9	402	ND	ND	5.1	13.6	199.0	8.1	2.0	26.6	9.8	5520.0	1580.0	1490.0	631.1	123.2	13.0	16.9	18.4
3	6.5	115	42.4	0.6	4.0	12.7	9.4	7.3	1.7	10.0	2.2	28.1	23.1	36.5	3.9	2.8	3.3	1.0	10.2
4	7.0	124	39.2	0.5	4.1	12.5	15.7	7.1	1.9	12.3	3.2	31.1	204.0	38.3	31.2	13.9	0.9	2.3	10.7
5	6.8	146	27.2	0.5	4.4	12.0	29.5	7.3	1.7	10.7	2.5	49.9	99.1	23.8	16.9	6.9	2.2	1.5	9.6
6	6.8	154	21.5	0.5	5.0	9.1	40.7	6.3	2.3	12.6	3.8	30.7	174.0	22.6	22.5	14.0	3.0	2.1	9.9
7	7.0	145	27.2	0.5	4.3	12.1	28.8	7.0	1.9	12.0	3.2	32.0	197.1	21.7	26.8	13.4	1.9	2.4	11.0
8	7.1	111	29.7	0.6	5.4	7.1	12.9	6.2	3.6	7.4	3.0	20.3	14.3	32.6	4.0	2.4	2.0	1.0	9.1
9	7.1	147	27.8	0.5	4.8	11.8	28.3	7.4	2.1	12.2	3.2	33.6	181.2	11.4	22.3	11.7	0.8	1.9	11.4
10	7.1	145	27.5	0.5	4.7	11.6	28.1	7.3	2.2	12.0	3.2	35.4	148.2	10.3	18.5	12.3	1.4	1.4	11.3
11	7.6	135	46.2	ND	4.7	7.8	11.1	7.1	2.1	12.4	2.6	14.8	21.8	29.0	3.9	2.8	1.2	0.9	8.9
12	7.5	141	29.7	0.5	4.7	10.5	23.0	7.3	2.1	12.3	3.1	35.7	111.5	14.1	12.7	7.2	2.1	1.5	13.2
13	7.5	146	45.6	ND	5.7	7.8	12.9	7.4	3.7	12.4	3.1	16.5	15.9	34.0	3.75	2.9	0.7	1.2	9.4
14	7.5	144	40.5	ND	5.0	9.2	18.2	7.6	2.8	12.7	3.1	27.8	65.5	22.7	8.9	4.9	ND	0.9	10.9
15	8.0	199	72.8	ND	5.6	13.7	20.6	10.8	2.9	20.7	4.0	26.2	33.5	15.4	4.0	3.3	2.5	1.4	10.9
16	7.6	192	62.6	ND	10.1	11.7	15.0	12.6	3.0	18.4	3.7	6.4	20.3	18.6	3.6	2.8	0.2	1.1	10.6
17	7.2	149	48.7	0.6	5.5	9.6	18.4	8.0	2.5	13.9	3.1	20.5	79.0	31.7	7.5	5.3	0.9	1.2	7.3
18	7.3	154	48.1	ND	5.5	9.0	18.4	8.4	2.7	14.3	3.3	17.3	83.8	42.6	6.8	4.5	1.1	0.8	7.6
19	7.4	164	53.8	ND	6.0	12.1	14.9	10.1	2.6	16.2	2.9	5.8	24.0	14.9	3.5	3.1	2.6	0.5	10.3
20	7.4	165	41.8	0.5	11.6	13.1	13.9	11.2	5.1	12.3	2.8	10.9	22.9	17.8	3.9	20.1	0.3	0.9	9.2
21	7.3	161	48.1	0.2	6.6	9.0	18.1	8.9	2.8	15.0	3.4	11.7	93.8	42.6	5.3	3.7	ND	0.4	6.0
22	7.1	192	55.4	0.3	7.2	16.0	23.7	10.5	6.3	16.5	4.3	5.5	74.3	13.1	4.3	29.2	5.0	1.1	14.9
23	7.3	162	50.0	ND	6.0	9.2	18.4	9.1	2.9	15.1	3.5	12.3	94.2	40.3	5.3	3.9	2.6	1.0	5.2

ND: not detected

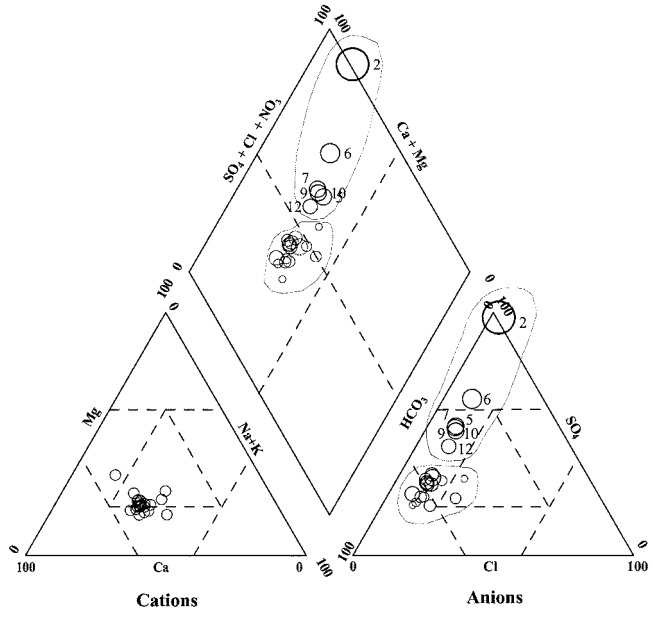

Fig. 2. Piper plot of the major cations and anions of the stream water samples from the watershed. The size of circles in the diagram represents for the relative concentration of SO_4^{2-}.

Ca-HCO_3 type. The stream water sample 5, 7, 9, 10 and 12 were collected from the main stream in the downstream of the sampling point 2. It indicates that they were affected by Guryong mine. The stream water sample 6 was collected at the tributary draining from the area of the andestic volcanic rock with an extensive disseminated sulfides and an abandoned mine. There was no evidence of mine waste and AMD discharge from the upstream to the sampling point 6 in the field. The field observation indicates that the chemistry of the stream water sample 6 is controlled by the regional geology. The SO_4^{2-} concentration of the stream water gradually decreased with increasing distance along the watercourse from 2 to 12 (199 to 23 mg L^{-1}). The stream water sample 2 also had the highest concentrations of metals (Al, Mn, Fe, Cu, Zn, Pb, Co, and Ni). The concentrations of Al, Mn and Fe of the stream water sample 2 exceeded the EPA surface water quality standard: 5.52 mg L^{-1} of Al (1.0 mg L^{-1}), 1.58 mg L^{-1} of Mn (0.05 mg L^{-1}) and 1.49 mg L^{-1} of Fe (0.3 mg L^{-1}). The acidity was neutralized and the concentrations of metals were reached to the average concentrations within 200 m of downstream from the sampling point 2.

The correlation coefficients of the concentrations of ions (15 variables) for the stream waters are shown in Table 3. Sulfate (SO_4^{2-}) showed a strong positive correlation with Ca, Mg, Si, Fe, Mn, Al, Cu and Zn, and HCO_3^- with Na, K and Sr. Bicarbonate (HCO_3^-) showed a strong negative correlation with SO_4^{2-}, Al, Cu, Zn, Mn and Fe. Eigenvector, factor loading, eigenvalue and variance in the principal component analysis (PCA) for the chemical properties of

Table 3. Correlation matrix of the concentrations of cations and anions in the stream water samples (n=23).

	HCO_3	Cl	NO_3	SO_4	Ca	Mg	Na	K	Si	Al	Cu	Sr	Zn	Mn	Fe
HCO_3	1														
Cl	0.383	1													
NO_3	-0.048	0.185	1												
SO_4	-0.584	-0.119	0.240	1											
Ca	0.180	0.217	0.274	0.672	1										
Mg	-0.351	0.013	0.233	0.948	0.822	1									
Na	0.687	0.781	0.340	-0.047	0.590	0.161	1								
K	0.443	0.640	0.113	-0.148	0.175	0.057	0.572	1							
Si	-0.108	0.049	0.548	0.703	0.721	0.745	0.356	0.016	1						
Al	-0.540	-0.079	0.234	0.981	0.661	0.933	-0.023	-0.142	0.731	1					
Cu	-0.563	-0.103	0.239	0.986	0.654	0.934	-0.045	-0.162	0.724	0.998	1				
Sr	0.579	0.348	0.181	0.255	0.870	0.468	0.758	0.267	0.446	0.249	0.233	1			
Zn	-0.557	-0.001	0.374	0.967	0.644	0.932	0.021	0.011	0.711	0.963	0.968	0.219	1		
Mn	-0.600	-0.154	0.243	0.990	0.644	0.935	-0.085	-0.194	0.689	0.982	0.991	0.212	0.967	1	
Fe	-0.531	-0.079	0.216	0.977	0.660	0.931	-0.024	-0.141	0.721	0.999	0.997	0.251	0.959	0.980	1

the stream waters are shown in Table 4. The first three components explained 88.2% of the data variation. Principal component 1 (PC1) accounting for 55.8% of the total variation reflects the typical AMD parameters such as SO_4^{2-}, Mg, Si, Al, Cu, Zn, Fe and Mn. Principal component 2 (PC2) including HCO_3^-, Cl^-, Na^+, K^+ and Sr^{2+} accounts for 25.0% of the total variation and is probably reflecting the regional geology. The principal component score biplot using the first two components, as they accounted for 80.8 % of the total variation, showed that the stream water sample 2 was governed by PC1 and characterized by higher concentrations of SO_4^{2-} and metals (Fig. 3). The PC2 positively affected on the chemistry of the stream water samples from the Pb-Zn mineralization zone but negatively affected on the chemistry of the stream water samples from the Cu mineralization zone. Some stream water samples collected from the tributaries (sample 15, 16 and 22 from Pb-Zn mineralization zone; sample 1 and 8 from Cu mineralization zone) showed a strong effect of PC2 either in positive or negative manner. The stream water samples collected near the boundary of the two mineralization zones (sample 11 and 13) had a moderate effect of PC2.

The stream water chemistry in the studied watershed was mainly controlled by the AMD from Guryong mine and the regional geology (the two mineralization zones). The chemistry of stream water (concentrations of ions, pH and EC) affected by Guryong mine were attenuated within a relatively short distance along the watercourse. The active quarry also affects the stream water chemistry but the effect (the concentrations of HCO_3^- and Ca^{2+}) was attenuated within 200 m of the downstream along the watercourse.

3.2. Stream Sediments

All stream sediments collected from the studied watershed had a similar mineralogical composition consisting of quartz, feldspar and mica as the major minerals and kaolinite, vermiculite, amphibole and chlorite as the minor minerals (Fig. 4). The stream sediment sample 15 contained a significant amount of dolomite. The stream sample 2 had a significant amount of noncrystalline Fe and Al hydroxide and oxide (confirmed by XRF data but not presented in this paper). However, the presence of Fe and Al hydroxide and oxide was not detected with XRD and it might be due to their poor crystallinity. The EDX data of SEM revealed that they contained a significant amount of heavy metals (Fig. 5). It implies that the heavy metals can be dispersed with them to the downstream.

The total Cu concentration of the stream sediment samples showed a spatial contrasting pattern with the total concentrations of Pb, Zn and Mn: a higher Cu concentration in the Cu mineralization zone and a higher Pb, Zn and Mn concentration in the Pb-Zn mineralization zone (Fig. 1 and 6). The stream sediment sample 2, 5, 6, 7, 9, 10, 12, 14, 17, and 19 had higher Cu concentration than the average level (150 mg kg^{-1}). The stream sediment sample 15, 17, 18, 21, 22 and 23 had higher concentrations of Pb, Zn and Mn than the average levels (Pb: 100 mg kg^{-1}, Zn: 400 mg kg^{-1} and Mn: 5,000 mg kg^{-1}). The stream sediment sample 2 had higher concentrations of Zn, Pb, Fe and Cd than their average levels of the watershed too. The stream sediment sample 15 had the highest concentrations of Mn, Pb and Zn among the sediment samples from the Pb-Zn mineralization zone.

The residual fraction was the dominant form of Cu, Cd, Zn and Fe for the stream sediment samples (Fig. 6). However, the stream sediment sample 15 contained about 40% of total Zn as the oxidizable fraction including sulfide and organic forms. The stream sediment sample 17, 18, 21 and 23 collected from the downstream of the sampling point 15

Table 4. Eigenvalue, variance, eigenvector and factor loading in the principal component analysis of the stream water chemistry.

Eigenvalues					
	PC1	PC2	PC3	PC4	PC5
Eigenvalue	8.368	3.744	1.114	0.962	0.420
% variance	55.785	24.957	7.428	6.413	2.802
Cumulative	55.785	80.742	88.170	94.584	97.385
Eigenvectors					
	PC1	PC2	PC3	PC4	PC5
HCO_3^-	-0.159	0.407	-0.309	0.090	0.187
Cl^-	-0.013	0.382	0.417	-0.327	-0.601
NO_3^-	0.117	0.146	0.504	0.709	0.071
SO_4^{2-}	0.339	-0.074	-0.006	-0.078	-0.016
Ca	0.262	0.286	-0.305	0.026	0.034
Mg	0.335	0.054	-0.074	-0.137	0.152
Na	0.032	0.501	0.047	0.042	-0.256
K	-0.028	0.346	0.393	-0.425	0.686
Si	0.276	0.138	0.036	0.370	0.132
Al	0.339	-0.062	0.004	-0.085	-0.063
Cu	0.340	-0.075	0.005	-0.072	-0.058
Sr	0.126	0.404	-0.434	0.071	-0.038
Zn	0.335	-0.034	0.179	-0.077	0.085
Mn	0.338	-0.096	-0.006	-0.055	-0.031
Fe	0.338	-0.062	-0.007	-0.101	-0.064
Factor loadings					
	PC1	PC2	PC3	PC4	PC5
HCO_3^-	-0.459	0.788	-0.327	0.088	0.121
Cl^-	-0.037	0.739	0.440	-0.320	-0.390
NO_3^-	0.337	0.283	0.532	0.696	0.046
SO_4^{2-}	0.982	-0.142	-0.006	-0.077	-0.010
Ca	0.758	0.553	-0.322	0.026	0.022
Mg	0.968	0.104	-0.078	-0.135	0.098
Na	0.093	0.970	0.050	0.041	-0.166
K	-0.081	0.670	0.415	-0.417	0.444
Si	0.798	0.267	0.038	0.363	0.085
Al	0.982	-0.120	0.004	-0.083	-0.041
Cu	0.983	-0.144	0.005	-0.071	-0.038
Sr	0.365	0.782	-0.458	0.070	-0.025
Zn	0.970	-0.065	0.189	-0.075	0.055
Mn	0.977	-0.186	-0.007	-0.054	-0.020
Fe	0.978	-0.120	-0.008	-0.099	-0.041

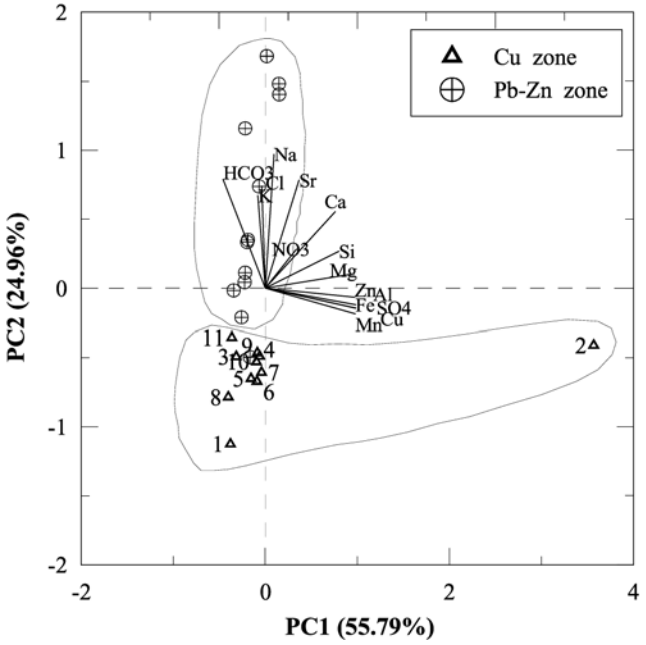

Fig. 3. Principal component score plot of the first two components (PC1 and PC2) accounting for 80.8% of the total variance of the stream water chemistry.

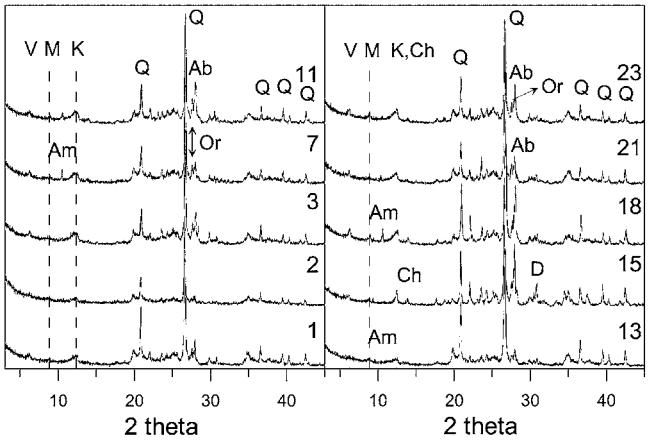

Fig. 4. XRD patterns of the selected stream sediment samples. V stands for vermiculite, M for mica, Ch for chlorite, Am for amphibole, K for kaolinite, Q for quartz, Or for orthoclase, Ab for albite and D for dolimite.

also contained a significant portion of oxidizable fraction of Zn. For Pb, the residual fraction was the dominant form for the stream sediment samples from the Cu mineralization zone but the reducible fraction was the dominant form for the stream sediment samples from the Pb-Zn mineralization zone. For Mn, the carbonate and residual fractions were the dominant forms for the all stream sediment samples.

The correlation coefficients of the total concentrations of Zn, Pb, Cd, Cu, Fe and Mn of the stream sediments are shown in Table 5. The total concentrations of Pb, Zn and Mn revealed a strong positive correlation each other and the total concentrations of Cu, Cd and Fe showed a strong positive correlation too. The total concentrations of Pb, Zn and Mn showed a negative or weak correlation with the total concentrations of Cu, Cd and Fe. Eigenvalue, variance, eigenvector and factor loading in PCA for the total concentrations of metals in the stream sediment samples are shown in Table 6. The result of PCA showed that the first three components explained 94.5% of the data variation. Principal component 1 (PC1) including Zn, Pb and Mn explains 48.8% of the total variation and PC2 (Cu, Fe and Cd) accounts for 33.8% of the total variation. The score

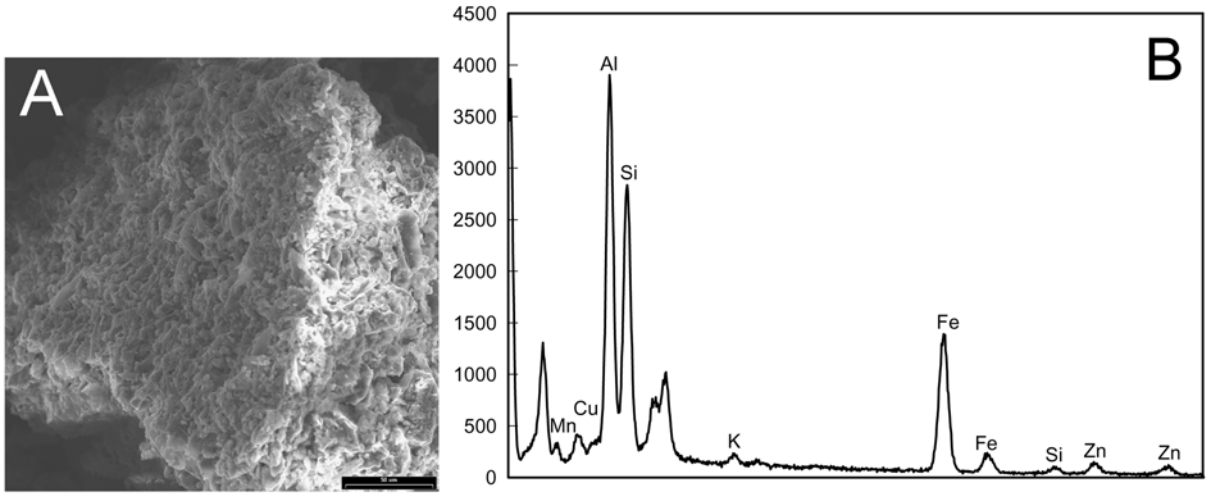

Fig. 5. SEM micrograph (A) and EDX data (B) of the stream sediment sample 2 collected nearby Guryong mine.

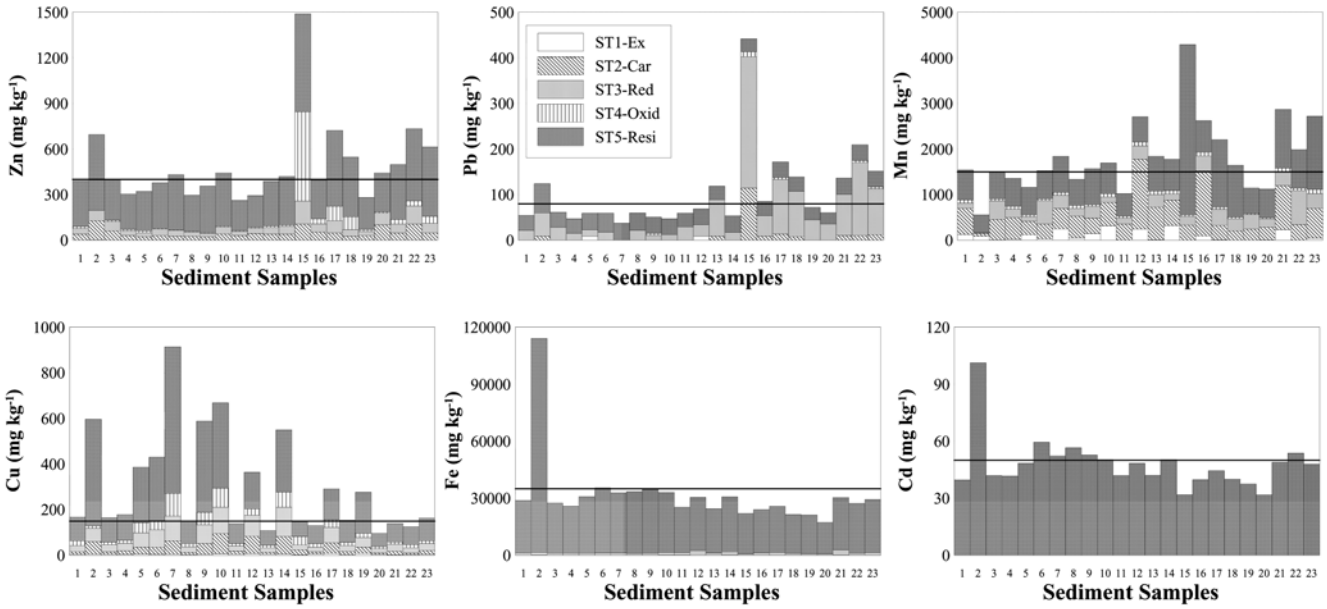

Fig. 6. Total concentrations and fractions of Cu, Pb, Zn, Cd, Fe and Mn of the stream sediment samples determined with the sequential extraction method. The solid lines in the figure stand for the background level of each metal.

Table 5. Correlation matrix of the total concentrations of Zn, Pb, Cd, Cu, Fe and Mn in the stream sediment samples (n=23).

	Cu	Cd	Pb	Zn	Fe	Mn
Cu	1					
Cd	0.501	1				
Pb	-0.326	-0.136	1			
Zn	-0.117	-0.012	0.950	1		
Fe	0.429	0.942	-0.042	0.100	1	
Mn	-0.215	-0.375	0.719	0.650	-0.352	1

biplot using the first two factors explaining 82.6% of the data variation showed that the stream sediment sample 15 was governed by PC1 and the stream sediment sample 2 by PC2 (Fig. 7). The other samples showed a mixed effect of PC1 and PC2 on the metal content.

Guryong mine and the active quarry were the major sources of metals in the stream sediments of the mainstream. The anomalous Cu concentration of the mainstream was mainly contributed from Guryong mine and the effect apparently lasted down to the sampling point 17 along the watercourse. The anomalous concentrations of Pb, Zn and Mn of the mainstream sediment samples in the Pb-Zn mineralization zone were due to the direct discharge of rock fragments from the active quarry into the stream. The metal loading from the active quarry impacted down to the sampling point 23 along the mainstream. The anomalous concentrations of

Table 6. Eigenvalue, variance, eigenvector and factor loading in the principal component analysis of the total concentration of metals (Zn, Pb, Mn, Cu, Cd and Fe) of the stream sediment samples.

			Eigenvalues			
	PC1	PC2	PC3	PC4	PC5	PC6
Eigenvalue	2.925	2.027	0.714	0.262	0.052	0.019
%variance	48.754	33.791	11.908	4.364	0.874	0.309
Cumulative	48.754	82.545	94.453	98.818	99.691	100.000
			Eigenvectors			
	PC1	PC2	PC3	PC4	PC5	PC6
Zn	0.403	0.480	0.012	-0.432	0.162	-0.628
Pb	0.472	0.390	-0.127	-0.227	-0.328	0.671
Cd	-0.385	0.494	-0.176	0.316	-0.641	-0.256
Mn	0.487	0.161	0.374	0.761	0.124	-0.048
Fe	-0.341	0.533	-0.273	0.148	0.663	0.253
Cu	-0.335	0.251	0.859	-0.247	-0.025	0.157
			Factor loadings			
	PC1	PC2	PC3	PC4	PC5	PC6
Zn	0.689	0.684	0.010	-0.221	0.037	-0.085
Pb	0.808	0.555	-0.108	-0.116	-0.075	0.091
Cd	-0.659	0.704	-0.148	0.162	-0.147	-0.035
Mn	0.838	0.230	0.316	0.389	0.028	-0.007
Fe	-0.584	0.759	-0.230	0.076	0.152	0.034
Cu	-0.573	0.357	0.726	-0.126	-0.006	0.021

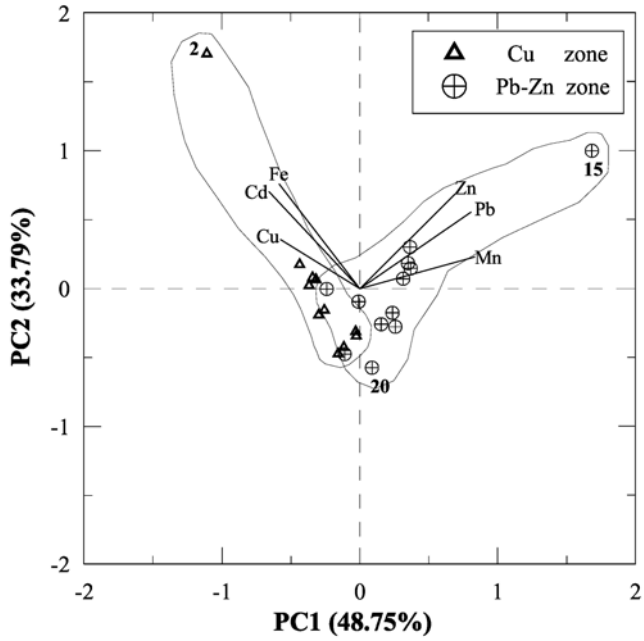

Fig. 7. Principal component score plot of the first two factors (PC1 and PC2) accounting for 82.6% of the variance of the stream sediment chemistry

metals of the sample 6 and 22 indicate that the abandoned mines located in the upstream of them have been loading metals into the stream even though there was a small amount of mine waste around the mines. The fractions of metals in the stream sediments indicate that the metals dispersed from Guryong mine to the downstream via oxide forms rather than sulfide. But the metals from the active guarry were loaded into the stream with rock fragments and they were slightly weathered to secondary forms during transportation along the watercourse.

4. CONCLUSIONS

The chemistry of the stream water and sediment in the studied watershed was mainly controlled by Guryong mine, the active quarry and the regional geology. The concentrations of SO_4^{2-} and heavy metals of the stream water were mainly controlled by from Guryong mine and the concentration of HCO_3^- was mainly controlled by the regional geology and the active quarry. The stream water sample collected nearby Guryong mine showed the highest concentrations of SO_4^{2-}, Ca, Mg, Al, Fe, Mn, Cu, Zn, Pb, Co and Ni and the lowest pH, and the sample collected from the tributary draining from the active quarry had the highest concentration of HCO_3^- and the highest pH. The effect of the historical mines and the active quarry on the stream water chemistry (concentration of cations and alkalinity) was attenuated in a relatively short distance along the watercourse (< 200 m). However, the SO_4^{2-} from the old mine had relatively longer lasting effect on the stream water chemistry comparing with heavy metals and HCO_3^-.

There were two distinctive spatial anomalous concentrations of Cu, Pb, Zn and Mn in the stream sediment samples:

higher Cu concentration in the Cu mineralization zone and higher concentrations of Pb, Zn and Mn in the Pb-Zn mineralization zone. The heavy metals from the abandoned mine, Guryong mine, was mainly dispersed to the downstream by Fe oxides and hydroxide. Heavy metals from the active quarry were mainly dispersed to the down steam by a direct loading of finely ground rock fragments into the watercourse. The signature of the mining activity and the regional geology in the stream sediment samples showed a relative longer effect than in the stream water.

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REFERENCES

Ahn J.S., Kim J.H., Kim J.G., Song Y. and Moon H.S., 2003, Laboratory investigation of the behavior of metals in paddy soils contaminated with mine tailings. Water, Air, and Soil Pollution, 150, 23–42.

Fukushima K., Nakajima R., Sato A. and Sakurai T., 2000, Relationships between stream water chemistry and catchment geology in a mountaineous region in Nagano Perfecture, Japan II: mid to southern part along the Median Tectonic Line. Limnology, 1, 117–127.

Garcia-Sanchez A. and Alvarez-Ayuso E., 2003, Arsenic in soils and waters and its relation to geology and mining activities (Salamance Province, Spain). Journal of Geochemical Exploration, 80, 69–79.

Gurrieri J.T., 1998, Distribution of metals in water and sediment and effects on aquatic biota in the upper Stillwater River basin, Montana. Journal of Geochemical Exploration, 64, 83–100.

Helgen S.O. and Davis A., 2000, Quantifying metal contribution from multiple sources to the Clark Fprk River, Montana, U.S.A. Journal of Environmental Forensics, 1, 55–62.

Helgen S.O. and Moore J.N., 1996 Natural background determination and impact quantification in trace metal-contaminated river sediments. Environmental Science and Technology, 30, 129–135.

Holloway J.M. and Dahlgren R.A., 2001, Seasonal and event-scale variations in solute chemistry for four Sierra Nevada catchments. Journal of Hydrology, 250, 106–121.

Leblanc M., Morales J.A., Borrego J. and Elbaz-Poulichet F. 2000, 4,500 year old mining pollution in southwestern Spain: Long term implications for modern mining pollution. Economic Geology and The Bulletin of The Society of Economic Geologists, 95, 655–662.

Meglen R.R., 1992, Examination of large database: a chemometeric approach using principal component analysis. Marine Chemistry, 39, 217–237.

Ohta A., Imai N., Terashima S. and Tachibana Y., 2005, Application of multi-element statistical analysis for regional geochemical mapping in Central Japan. Applied Geochemistry, 20, 1017–1037.

Pinol J., Avila A. and Roda F., 1992, The seasonal variation of stream water chemistry in three forested Mediterranean catchments. Journal of Hydrology, 140, 119–141.

Pirrie D., Power M.R., Wheeler P.D., Cundy A., Bridges C. and Davey G., 2002, Geochemical signature of historical mining: Fowey Estuary, Cornwall, UK. Journal of Geochemical Exploration, 76, 31–43.

Pirrie D., Camm G. S., Sear L.G. and Hughes S.H., 1997, Mineralogical and geochemical signature of mine waste contamination, Tresillian River, Fal Estuary, Cornwall, UK. Environmental Geology, 29, 58–65.

Prusty B.G., Sahu K.C. and Godgul G., 1994, Metal contamination due to mining and milling activities at the Zawar zinc mine, Rajasthan, India. Chemical Geology, 112, 275–291.

Wenchuan Q. and Kelderman P., 2001, Heavy metal contents in the Delft canal sediments and suspended solids of the River Rhine: Multivariate analysis for source tracing. Chemosphere, 45, 919–925.

Wilson B., Lang B. and Pyatt F.B., 2005, The dispersion of heavy metals in the vicinity of Britannia mine, British Columbia, Canada. Ecotoxicology and Environmental Safety, 60, 269–276.

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