Groundwater quality in the Shallow Aquifer nearby the Gubong gold-mine Tailings

구봉 금광산의 광미 인근지역의 천부지하수 수질특성

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Abstract : Gubong gold-mine, previously one of the largest gold mines in Korea, is located at the mid-west of the South Korea. In the areas nearby the mine, the shallow groundwater was the major source for domestic and farming water-supply. Soil contamination by Cd, Cu, Pb and Zn was previously known in this area. This study is objected to identify quality of the shallow groundwater, possibly affected by the mine tailings. Samples were collected from a nearby stream, shallow groundwater and seepage from the tailings. Chemical analysis for the water quality includes major cations such as Na, K, Ca, and Mg, anions as F, Cl, NO_3, SO_4, HCO_3, and trace elements as Al, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Pb, Se, As, Hg. Water types could be drawn into four groups from the plots of Piper, Stiff diagrams and cluster analysis. SAR-Conductivity plot indicates the water does not pose either alkalinity or salinity hazards for irrigation. Major contaminant in groundwater appeared to be arsenic, released from arsenopyrites in tailings by oxidation. Dredging of buried tailing materials could stimulate the release of arsenic from the sediments to the groundwater.

요   약 : 구봉광산은 과거 남한의 최대 금광중의 하나였다. 광산 주변 지역에서는 천부 지하수를 생활용과 농업용 수원으로 사용하여 왔다. 이 지역에서 Cd, Cu, Pb 및 Zn에 의한 토양오염이 보고되었으며, 이로부터 이 지역의 천부지하수의 수질과 광미로 인한 영향을 규명하고자 본 연구가 시작되었다. 인근의 하천수, 지하수 및 광미지역의 침출수 시료를 채취하여 Na, K, Ca, Mg 등의 주양이온과 F, Cl, NO_3, SO_4, HCO_3 등의 음이온 및 Al, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Pb, Se, As, Hg 등의 미량 오염원소등을 분석하였다. 분석결과로부터 4가지 유형의 수질특성을 구분하였으며, 이 지역의 지하수는 알칼리니티와 염도에 의한 농업용수로서의 위해성은 없는 것으로 판명되었다. 지하수 중의 주오염물질은 비소였으며, 유비철석(arsenopyrite)의 산화로부터 기인되는 것으로 사료된다. 따라서 기매립된 광미와 퇴적물을 파내는 것은 비소성분의 지하수로의 이동을 유발할 수 있다.

Introduction

Gubong gold mine is located in the middle of South Korea, and it is previously one of the largest gold mines in Korea (Figure 1). Bedrocks of the area consist of mica-schists and amphibole-schists. Shallow aquifer in this area is developed down-gradient from the mining facility.

The mine had managed several tailing ponds on site without bottom linings during approximately 50 years of operation period (KMPC, 1987). After closure, the mining company left out all the tailings in the ponds and, still more, filled up a nearby small valley with tailings. The tailings consist of fine sands to silty clays in size. They have dispersed into the nearby environments through the air as dust particles, along the stream with surface run-off and possibly through the groundwater carried by infiltration.

Farmers living in nearby and down-gradient areas have found that the crop declines when tailing dusts precipitate onto it. Until 1996, the shallow groundwater was the major source for drinking- and domestic-water supply. Recently people in the area drilled a deep well in the up-gradient area to supply their drinking water. However, still the groundwater is the major water source for domestic and agricultural activities.

A couple of studies in this area indicated the relatively high concentrations of Cd, Cu, Pb and Zn in soils (Kim *et al.*, 1995, 1997). However, no study was on the mineral phases, mobility, transport mechanisms, and reactions of those contaminants in the groundwater system. In addition, the local administration started removing open tailing materials. However, for the buried tailings, no strategy was made and they are looking for the methods of stabilization.

Therefore, in this area, major problems still remain to be answered including, 1) the effects of soil and water contamination on groundwater use in domestic and agricultural activities,

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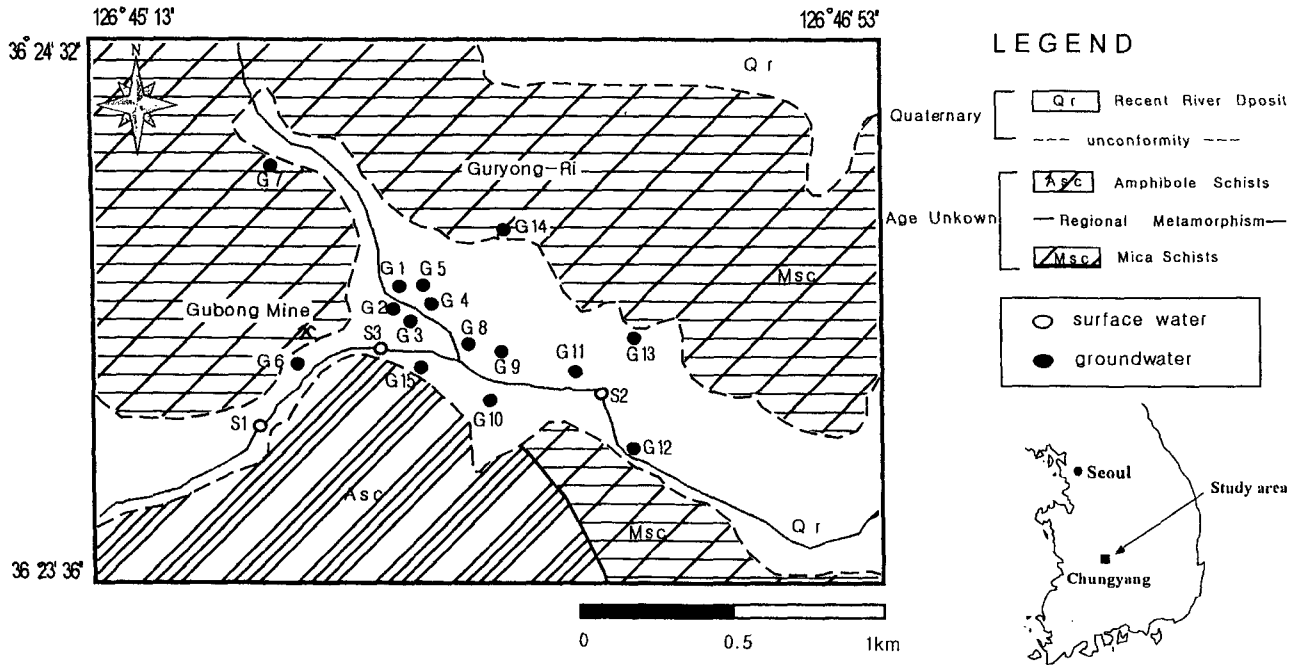
Figure 1. Geologic map and water-sampling locations of the study area.

2) how to properly manage tailing materials distributed in the area. To answer these questions, this study was initiated with the objectives of surveying the groundwater quality for the purposes of agricultural and domestic uses, and identifying groundwater contaminants, their sources, and transport mechanisms.

Methods

Ground- and surface-water samples were collected at 15 sites and three locations, respectively. On sites were measured pH, EC, Temperature, and ORP, using portable multisensor, and alkalinity by titration. Each 500 mL of water samples were separately preserved for cation and anion analyses with addition of concentrated nitric acid and refrigeration, respectively, after filtering through 0.45 μm membrane filter papers.

In the laboratory, water samples were analyzed for major cations (Na, K, Ca, Mg), anions (F, Cl, NO_3, SO_4, HCO_3) and trace elements (Al, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Pb, Se, As, Hg). Cations and trace metals were analyzed, at the Korean Basic Science Institute at Daejeon using ICP-AES. For Se, As, and Hg, hydride-generation process was incorporated with the ICP-AES analysis. Anions were analyzed from HPLC at Yonsei University, and the concentrations of bicarbonate ion were converted from the alkalinity titration results. To understand general groundwater quality, laboratory analytical results were plotted on various diagrams including Piper, Stiff, and SAR-Conductivity, and grouped by cluster analysis using SAS (Statistical Analysis Software) (Sung, 1997).

Results and Discussion

Water types

Analytical results of the major cations and anions are shown in the Table 1. Plots on the Piper diagram indicate the major cations of Ca and Mg (Figure 2). Anions varies fairly among carbonate, sulfate and chloride ions. This results imply that groundwater in the area is significantly affected by the local conditions.

Water types can be grouped based on the shape of Stiff diagrams. Hounslow (1995) clearly shows the examples of difference in Stiff diagrams of waters originated from various rocks. In the study area, four types could be easily identified (Figure 3): G6 (seepage from tailings), G14 (probably originated from shale), G1-5 and G8-9 (with carbonate origins) and the rest (with small amount of dissolved solids). G7, G10-13, and G15 show very similar compositions with stream samples (S1-3), indicating the origin of induced recharge of stream water.

Using the SAS, water samples were clustered each other based on the laboratory analytical results. Dendrogram (Figure 4) indicates the similarity of the water quality of the samples among surface water samples and G11, G12, G13 and G15. Again, G6 and G14 were separated from all the others. This result conforms the grouping from the Stiff diagrams.

Water quality for irrigation

Since groundwater in this area is the major water-supply source for vegetation and farming, suitability of the water

Table 1. Concentrations of major contaminants in water samples (meq/L)

| Sample name	pH	EC (μs/cm)	Eh (mV)	Na	Mg	Ca	K	F	Cl	SO₄	HCO₃
S1	6.74	59	445	0.244	0.237	0.455	0.002	0.012	0.283	0.130	0.490
S2	6.60	94	437	0.292	0.372	0.857	0.002	0.017	0.301	0.457	0.655
S3	6.83	81	427	0.260	0.299	0.719	0.001	0.020	0.270	0.384	0.554
G1	6.28	166	451	0.517	0.963	1.535	0.001	0.019	0.241	0.562	1.896
G2	6.30	377	427	0.550	1.832	4.651	0.002	0.020	0.250	2.800	3.437
G3	6.51	366	419	0.538	1.654	4.456	0.004	0.058	0.322	3.030	2.946
G4	4.60	270	451	0.440	1.279	3.084	0.003	0.043	0.575	1.387	2.313
G5	6.31	255	448	0.785	1.084	2.112	0.003	0.020	1.049	0.731	1.673
G6	7.33	553	414	0.105	2.032	8.568	0.006	0.023	0.150	8.914	0.820
G7	6.03	99	442	0.609	0.394	0.378	0.000	0.015	0.357	0.152	0.620
G8	5.98	168	442	0.620	0.701	1.327	0.005	0.019	0.919	0.457	0.915
G9	5.82	202	445	0.699	0.895	1.611	0.003	0.029	1.212	0.664	1.043
G10	5.42	76	443	0.344	0.336	0.553	0.001	0.020	0.333	0.175	0.494
G11	5.71	138	442	0.533	0.578	1.206	0.002	0.018	0.619	0.458	1.173
G12	6.03	127	443	0.426	0.571	1.048	0.002	0.017	0.553	0.617	0.702
G13	5.92	145	447	0.678	0.553	0.984	0.001	0.009	0.716	0.100	0.531
G14	5.56	234	453	1.309	1.064	0.893	0.006	0.012	1.756	0.050	0.248
G15	6.45	104	437	0.453	0.351	0.676	0.002	0.015	0.524	0.236	0.281
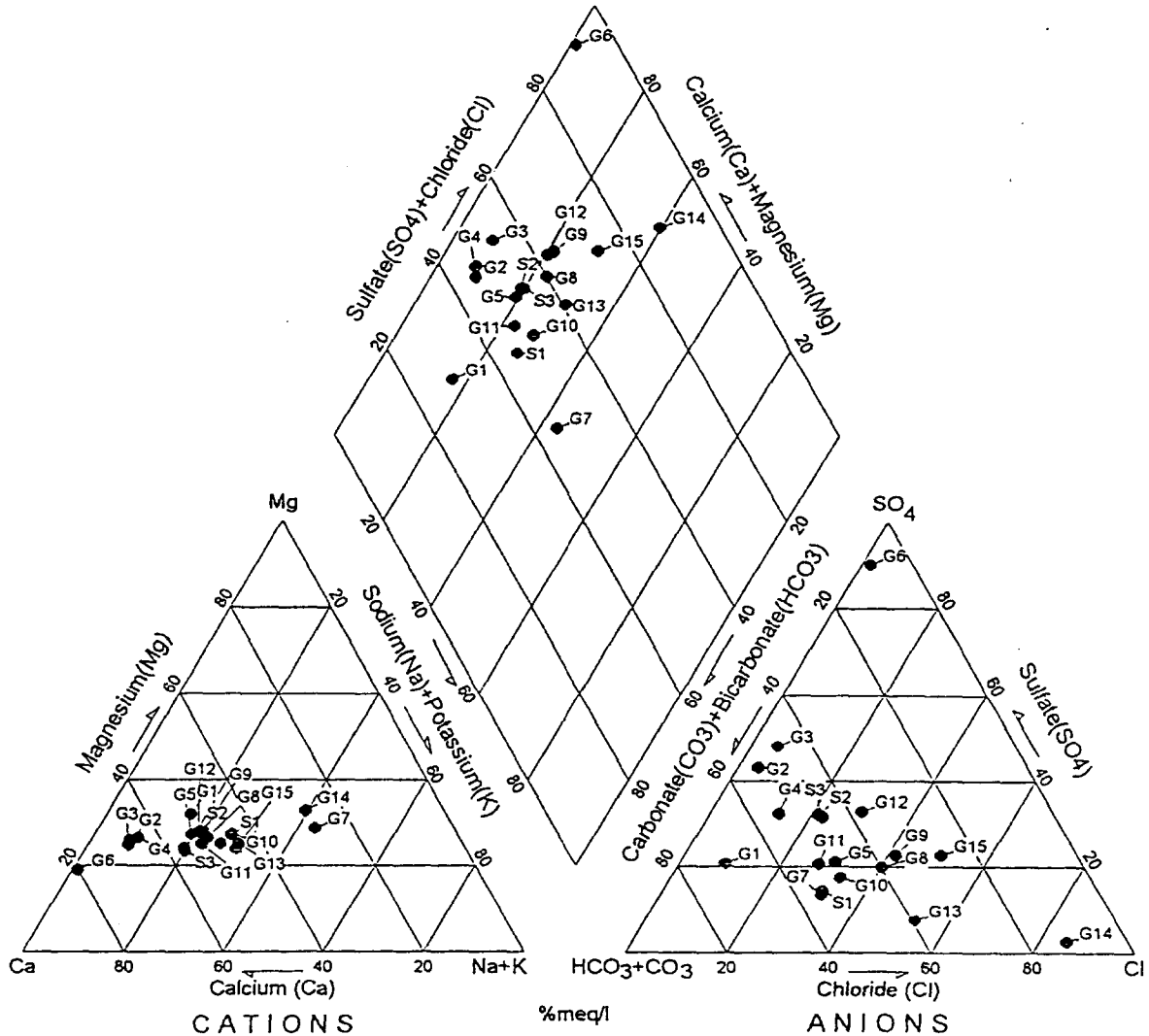
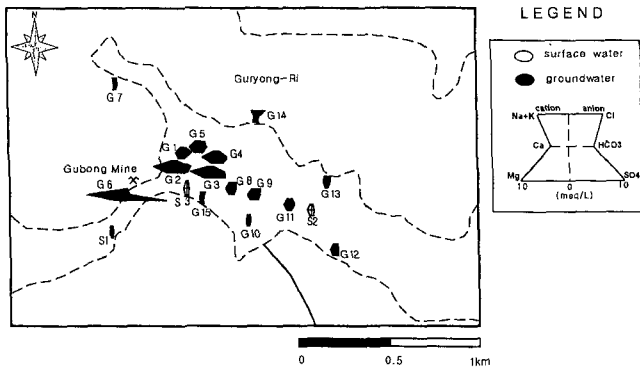**Figure 2.** Water quality by the piper diagram.

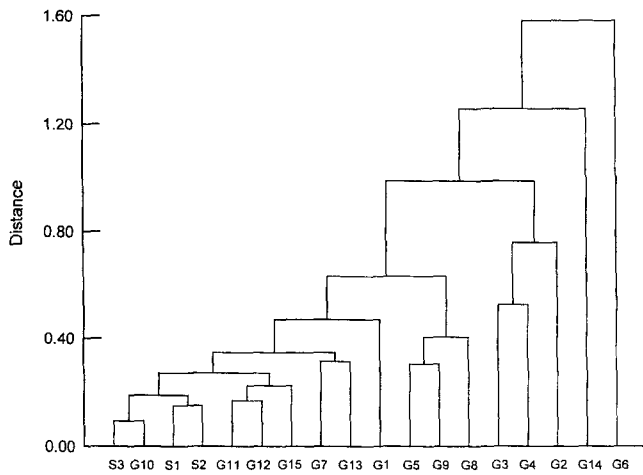**Figure 3.** Water type of the groudwater samples by the stiff diagram.

Figure 4. Dendrogram of the water samples.

quality for irrigation was evaluated on the alkalinity hazard (noted by the sodium adsorption ratio; SAR) vs. salinity hazard (noted by conductivity or TDS) diagram (Figure 5; Hem, 1992). The SAR of a water is defined as following,

$$SAR = \frac{Na^+}{\sqrt{\dfrac{Can^{2+} + Mg^{2+}}{2}}}$$

where the ion concentrations are expressed in meq/L (Richards, 1969).

SAR value measures the degree to which sodium in irrigation water replaces the adsorbed $(Ca^{2+}+Mg^{2+})$ in the soil clays, and thus damages the soil structure. All samples appear to be low-sodium waters with low to medium salinity, indicating that the groundwater does not pose any potentials for alkalinity and salinity hazards in irrigation.

Contaminants in Groundwater

To identify existing contaminants in water, samples were analyzed for a total of 12 trace elements including Al, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Pb, Se, As, and Hg. Four of them, Cd,
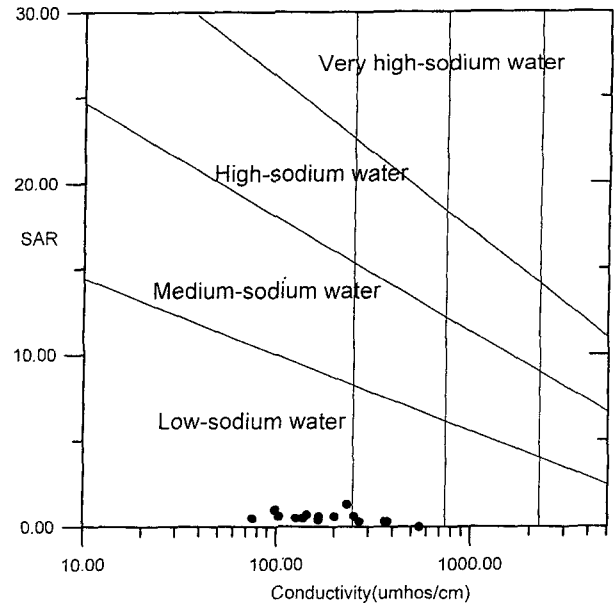

Figure 5. SAR-conductivity plots of the water samples.

Cu, Pb and Zn, were previously known to exist in soils with relatively high concentrations. Table 2 shows the concentrations of only eight potential contaminants, Mn, Fe, Cu, Zn, Cd, Pb, As, and NO_3-N. Other elements were almost in the concentrations of below the detection limits. Even in this table, shaded samples are only ones of higher concentrations

Table 2. Concantrations of contaminants in water samples

(mg/L)

Sample name	Mn	Fe	Cu	Zn	Cd	Pb	As	NO_3-N
Drinking water standard	0.30	0.30	1.00	1.00	0.01	0.05	0.05	10.00
Detection limit	0.005	0.010	0.009	0.002	0.001	0.012	0.001	0.219
S1	0.074	0.111	BDL	0.005	BDL	BDL	BDL	1.470
S2	0.150	0.044	BDL	0.025	0.001	BDL	0.039	1.585
S3	0.152	0.112	BDL	0.003	BDL	BDL	0.002	1.610
G1	0.006	0.043	BDL	0.011	BDL	BDL	BDL	0.587
G2	0.455	BDL*	0.005	1.080	0.039	BDL	0.057	0.847
G3	BDL	BDL	0.009	0.378	0.012	BDL	0.167	2.147
G4	0.049	BDL	0.010	0.043	BDL	BDL	0.086	6.892
G5	0.206	0.054	BDL	0.005	BDL	BDL	0.026	8.332
G6	0.067	BDL	BDL	0.127	0.015	BDL	0.070	1.258
G7	BDL	BDL	0.001	0.015	BDL	0.013	0.003	7.135
G8	BDL	BDL	BDL	0.054	BDL	BDL	0.001	7.553
G9	BDL	BDL	BDL	0.006	BDL	BDL	0.001	5.354
G10	BDL	BDL	BDL	0.012	BDL	BDL	BDL	3.940
G11	0.013	BDL	BDL	0.044	BDL	BDL	0.002	0.605
G12	BDL	BDL	BDL	0.006	BDL	BDL	0.001	2.518
G13	BDL	BDL	BDL	0.007	BDL	BDL	0.001	4.984
G14	0.016	0.012	BDL	0.057	BDL	BDL	0.001	27.311
G15	0.006	BDL	BDL	1.249	0.023	BDL	0.001	9.976

*BDL denotes the below detection limit of each element.

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than the drinking water standards.

Zn and Cd, previously known at soils, were found also in groundwater, with slightly higher concentrations than the standards of 1.0 mg/L and 0.01 mg/L, respectively. However, in all samples, Pb was below the method detection limit of 0.01 mg/L, and Cu slightly higher than the method detection limit of 0.003 mg/L. Instead, arsenic was found at the 15 samples out of 18, and four of them shows over the drinking water standard of 0.05 mg/L. For arsenic, the method detection limit was 0.0005 mg/L (=0.5 µg/L).

In terms of metal contaminants including Mn, Zn, Cd, and As, G2, G3, G4, and G15 wells show higher concentrations than the drinking water standards. Waters from G2, G3, G4 and G6 wells contains higher arsenic concentrations than the drinking water standard (Figure 6). Cadmiums were higher at wells of G2, G3, G6 and G15. These distributions show that contaminations are generally higher at the areas close to the mine.

However, although their distribution look similar, arsenic appears to be controlled by different chemistry in groundwater system from Mn, Zn, and Cd. Multiple correlation study of the elements shows that among the contaminants, Zn, Cd and Mn are correlated each other in 95% of confidence level, implying that their occurrences in groundwater are closely related (Table 3). However, arsenic shows correlations with F and SO₄, but no correlations with Zn, Cd and Mn. The differences in behavior in water of these ions need further study. The major difference may be the forms of these ions in water, since arsenic exists as anions ($H_2AsO_4^-$, $HAsO_4^{2-}$) and Zn, Cd, and Mn as cations (WHO, 1981). Since the other trace elements such as Al, Cr, Fe, Ni, Cu, Pb, Se, and Hg were almost in concentrations of below detection limits, they were omitted in multiple correlations.

Recently, in the study area, Song et al. (1998) and Kim (1998) identified arsenopyrites (FeAsS) enriched in the mine tailings and the stream sediments. Kim (1998) reported that the total concentrations of arsenic in those samples ranging from 380 to 438 mg/kg. Lee at al. (1998) reported highly concentrated arsenic in the soil and stream sediments at Samkwang Au-Ag Mine area, which is located about 20 km away from this study area and of the same geological environment for the ore deposits. In 1982, Kim also reported
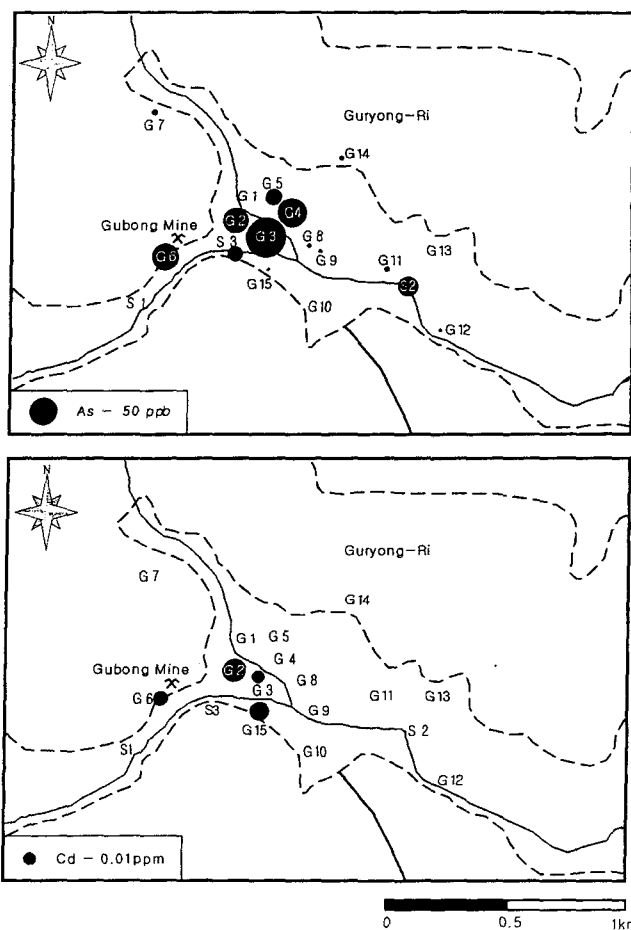

Figure 6. Concentrations of the arsenic and cadmium in the water samples.

that arsenopyrite is contained in the vein type gold ores associated with trace minerals such as galena, spalerites, pyrites, and chalcopyrites. Therefore, arsenopyrites appeared to be the major source of arsenic in groundwater in the study area.

Arsenic pollution of groundwater originated from the arsenopyrite was reported in Nova Scotia, Canada (Grantham and Jones, 1977). Arsenopyrite was present in gold-bearing rocks in that area, and oxidation of it in mining wastes exposed to the air released arsenic. The highest As-concentration reported was 5 mg/L.

Marron (1986) showed the metal-contaminated sediments from the gold-mine tailings with the highest in arsenic

Table 3. Correlations of major contaminants with other constituents in water samples

ions	Na	K	Ca	Mg	F	Cl	SO₄	HCO₃	As	Zn	Cd	Mn
As	-0.1723	0.3363	0.6385*	0.6278	0.8791	-0.2911	0.5278	0.6755	1.0000	0.1992	0.3453	0.1625
Zn	-0.0394	-0.0367	0.2227	0.2541	0.0579	-0.1896	0.1525	0.3333	0.1992	1.0000	0.9058	0.4118
Cd	-0.1432	0.1115	0.5357	0.5360	0.1200	-0.3119	0.4623	0.4983	0.3453	0.9058	1.0000	0.6095
Mn	-0.0901	-0.0801	0.3086	0.3679	-0.0708	-0.2118	0.1990	0.5190	0.1625	0.4118	0.6095	1.0000

*Shaded numbers indicate significant relationships in 95% confidence level.

concentration, ranging from 500 to 10,000 mg/kg. She noted that much of the arsenic is transported to the floodplain as primary sulfides in the crushed mine tailings. Then, arsenic is released due to the oxidation of sulfides, and reattached to the floodplain sediments in association with oxide and hydroxide minerals.

To examine the principal components of the water, the SAS was used with the concentration data of Na, Mg, K, Ca, F, Cl, HCO_3, SO_4, Zn, Cd, Mn, and As (Table 4). In this analysis, we tried to examine the first three principal components (Table 4(a)). The three associations explains about 78% of the total data distribution. The first factors, the association of Ca, Mg, HCO_3, SO_4 and As, can cover the about 43% of the total data distribution (Table 4(b)). The second factors including Na, K, and Cl, and the third Zn, Cd, and Mn cover the data distributions of 19% and 15%, respectively.

The eigenvectors of the principal components indicate that two groups of major water types can be separated as the first being Ca, Mg, HCO_3, and SO_4 type and the second Na, K, and Cl type (Table 4(b)). In addition, arsenic is associated with Ca, Mg, HCO_3, and SO_4 type water. Zn, Cd, and Mn appear to behave closely together. However, their association with Na and Cl seems not to be realistic, because contributions of Na and Cl on the data distribution were already separated as the second principal component. So we considers the eigenvectors of Na and Cl for the third components without any practical meanings.

Lee et al. (1998) found the arsenic concentrations much higher at the stream sediments that at soils, implying that the arsenic released from the rocks or minerals were fixed into the sediments. More detailed and integrated studies are in progress to identify the exact pathways of arsenic in this area. However, at this point, we can suggest that arsenic in groundwater could be secondarily released from sediments, on which arsenic was concentrated after the primary release of arsenic-bearing sulfides such as arsenopyrites.

Several researchers also reported that arsenic might be in very low concentrations in water due to the adsorption by hydrous iron oxide or coprecipitation, or combination with sulfide in reduced bottom mud (Pierce and Moore, 1980; Masscheleyen, et al., 1991; Kobayashi and Lee, 1978). Therefore, dredging out of buried tailing materials might not be wise choice for the management of contaminated sediments. A significant amount of arsenic could be released from the sediments to the groundwater because of changing pH-redox conditions, resulting in desorption of arsenic from oxides and hydroxides. Furthermore, the residual sulfide minerals could be oxidized and release arsenic, subsequently.

Another common groundwater contaminant in the study area was NO_3-N. As shown in the Table 2, nitrate-nitrogen concentrations were mostly below the drinking water standard of 10 mg/L, except for the well G14 with about 27 mg/L. However, wells G4, G5, G7, G8 and G14 also show various amounts of NO_3-N detections with spatially random distribution. This implies that nitrate is different from other metal contaminants in their sources, such as domestic sewage or livestock manures.

Summary

Based on this study, several conclusions can be made as followings:

1) Water types could be drawn into four groups, and SAR-Conductivity plot indicates the water poses neither alkalinity nor salinity hazards for irrigation.

2) Major contaminant in groundwater is arsenic, previously unknown soil contaminants. It is closely related to the Ca, Mg, HCO_3, SO_4-type water, and independent from Zn, Cd, and Mn, which behave closely together.

3) Arsenopyrites in tailing materials appear to be the ultimate sources of arsenic in water. Arsenic movement in the groundwater system can be summarized as follows; oxidation of this minerals, resulting the release of free arsenic to the environment, following fast but unstable adherence to the sediments, and subsequent remobilization to the water.

4) Therefore, dredging of buried tailing materials probably containing lots of arsenopyrites might stimulate the release of arsenic from the sediments to the groundwater system.

At this moment, we still need to study followings in the on-going project:

Table 4. Results of the principal component analysis

(a) Eigenvalues of the Correlation Matrix

	Eigenvalue	Difference	Proportion	Cumulative
PRIN1	5.17925	2.86880	0.431604	0.431604
PRIN2	2.31045	0.48203	0.192537	0.624141
PRIN3	1.82842	·	0.152368	0.776509

(b) Eigenvectors of each Principal Components

	PRIN1	PRIN2	PRIN3
Na	-0.110910	0.430744	0.465207
Mg	0.394036	0.224646	0.086233
K	0.188929	0.486149	0.017044
Ca	0.400980	0.103027	-0.106792
F	0.276337	0.164259	-0.263118
Cl	-0.154857	0.512965	0.353624
HCO_3	0.327916	-0.037469	0.122654
SO_4	0.355836	0.073644	-0.194547
Zn	0.198758	-0.277759	0.443857
Cd	0.310500	-0.255541	0.380868
Mn	0.202491	-0.261705	0.371561
As	0.352911	0.095684	-0.192745

1) forms of fixed and mobile species of arsenic and other metal contaminants, 2) controlling factors of those speciation in terms of pH and redox conditions, and 3) suggestions for the proper management of tailing materials in this area.

Acknowledgement

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