

Contamination of Stream and Reservoir Waters with Arsenic from Abandoned Gold Mine

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Abstract

Levels of arsenic in stream and reservoir waters affected by an abandoned gold mine were examined. The abandoned mine has been left without proper civil and remedial works preventing potential environmental hazards. Field and laboratory chemical analyses revealed that the stream waters downgradient from the mine area were severely contaminated with arsenic and furthermore the reservoir water, 2-3 km away from the mine, also contained substantial levels of As, far exceeding the Korean stream water standard. Relatively higher pH values (6.5-9.4) enhanced mobility of As and mainly sustained substantial As concentration in waters. Chemistries of the stream water, groundwater and reservoir water were dominated by two main factors including effects of mine effluent and anthropogenic agricultural activities. Considering that there has been a substantial As input to the reservoir and the reservoir water has been used for agricultural and domestic uses, immediate remedial works are essentially required.

Keywords: Abandoned mine, Mine tailings, Heavy metals, Arsenic, Stream water, Reservoir

1. Introduction

Heavy metals from uncontrolled abandoned metal mine would pose a threat to ecological community and human health. Especially arsenic shows a cancer risk. There are about 900 abandoned metal mines in Korea.¹⁻³⁾ The measures to the abandoned mines have been focused on civil works including concrete walls preventing mine tailings and waste rocks from collapsing and washing out away during heavy rain season, and partially surface capping preventing rainfall infiltration into the mine tailings. Even though these minimal technical measures are partly effective, leaching of hazardous heavy metals from the mining wastes would be inevitable. Furthermore, a large number of the metal mines were left without even the minimal treatment or remediation.

A relevant governmental authority of Korea has undertaken a multi-year consecutive project to tackle the environmental problem potentially caused by the abandoned metal mines, which was enforced by a new law named "Mining Hazards Protection Law" enacted since 2006. With the help of the law, a large quan-

tity of budget (100 million dollars per year) was secured for the project. The project includes environmental investigation of the abandoned mines, remediation of the contaminated soil and groundwater and relevant civil works. As a first step for the project, a remediation priority for the abandoned mines was listed. The priority was determined by considering contamination levels of soil and groundwater, proximity to residential area, land use of surrounding area, amount of groundwater use, hydrogeological characteristics such as subsurface permeability and many others.⁴⁾ These data were extensively collected from many previous studies for the mines and the exploratory or preliminary investigations.

The Samgwang mine of this study, which is an abandoned gold (Au) mine, ranked the first in the priority list and it means that the mine should be urgently treated and remediated. The studied mine started to operate in 1938 and it closed in 1996. Since the closure, there have been neither remediation efforts nor appropriate civil works for the abandoned mine. Furthermore, there are a large amount of waste rocks and mine tailings untreated and open to air. According to a preliminary investigation,⁴⁾ soil and stream water within and around the abandoned mine were highly contaminated with heavy metals, especially As whose levels far exceeding the Korean soil and stream water

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standards.

This study, as a component of basic remediation plan for the mine, re-evaluated the contamination level of stream water, groundwater within and around the mine and water of a reservoir, about 2 km downstream from the abandoned metal mine and seasonal variation of the contamination levels for dry and wet seasons were evaluated.

2. Materials and Methods

2.1. Abandoned Gold Mine

The abandoned gold mine is located 110 km south of Seoul, capital of Korea (Fig. 1(a)). The mine was operated intermittently in 1938-1942, 1952-1959 and 1994-1996. During the opera-

tion period, about 980 kg of gold was produced. Closure of the mine initially left a large volume of waste rocks and 1,125,000 m³ of mine tailings.⁴⁾ The waste rocks were stacked mainly below and left side of the mine adits (Fig. 1(b)). Now there are two mine tailings stacks because some of the mine tailings in the original main stack were moved to another location, where a mineral company is extracting silica from the mine tailings and byproducts of the process were dumped at the site. Volume of the main mine tailings is 226,468 m³ while that of the secondary is about 197,701 m³. The stacks are open to air without any surface cover and they are soaked below the water during the heavy rainstorm. Much of the mine tailings were lost due to torrential rains in the wet seasons for many years.

There are three mine adits and the mine drainages are still occurring at two of the three. But amount of the seepage are

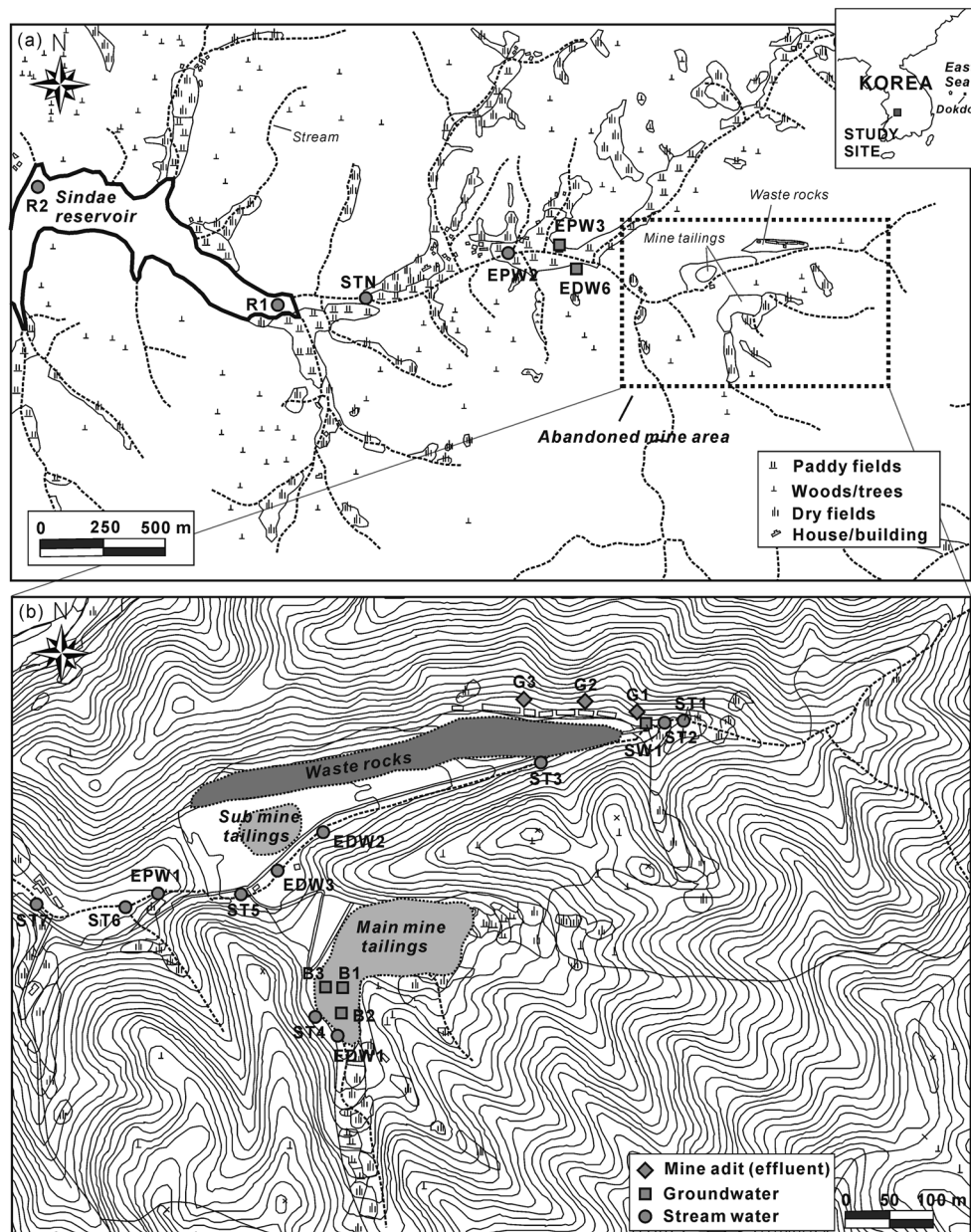


Fig. 1. Location of the studied mine showing water sampling locations.

small. Adjacent to the mine adit (G1), a stream runs from east to west. Water of the stream is flowing for all seasons with very varying flow rates. Waters of many subsidiary streams join the main stream, finally reaching a reservoir (see Fig. 1(b)). The Sindae reservoir covers about 0.25 km² of surficial area and water of the reservoir has been generally used for agricultural irrigation and domestic use.⁴⁾ Water for drinking and domestic use was largely supplied from groundwater but now it is mainly supplied with pipes from uppermost area. Some residents within 2 km from the mine still use groundwater for drinking and domestic purposes. Some parts of the area between the abandoned mine and the reservoir have been used for cultivation of rice, hot peppers and corns. Irrigation waters are obtained from near-by streams.

The mine is situated in a valley surrounded by relatively high elevations mountains. The geology of the mine and surrounding areas are composed of pre-Cambrian granitic gneiss and meta-sedimentary rocks, which were intruded by pegmatite and basic dykes. The granitic gneiss with high biotite content is intermediately or coarse grained and it shows generally foliation structures. Quartz veins filling fractures in the granitic gneiss contain gold (Au) and silver (Ag). The veins also include minerals of pyrite, galena, sphalerite, arsenopyrite and chalcopyrite. Hydro-geologic investigation revealed that groundwaters in this area occur mainly in fractured bedrock aquifer. Hydraulic conductivity of the bedrock aquifer is in the order of 10⁻⁴ cm/sec.⁵⁾ The nearby streams have been losing and gaining in the dry and the wet seasons, respectively.⁶⁾ Annual precipitation in this area averages 1,400 mm and over 60% of them occur in the wet months (June-September). Rainfall in the wet season becomes often torrential.

2.2. Field Investigation and Chemical Analysis

To evaluate the contamination levels of the stream and reservoir waters and groundwaters, multiple field measurements and three times of laboratory analysis were performed in 2006-2007. In the sampling campaign, two points of mine effluent (G1 and G2), seven points of stream water (ST1, ST3-ST7, STN), three points of groundwater (SW1, B3, EW) and two points of reservoir water (R1 and R2) were included. The ST4 is water from ditch bypassing the main tailings stack. Prior to measurement of physico-chemical field parameters, flow rates of the stream water were measured using a weir system or a flowmeter (FP101, Global Water). Then the field parameters including pH, EC (electrical conductivity), ORP (oxidation-reduction potential), DO (dissolved oxygen) and temperature were measured using a multi-probe device (556MPS, YSI) under flowing condition. For analysis of multi-elements including heavy metals, 125 mL of water sample was collected in a HDPE bottle after 0.45 µM filtration and it was preserved using ultra-pure (65%) HNO₃. For other constituent including anions and alkalinity, water was collected in a 1 L HDPE bottle after filtration (0.45 µM). Until the laboratory analysis, the water samples were stored at 4°C in a portable refrigerator. Groundwater was sampled using a disposable bailer after purging three well volumes.

Alkalinity was determined by titration in the sampling day. Cations and heavy metals were analyzed using ICP (VISTA-MPX) and ICP/MS (ICP-MS, Varian) following USEPA standard methods and anions were analyzed using ion chromatography (IC, DX-120). The laboratory analysis was conducted at Natural Science Research Supporting Center of Sangji University in Wonju, Korea, which is a nationally authorized water analysis center.

3. Results and Discussion

3.1. Results of Field Measurements

Fig. 2 shows water levels of the monitoring wells and the reservoir. The groundwater levels including the reservoir level were the highest in July due to heavy rainfall of the wet season. The amount of rainfall was closely related with the water levels. Thus a great quantity of groundwater recharge and increase of stream flow were expected. Fig. 3(a) shows results of field measurement of water quality in 2006 (5 times) to 2007 (single time). Water temperatures ranged between 7 and 23°C and they showed the most distinctive seasonal variation, that is, the highest in summer while the lowest in winter. Ambient air temperature influenced mostly the water temperature.

The pH variation is presented in Fig. 3(b). The pHs ranged between 6.5 and 9.4 (except for 4.4 at an existing well EW), which are not so low (not so acidic). In many cases, the stream waters where acid mine drainage occurs would show very low pH values such as 2-4.^{7,8)} Relatively high pH values in this abandoned mine area may be derived from deficiency or less abundance of sulfide minerals in the bedrock. Thus not much sulfate was generated from oxidation of the sulfide minerals, which did not substantially lower the pHs of the waters. These neutral or slightly alkaline conditions greatly affected mobility of arsenic in the waters.⁹⁾

The EC values of the waters ranged from 62 to 798 µS/cm (Fig. 3(c)), which were considered quite similar values compared with those in other abandoned metal mines.⁵⁾ The highest EC values were measured at mine effluents (G1=754, G2=798 µS/cm). The lowest EC values in July are attributed to dilution due to heavy rains in the wet season. The lowered EC values increased again in next dry season (November). The ORP values,

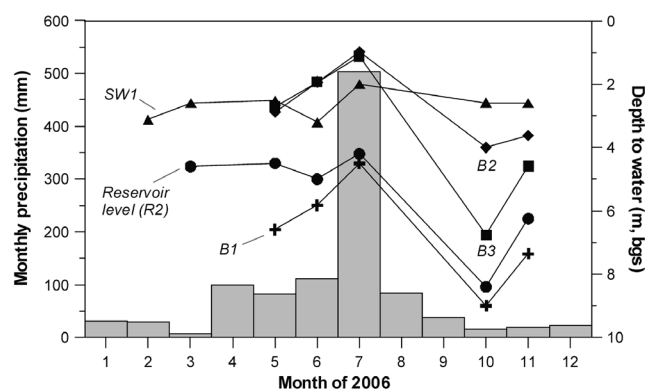


Fig. 2. Water levels of the monitoring wells with precipitation data.

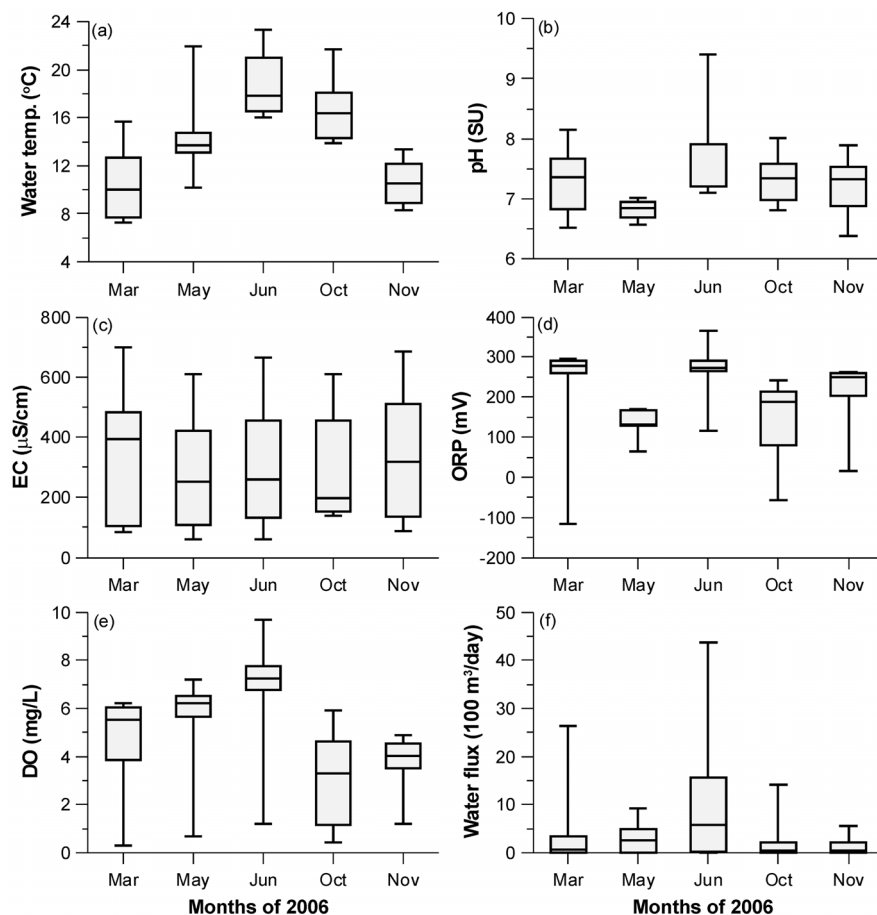


Fig. 3. Box plots of the field measured parameters, mostly showing seasonal variations.

indicative of redox condition, ranged from -117 to 365 mV. Except for the values of groundwaters, they were mostly positive (> 0 mV), which indicates prevailing oxidative water conditions throughout the year.

Dissolved oxygen also showed very distinctive seasonable change (Fig. 3(e)). It was the highest in summer and the lowest in winter, which is the same variation trend as the water temperature. However, it was somewhat contrary to our expectation because low temperature is closely associated with high solubility of oxygen into water. Even in the hot summer (coincident with wet season), DO in water can be elevated by enhanced aeration due to accelerated stream water flow or turbulent flow (Fig. 3(f)). High DO values and ORP levels implies oxygenated environment and hence existence of As as pentavalent arsenate, less toxic than arsenite.⁹⁾

Variations of the field parameters along stream flow paths are shown in Fig. 4. Water temperatures generally increased along the flow path mainly due to increase of contact time between the air and the stream water. Average water temperature of 14.5°C at ST1 increased to 21.2°C at the lowermost reservoir (R2). Levels of pH, ORP, DO and water flux showed increasing trend. But EC exhibited a decreasing trend due to dilution or mixing with additional waters supplied from rainfall or adjoining tributaries. Uncontaminated bypass ditch water (ST4) showed the lowest EC values.

3.2. General Water Chemistry

General water chemistry comprised of major cations and anions is shown in Fig. 5. The most dominant cations are Ca^{2+} and Mg^{2+} while the most abundant anions are HCO_3^- and SO_4^{2-} . Mine drainage (especially G1) is classified as Ca (+Mg)- SO_4 type while most of the stream waters are Ca + Mg- HCO_3 type, in which proportions of HCO_3 and SO_4 are much varying. The two end members, SO_4 and HCO_3 are indicative of effects of mine drainage and aeration of stream water during downstream flow, respectively. Thus it is reasonably inferred that these two factors control major composition of the stream waters.

3.3. Occurrence of Arsenic

Fig. 6 shows arsenic concentrations in stream waters and soils measured in 2004 (see sample locations in Figs 1(a) and 1(b)). In the soils of the abandoned mine, very high As concentration (up to 68 times greater than the Korean soil action level=15 mg/kg As) was observed. Except for As, Cu, Pb, Cd, Ni and Zn greatly exceeded the soil action levels.⁴⁾ Two stream sediments collected at ST6 revealed severe heavy metal contamination (As=547.3, Cd=5.7, Cu=100.5, Ni=55.1, Pb=200.5, Zn=496.7 mg/kg). Even at distance of about 1 km from the mine, As concentration in soil reached almost the action level. Levels of

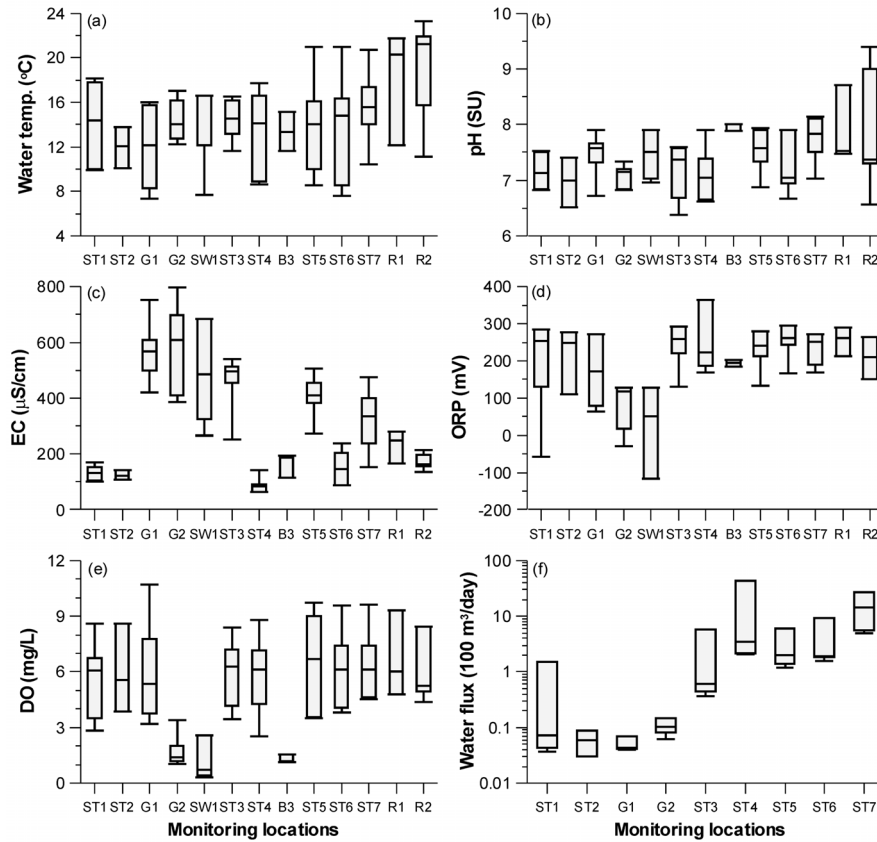


Fig. 4. Levels of the field measured parameters at each monitoring location. ST1 and ST2: upgradient stream waters, G1 and G2: mine effluents, SW1 and B3: boreholes, ST4: bypass ditch of the main tailings stack, R1 and R2: reservoir waters.

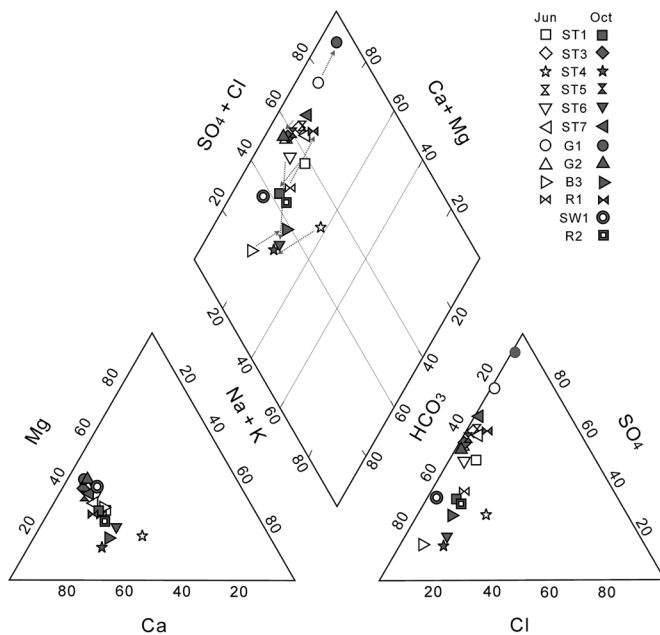


Fig. 5. Piper diagram of the water samples for two sampling rounds in 2006.

As in stream water also exceed the Korean standard ($=0.05$ mg/L). At lowermost location (EPW2) sampled in 2004, As concentration greatly exceeded the stream water standard.

Fig. 7 shows levels of As, SO_4^{2-} , and NO_3^- for three sampling

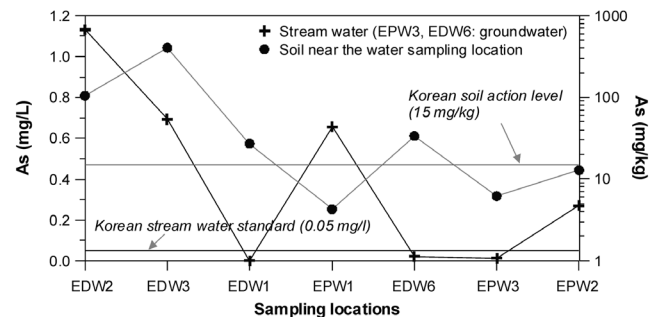


Fig. 6. Arsenic concentrations in stream waters and soils measured in October-December of 2004. Data are from MOE.⁴⁾

rounds at each location (approximately along flow path). Except for water of the bypass ditch around the main tailings stack (directly discharging waters from upgradient surrounding areas), all waters contained substantial levels of As exceeding the water standard (Fig. 7(a)). But any systematic seasonable variation was not found. The highest content (18.427 mg/L) was found at the mine effluent (G2). The As levels in waters generally decreased with distance from the mine adit. Compared with the peak levels at the mine adit, As level in the reservoir water was much lower by average 80 times, which is still greater than the water standard. As an indicator for effect of acid mine drainage, SO_4^{2-} was examined (Fig. 7(b)). The levels of sulfate showed a similar variation pattern of As. The highest concentrations were observed at the mine adit (G1) and they generally decreased with

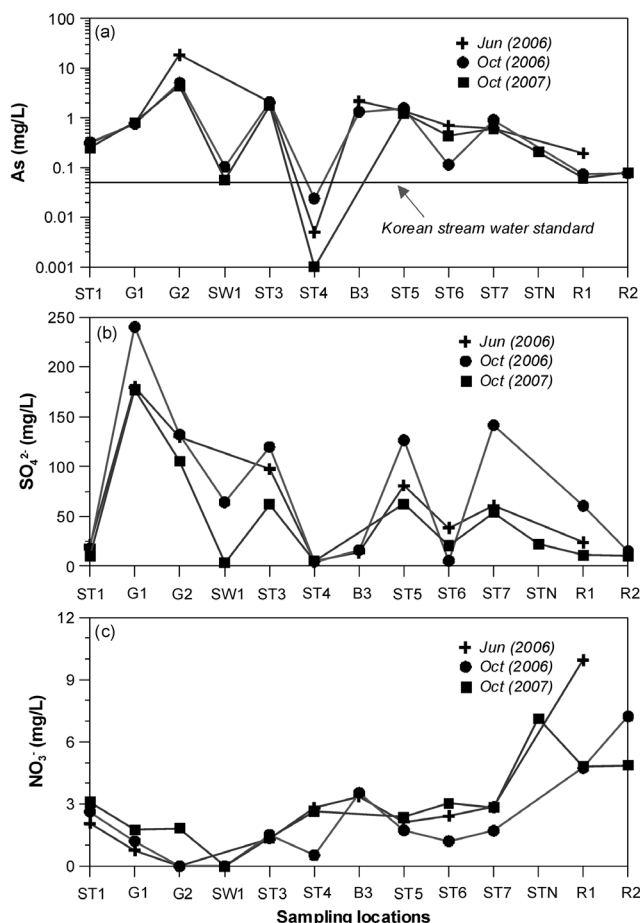


Fig. 7. Concentrations of arsenic, sulfate and nitrate measured in June, October of 2006 and October of 2007. The Korean stream water standard of arsenic is 0.05 mg/L. ST1: upgradient stream water, G1 and G2: mine effluents, SW1 and B3: boreholes, ST4: bypass ditch of the main tailings stack, R1 and R2: reservoir waters.

distance. The levels of As and SO_4^{2-} are somewhat positively correlated ($r=0.55$ at $p=0.06$). Oxidation of the sulfide minerals releases arsenic and sulfates, resulting in acidification of water.¹⁰⁾ The lowering of the sulfate level was mainly derived from mixing of the mine effluent with surrounding unaffected waters from many adjoining streams.

Nitrate concentration showed very different variation with those of the previous two parameters (As and SO_4^{2-}) (Fig. 7(c)). Therefore As and nitrate was negatively correlated ($r=-0.42$ at $p=0.01$). The lowest levels of nitrate were observed at the mine adit (G2) and it generally increased with distance from the adit. At the reservoir, it was elevated to about 7 mg/L. The nitrate in this area is largely related to many agricultural activities such as application of manure and nitrogen fertilizers and thus it is indicative of anthropogenic contamination.¹¹⁾ Consequently, qualities of the stream and reservoir waters were mainly affected by the mine effluent and the anthropogenic activity.

Fig. 8 shows relationship of As with pH, EC, ORP, DO, total Fe and HCO_3^- for data of the three sampling rounds. As previously described, pH ranged between 6.6 and 9.0 (average \pm std. deviation = 7.4 ± 0.6 , $n=34$) (Fig. 8(a)). These relatively higher pH values (slightly acidic to alkaline) would enhance mobility

of As in stream waters.¹²⁾ Most of hazardous cationic heavy metals including Pb^{2+} , Cu^{2+} , Zn^{2+} , and Cd^{2+} , generally sorb to a greater extent with increasing pH, whereas most oxyanions including arsenate and selenate, would sorb to a greater extent with decreasing pH.¹³⁾ In other words, arsenic behaves as an anion in water and does not necessarily follow the pattern of being more mobile at low pH.⁹⁾ Therefore, these high pH values sustained substantial As levels in stream waters sustained high pH values. In this context, deficiency of the cationic heavy metals in these stream waters can be understood.

Concentration of arsenic showed a positive correlation with EC, which means that higher EC values indicate higher As concentrations (Fig. 8(b)). The lowest EC value (threshold value) where substantial As is detected is found as about 100 $\mu\text{S}/\text{cm}$. The As concentration showed a slightly negative correlation with both ORP and DO (Figs 8(c) and 8(d)). The two parameters are indicative of redox condition of waters. Thus highly positive ORP and high DO values indicate oxidic condition. Fate of As is primarily dependent on pH and ORP (or Pe) levels. The highly positive ORP levels may reduce sustainability of dissolved As in waters. The dissolved As strongly sorbs to surfaces of iron oxides in acidic and near-neutral pH condition, which reduces As and Fe concentrations in waters.^{14,15)} Thus As concentration can show a positive correlation with iron dissolved in water (Fig. 8(e)). Fig. 8(f) shows a relationship between As and HCO_3^- (alkalinity). The two parameters revealed a positive correlation. That is, higher alkalinity is related to higher As level. High alkalinity would prevent pH from being lowered by acidic mine effluent, thus high pH values can be sustained, which consequently results in high As levels.

In the meanwhile, considering the fact that there has been an important As input to the reservoir and it has been widely used for agricultural activities and domestic uses, the stream water flow from the abandoned mine area is a substantial risk to environment and human health when compared with relatively small volume of the reservoir. Therefore, immediate remedial action is required to reduce environmental and health risks poised by the substantial arsenic input to the reservoir.

4. Conclusions

This study evaluated levels of arsenic in stream and reservoir waters affected by the abandoned gold mine. The abandoned mine has been left without appropriate civil and remedial works preventing potential environmental hazards. Stream waters down-gradient from the mine area were severely contaminated with arsenic and furthermore the reservoir water, 2-3 km away from the mine, also contained substantial levels of As, exceeding the Korean stream water standard. Relatively higher pH values (near neutral to slightly alkaline) mainly sustained substantial As concentration in waters. Chemistries of the stream water, groundwater and reservoir water were dominated by two main factors including effects of mine effluent and anthropogenic agricultural activities. Considering that there has been a substantial As input to the reservoir and the reservoir water has been used for agricultural and domestic uses, immediate remedial works are essen-

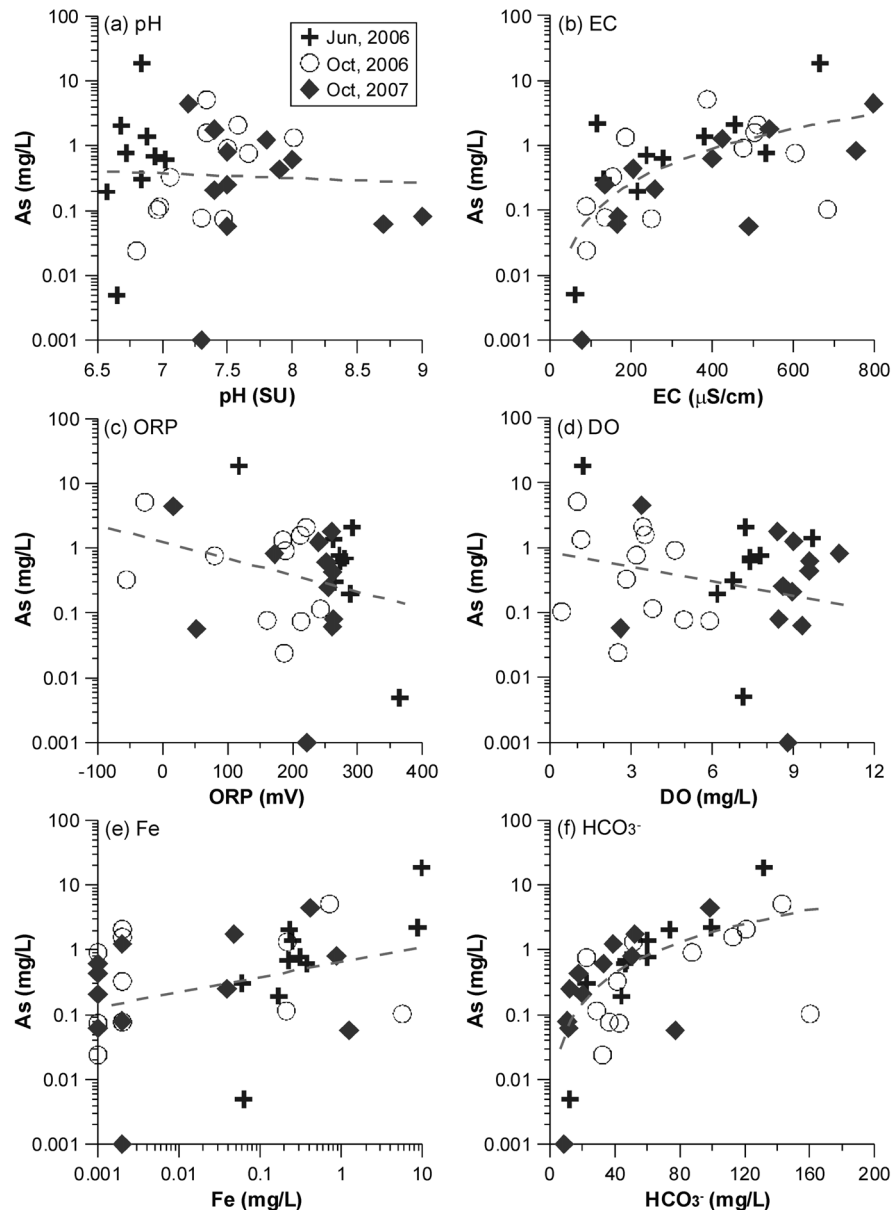


Fig. 8. Relationship between As concentration with other parameters including pH, EC, ORP, DO, Fe and HCO_3^- .

tially needed. In the meanwhile, examination of arsenic levels in the reservoir sediments deserves a further study.

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