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Geochemical and eco-toxicological characteristics of stream water and its sediments affected by acid mine drainage

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ABSTRACT

In assessing the adverse effects of acid mine drainage (AMD), the chemistry of AMD and stream water (i.e., pH and toxic metal concentrations) has been accounted as important monitoring parameters and its characteristics are regulated in many countries. Yet for the precise evaluation of eco-toxicological effect on AMD receiving streams, a more comprehensive evaluation parameter has to be recognized as a mandatory parameter. In this study, eco-toxicological correlations between chemical properties of water and sediments collected from an AMD receiving stream were investigated at an abandoned mine site in Korea. The stream water in the AMD watercourse near the mine adit that is highly acidic and contains high concentrations of heavy metals, has been neutralized as the AMD became diluted with nearby natural stream water. The toxicity of stream water showed a relatively strong correlation with the pH and dissolved metal concentrations of water implying the toxic effects of stream water on its stream biota. In contrast, the toxicity results obtained from stream sediments hardly showed close correlation with the composition of toxic elements, particularly with enriched arsenic.

1. Introduction

Acid mine drainage (AMD) is the most commonly documented unwanted consequence of mining activities. The primary cause of AMD generation is the oxidation of sulfur-bearing minerals such as pyrite during excavation. The generated acidic water elevates the level of dissolved metal concentration of the AMD receiving stream and negatively influences stream biota. Among the physical and chemical properties of AMD, pH is the most influential factor controlling the release of dissolved metals and metal hydroxide precipitations. The pH of AMD shows a wide variation ranging from 1.5 to 6 depending on the various geological characteristics of the particular region (Nordstrom, 2009; Skousen et al., 1998). The eco-toxicological influence of stream water in the AMD watercourse and its sediments are complicated and the individual effects of geochemical parameters such as acidity, dissolved metals, precipitated metal hydroxides, and the original sediment in the particular region is difficult to investigate separately (Hogsden and Harding, 2012). Moreover, the chemical properties of stream sediments were often reported to be one which is not strongly boned with the chemical properties of its overlying water body (Williams, 2001).

Ilgwang mine, located in Busan, Korea, is an abandoned Cu mine which generates highly acidic mine drainage (pH ≈ 2.5). The AMD watercourse of this site displays a typical yellow boy symptom. Visible biota in the surrounding stream seems to be scarce due to the effects of acidity and precipitated metal hydroxides. In Korean mining management, there is no legal standard regulating the water quality of mine drainage from abandoned mine sites. Instead, Mine Reclamation Corp. (MIRECO, Seoul, Korea) provides a recommended standard for the water quality of treated AMD, which includes the criteria for pH and 19 other elements or chemical compounds (Cd, As, CN, Hg, Pb, Cr, Cr^{6+}, dissolved Fe, Zn, Cu, dissolved Mn, F, Al, Na, Ca, K, Mg, SO_4^{2-}, and Cl^-). Yet, MIRECO's criteria on AMD do not consider the comprehensive effect of effluent toxicity as a whole. The whole-sediment toxicity testing has been published by ASTM (2010), OECD (2004, 2007), and USEPA (2000) to characterize the bioavailability and toxicity of sediment associated contaminants.

In evaluating the adverse environmental effects of AMD, chemical properties of sediments in the AMD watercourse has not been highlighted compared to those of stream water. Stream sediments however, to some extent affect the water quality of its overlying water body by continuously releasing or precipitating metal species (Hogsden and Harding, 2012). Also, the eco-toxicological effects of the sediment-associated contaminants are often overlooked in the evaluation of AMD on stream biota due to the low concentration of those contaminants when measured in aqueous phase. However, even the contaminants associated with sediments can be taken by fish and aquatic biota (Williams, 2001). Although the accumulated metal precipitates with low solubility reduces the aqueous toxicity of AMD impaired stream water, the accumulated metal precipitates can toxify benthic invertebrates (Canfield et al., 1994). The toxic effects may further be

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extended to far downstream via bioaccumulation within the food chain (Cain et al., 2004).

Accordingly, the importance of sediment composition has a potential significance in evaluating the eco-toxicity of AMD impaired stream biota. A stream affected by AMD commonly contains massive amounts of metal precipitates and therefore, the effect of stream sediments on its aquatic biota is critical. In this study, Microtox® toxicity test which uses luminescent bacteria (*Aliivibrio fischeri*) as a toxic receptor was used to test the toxicity of stream water and sediments. In evaluating the toxicity of a solid sample such as stream sediment, the aqueous extract of the solid sample was often used (Park and Hee, 2001; Parvez et al., 2006). In this study, both the sediment suspension with solid particles and the aqueous extract of sediment suspension were simultaneously evaluated and the results were used to find the correlation between the sediment composition and its toxicity. The correlation of geochemical properties and toxicity results was investigated for the stream water as well. The objectives of this study are to investigate the chemical and eco-toxicological effects of Ilgwang mine AMD and examine the correlation between toxicity test results and the geochemical properties of analyzed stream water and sediment samples. The results of this study would highlight the importance of stream sediment in studying the eco-toxicological evaluation of an AMD affected stream.

2. Materials and methods

2.1. Study area and samples

Ilgwang mine, located in Busan (Southeast part of the Korean Peninsula) (Fig. 1), was one of the biggest copper mines in Korea from 1938 to 1945. This mine had been also mined for W, Au, and Ag until its shutdown in the early 1990s. After mining was completed, mine reclamation actions were enforced from 1999 to 2002. The reclamation actions included disposal of mine tailing, clearance of concentrators, reinforcement of slopes, waste rock disposal, and installation of impermeable barrier walls and artificial wetlands. However, when the enforcement of reclamation actions had stopped since 2002, 100 t/day of highly acidic mine drainage (pH < 3) has been produced from the abandoned adit of the mine. The recorded average daily release of heavy metals was 53.4 kg Fe, 6.25 kg Cu, 5.26 kg Zn, 2.13 kg Mn, 0.14 kg As, 0.04 kg Cd (Kang et al., 2010). At the time of sampling, strong AMD was being discharged from the semi-closed adit and flowed into the downstream river, overflowing the abandoned AMD treatment facility.

The stream water and sediment samples were collected at various locations, from the mine adit to the downstream of the AMD flow (Fig. 1). The stream affected by AMD extended to around 1.5 km downstream where it joins a much larger river and therefore the AMD influence is weakened. The sampling site was assigned different reference codes based on the origin of the stream water. "A" stood for AMD and "B" for background natural stream. Stream water samples were assigned as "W", sediment samples as "S", and sediment suspension as "SE" (sediment extract), respectively. The codes were then followed by its origin code where, for example, the stream water affected by AMD would be named AW-# and the stream water in the adjacent natural stream would be named BW-#. The sample codes ASE and BSE stood for AMD sediment aqueous extract and background sediment aqueous extract. Note that there are no sediment samples at the water sampling points of A-2 and A-3 because those points were concrete ditches and sediment sampling was not possible.

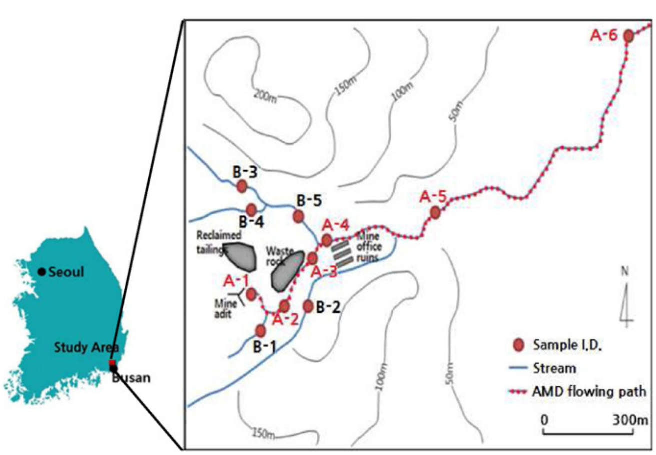

Fig. 1. Location of the study mine and the sampling sites.

2.2. Sample preparation and chemical analysis

For stream water samples, pH and electrical conductivity (EC) were measured at the sampling site. The stream water was then filtered with 0.45 μm filter and acidified with concentrated HNO_3 for cation analysis. Stream water samples for anion analysis and toxicity test were transferred to the laboratory without pretreatment and stored in 4 °C until use. The concentration of cation and anion were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkin Elmer) and ion chromatography (IC, Agilent), respectively.

The collected sediment samples were wet-sieved (#100 standard sieve) at the sampling site with the stream water to collect sediments with particles smaller than 150 μm and transferred to the laboratory. The samples were then dried at 40 °C and pulverized to a fine powder. A 0.1 g portion of each sample was digested for total metal content analysis using HF, HNO_3, and $HClO_4$ solutions at 130 °C for 24 h. The digested product was evaporated to dryness under 220 °C, and the residue was then dissolved in HNO_3 solution. The labile portion of metals were measured by 1 N HCl extraction test with 1:10 solid:solution ratio and 4 h of mixing time using an end-over-end rotator. The concentration of selected metals (Fe, Al, Mn, As, Cu, Pb, and Zn) was determined using ICP-AES. To validate the analysis, blind duplicates and the certified reference material for sediments (NCSDC73308) were analyzed. The prepared sediments were mixed with 2% NaCl solution with 1:4 solid to solution ratio for 1 h and the extracted metal concentrations were also determined with 0.45 μm filtered aqueous solution using ICP-AES.

2.3. Data analysis

To evaluate the degree of metal pollution of sediment by comparison to the base line metal concentration of the surrounding area, the geoaccumulation index was used. The geoaccumulation index is defined as,

$$\text{Geoaccumulation index} = \log_2(C_n/1.5B_n) \quad (1)$$

where C_n is the toxic element concentration in a sample and B_n is the measured concentration of the element in unpolluted sediments. This parameter has been used in other studies to characterize the pollution of sediments (Sarmiento et al., 2011). In this study, the metal concentration of sampling sites B-1, B-2, B-3, and B-5 was used to determine B_n. The results of the sampling site B-4 were excluded due to its geochemical anomaly.

The metal concentrations were also compared with the sediment quality guidelines (SQGs) for metals in freshwater ecosystems. In SQGs, samples can be grouped into two categories: threshold effect concentrations (TECs) and probable effect concentrations (PECs). The TECs are the concentrations below which harmful effects are unlikely to be observed and the PECs are the concentrations above which harmful effects are likely to be observed. Particularly in this study, the consensus based SQGs were used to predict the presence, absence and frequency of sediment toxicity (MacDonald et al., 2000).