

# Natural attenuation of arsenic in the wetland system around abandoned mining area

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## Introduction

Arsenic (As), a ubiquitous and carcinogenic element, has become an emerging issue because of its high concentrations around the world. For example, naturally high concentrations of As in the drinking water and groundwater in Bangladesh, India (West Bengal), Inner Mongolia, Vietnam, Argentina, Chile, Nepal, and Taiwan have caused serious concerns (Smedley and Kinniburgh 2002; Bhattacharya et al. 2006; Tandukar et al. 2006). In particular, mining activities result in problems, such as mine tailings, waste water, rocks, or ore, which may contain the relatively high magnitude of toxic elements such as As (Nriagu 1994; Loebenstein 1993; Gebel 1997; Laura and Dave 2008). In South Korea, there are about 1,000 abandoned metal mines (Kim et al. 2003) and little attention has been paid to the management of these abandoned mines, which are contaminated with As and heavy metals causing environmental hazards to agricultural soils, plants, and groundwater as well as human health (Smith et al. 1999; Kapaj et al. 2006).

Wetlands have been well recognized as important ecosystems (Mitsch and Gosselink 2007). Wetlands increase the retention time of contaminants by a water flow control of wetland plants and then reduce the diffusion of pollution to surrounding environment.

In addition, because of their sequestrable functions for contaminants such as heavy metals and As (Otte et al. 1991), in mining areas, they are constructed at the end of the interface with another land use as a last step of remediation technologies after physicochemical treatments are applied.

Wetland plants can alter the reducing sediment conditions to oxidizing sediment conditions by radial oxygen loss that plants release oxygen to the rhizospheres (Armstrong 1964; Mei et al. 2009; Deng et al. 2010). Thus, reduced Fe(II) can be changed to oxidized Fe(III) and then forms iron (oxy)hydroxides in rhizosediments, as well as the formation of iron plaques occurs on the roots and rhizomes of wetland plants (Hansel and Fendorf 2001; Batty et al. 2000). Accordingly, As can be attenuated by adsorption and/or co-precipitation on iron (oxy)hydroxides in the rhizospheres (Jain et al. 1999; Raven et al. 1998; Belzile and Tessier 1990; Jacobs et al. 1970; Majzlan et al. 2004; Pierce and Moore 1982; Wilkie and Hering 1996).

It has been recognized that wetlands can be employed as a passive treatment system from its capacity of natural attenuation. However, no attempts have been made for the potential use of wetlands to mitigate As contaminated lithosphere in South Korea. Thus, in order to examine the function for natural attenuation of As in wetlands, the study was carried out in selected natural wetland located in the vicinity of Myungbong mine heavily contaminated with As. The objectives of this study are (1) to investigate the contamination level of As and heavy metals, (2) to examine the ability to effectively attenuate As contamination in the studied wetland through accumulation in plant tissues and adsorption and/or coprecipitation on iron (oxy)hydroxides, in addition and

then (3) to characterize the stability of As in the wetland sediment for the assessment of capacity of the wetland to prevent diffusion of As.

## Materials and methods

### Site description

Water, sediment, and plant samples were collected during May 2008 at a natural cattail wetland situated downstream of Myungbong mine (Fig. 1), which is located in Jeonnam Province in South Korea and had Au–Ag production from 1910 to 1970 (Ko et al. 2003). The wetland received large quantity of As derived from approximately 6,000 m<sup>3</sup> size of mine tailings pile, which had been abandoned without any management and contained a high As content (up to 6,830 mg/kg) but relatively low concentration of other heavy metals (Kim et al. 2003; Ahn et al. 2003; Ko et al. 2003; Lee et al. 2005). The major sulfide mineral is pyrite (FeS<sub>2</sub>) and arsenopyrite (FeAsS) (Ko et al. 2003) mainly observable in Au–Ag mine tailings. Most of As phases in tailings were presented predominantly as co-precipitated with iron oxyhydroxides (98.8%), primarily as amorphous forms



Fig. 1 Location of the natural cattail wetland and Myungbong Mine

(93.8%) based on the sequential extraction results (Ahn et al. 2003) with indicating most of tailings are composed to highly weathered-pyrite and can be potentially changed to the mobile or bioavailable phases depending on the environmental conditions.

#### Sample collection and analysis

Surface water samples were collected above the sediment–water interface at five sampling locations. Measurement of pH and oxidizing-reducing potential (ORP) was accompanied in the field (Consort, model C562). Then, the samples were immediately filtered through a 0.45- $\mu$ m nylon syringe filter (Whatman), acidified by  $\text{HNO}_3$  for dissolved As and heavy metals analysis. Aliquots of pore-water samples were

obtained by centrifugation of sediments for 20 min at 3,000 rpm and followed in the same way as above water samples. The As and heavy metal concentrations of all filtrates were determined by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500 CE).

Wetland sediment samples, which were black colored with stink and became entangled with decayed roots, were collected simultaneously at the surface water sampling points. The samples were oven-dried at 40\_C for the physicochemical characterization and a part of sediment was freeze-dried for the additional spectroscopic analysis. After removal of large roots, samples were pulverized and subsequently sieved to less than 180  $\mu\text{m}$ . In order to obtain rhizosediments, plants were thoroughly shaken away to remove clinging sediment from the roots. The sediment remaining on the roots, regarded as rhizosediments, had been removed by hands (a layer about 2–5 mm thick). The roots were put into a beaker to be washed with about 100 mL of deionized water and then oven-dried at 40\_C and sieved (revised Doyle and Otte 1997).

The homogenized sediments and rhizosediments (0.2 g) were digested using 2 mL of acid mixture (3:1 HCl : HNO<sub>3</sub> by volume) followed by heating at 70\_C for 1 h (Ure 1995). The digests were then analyzed for As by graphite furnace-atomic absorption spectrometry (GF-AAS, Perkin Elmer 5100 PC) and heavy metals by inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin Elmer 5300 DV) and flame-atomic absorption spectrometry (Flame-AAS, Perkin Elmer 5100 PC).

Five fresh plant samples collected at each sampling location were separated into shoot and rhizome portions, then washed thoroughly with tap water to

remove residual sediment, and rinsed several times with deionized water. Plant tissues were freeze-dried and then homogenized using a mill by sieving to less than 1 mm.

As and total metal concentrations in plant tissues were determined using a wet digestion procedure described previously by Hansel et al. (2002). Aliquots of plant tissues (0.1 g) were digested in 15-mL polypropylene centrifuge tubes with 2 mL of 60% HNO<sub>3</sub> for 24 h. Successive additions of 30% H<sub>2</sub>O<sub>2</sub> (total 2 mL) was then followed by heating at 100 ± 2 °C for 30 min and carried on until plant residues disappeared. Total concentration was then analyzed by ICP-MS (Agilent 7500 CE).

In order to study the possible association of As with iron plaques in the rhizomes of cattail, a small portion of freeze-dried rhizome tissue was mounted on an ion sputter (E-1030), coated white gold for electrical conductivity and then determined by scanning electron microscope (SEM, Hitach S-4700), and the elemental chemical composition of samples was examined by energy-dispersive X-ray (EDX, Horiba) microanalysis.

#### Leaching experiment

In order to determine a water soluble form and stability of As in the wetland sediment, leaching experiment was conducted for 4 weeks. Paddy soil collected from just beside of the wetland and uncontaminated wetland sediment located 20 km far away from Myungbong mine were added as comparative samples. The paddy soil was also impacted by Myungbong mine tailings; As enrichment was shown about 84.7–130 mg/kg (Lee et al. 2006). Therefore, we investigated As stability in the wetland by leaching experiment using sediments

and paddy soils contaminated the same source. Approximately 10 g of samples was weighed into each 200-mL glass serum bottle, to which 100 mL of deionized water was added. The samples were then agitated on a rotating shaker (150 rpm) at 25 °C under anoxic conditions—the same as a wetland environment. In order to create anoxic conditions, air in the serum bottles was flushed by nitrogen gas (99.99% N<sub>2</sub>) through the medium for 1 min. The procedure was repeated thrice to reach a complete anoxic condition.

The aliquot of solution was sampled by extraction at 18 h and 7, 14, 21, and 28 days after incubation. The extracted solution was filtered and then immediately passed through a silica-based anion-exchange cartridge (LC-SAX SPE Tube, Supelco) to separate As(III) and As(V) (Le et al. 2000). Concentrations of total As and As(III) were determined by GF-AAS and Fe by Flame-AAS.

#### Sequential extraction

Sequential extraction scheme is common procedure to present useful information regarding general partitioning of trace elements within soils and sediments (Laforce et al. 2000). As in sediments and paddy soils was estimated using the method modified from Wenzel et al. (2001) (Table 1). Aliquots of dried samples (0.4 g) were collected in 15-mL polypropylene centrifuge tubes and then sequentially treated in duplicates to apportion five As pools: (1) non-specifically sorbed, (2) specifically sorbed, (3) amorphous and poorly crystalline hydrous oxides of Fe and Al, (4) well-crystalline hydrous oxides of Fe and Al, and (5) residual phases. After each step, aqueous As was analyzed by GF-AAS after centrifugation at 3,000 rpm for 10 min, filtration (0.45 μm nylon syringe filter, Whatman).

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