



Hydrochemical, mineralogical and isotopic investigation of arsenic distribution and mobilization in the Guandu wetland of Taiwan



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SUMMARY

This study explores the distribution and mobilization of As in the ecosystem of the Guandu wetlands, Taiwan. The chemical parameters, chemical sequential extraction, mineralogical compositions, and sulfur isotopic compositions (i.e., $\delta^{34}\text{S}_{[\text{SO}_4]}$ and $\delta^{18}\text{S}_{[\text{SO}_4]}$) of porewater and two sediment core samples (S2 and S5, locate in the inner and outer sites of the Guandu wetland) were analyzed to characterize As spatial distribution. The crucial mechanisms of the biogeochemical processes that control As mobility in wetland ecosystems were inferred. Based on factor analysis and cluster analysis, the vertical distributions of the redox zones in S2 and S5 were classified as oxidizing, transitional, and reducing zones, respectively. The mineralogical characteristics showed that adsorption and desorption are the major processes which control As retention in the surface sediment under cyclic aerobic/anaerobic conditions. Aqueous As and Fe were restrained because of oxidation, whereas aqueous Fe precipitated as amorphous metal oxides (i.e., FeO, FeOOH, and Fe₂O₃). Subsequently, aqueous As was adsorbed onto the surfaces of Fe(hydr)oxides, resulting in a high solid As content in the oxidizing zone. The high aqueous As content in the boundary of the transitional and reducing zones was caused by the reductive dissolution of highly dissolved Fe compounds through the microbial respiration of organic matter (OM). In the reducing zone, As³⁺ can be constrained by the formation of FeS₂ in sediment during bacterial sulfate reduction that is governed by the relative enrichment of the $\delta^{34}\text{S}_{[\text{SO}_4]}$ and $\delta^{18}\text{S}_{[\text{SO}_4]}$ values. Sulfur disproportionation and the redox of elemental sulfur (S⁰) are additional reaction paths that cause As cycling. Arsenic mobility in the Guandu wetland is primarily caused by the reductive dissolution of As-containing Fe-oxyhydroxides and the redox cycling of sulfate/sulfide, accompanied by the respiration of OM.

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1. Introduction

Wetlands can accumulate nutrients and anthropogenic substances in downstream eutrophication ecosystems. Solid Fe and Mn oxyhydroxides act as a sink for many trace elements in reducing environments (Carroll et al., 1998; Lytle et al., 1998). Arsenic in organic-rich wetlands can limit transformation and mobilization (La Force et al., 2000; Bauer et al., 2008; Du Laing et al., 2009). The redox cycling of As in wetland systems is largely determined by (1) in situ redox conditions, (2) the dissolution–precipitation of minerals with arsenic as a constituent ion, and (3) sorption–desorption (La Force et al., 2000; Mandal et al., 2009, 2012). The redox states of solid As stability complexes (Goldberg, 2002) and co-precipitates (Waychunas et al., 1993) are thermodynamically controlled. The geochemical characteristics of As mobility are

strongly influenced by iron, sulfur, and carbon redox processes, which may be primarily governed by the metabolic activity of bacteria (Pierce and Moore, 1982; Wilkin and Ford, 2006; Mukherjee and Fryar, 2008). A strong correlation of aqueous As³⁺ and Fe²⁺ concentrations are observed in low-level redox potential. For example, the binding of As and Fe in the same solid phase pools has been found in strongly minerotrophic and Fe-rich fen. Redox-related processes in aquifers/wetlands are largely controlled by the reduction of FeOOH in the presence of organic matter (OM) during bacteria respiration, serving as electron donors (McArthur et al., 2001, 2004; Harvey et al., 2002; Zheng et al., 2004; Cancès et al., 2005; Hossain et al., 2012).

In oxidizing conditions, low As mobility is caused by the formation of As⁵⁺ and its subsequent adsorption of metal oxides. Arsenic anions can sorb or bind using carbonates (Bauer et al., 2008; Rothwell et al., 2009) and silicates (Goldberg, 2002), but Al, Mn, and especially Fe oxides are the most crucial As sorbents in oxic conditions because of their large reactive surface areas (Smedley

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and Kinniburgh, 2002; Wang and Mulligan, 2006, 2008). The oxygenation of Fe^{2+} containing water to induce iron precipitation is used for sorbing and removing of As during As-contaminated water treatment processes (Jessen et al., 2005). Analytical methods have been used to accurately determine As oxidation states and local coordination environments in various solid phases and its possible presence as a surface-bound or adsorbed species. The chemical sequential extraction method is frequently used to determine operationally defined fractions. Spectroscopic methods, including X-ray techniques and vibrational spectroscopy, entail measuring the amount of energy absorbed or emitted by a system in response to an external perturbation in the form of electromagnetic radiation. The local coordination environments of As^{3+} and As^{5+} sorbed to natural or synthetic iron oxides of varying crystallinity have been widely investigated and compared with X-ray absorption near-edge structure (XANES) spectroscopic techniques (Manning et al., 2002; Sherman and Randall, 2003). The varying affinities of As^{3+} and As^{5+} can affect the extent of their sorption in sediment. The various capacities for As sorption onto sediment may affect As' concentration in water. In anoxic sediments, dissolved sulfates are terminal electron acceptors and are used by sulfate-reducing bacteria (SRB) during the heterotrophic respiration of OM (Jørgensen, 1982). A crucial pathway regarding trace metal behavior in sediments is the reaction of dissolved sulfide with ferrous iron to precipitate Fe sulfides, which may be responsible for metal uptake through sorption and/or co-precipitation (Xia et al., 1998; Wang and Mulligan, 2008; Langner et al., 2012). Fe disulfide and pyrite are important carriers of As (Dellwig et al., 2002; Bostick and Fendorf, 2003). Most metal sulfides provide a potential sink for As in anoxic sediments (Dellwig et al., 2002). Under sulfate-reducing conditions, As adsorption on the surfaces of metal sulfides and/or co-precipitation is the most crucial uptake process (Farquhar et al., 2002; Wolthers et al., 2005). Numerous studies have indicated that isotopic techniques are useful for understanding the influence of sulfur cycling geochemical environmental conditions on As mobility (Lipfert et al., 2007; Mukherjee and Fryar, 2008; Kao et al., 2011).

High As concentrations occur naturally in geothermal areas because of volcanic activity, resulting in pollution in groundwater, geothermal spring water, and downstream of the Guandu wetland ecosystem. However, the distribution and mobilization of As in the wetland ecosystem are not well understood. This study examines the geochemical processes of As in the Guandu wetland. We investigate the geochemical characteristics and processes of As in wetlands using advanced technologies, including chemical analyses, stable isotopic analyses, and spectroscopic methods. Finally, a conceptual model for the biogeochemical processes of aqueous and solid As cycling in the Guandu wetland is proposed.

2. Materials and methods

2.1. Study area

The Guandu wetland is located in the northern part of the Guandu Plain in Taipei, Taiwan, which is the downstream of the Beitou geothermal spring (Fig. 1). In the 1960s, many geothermal fields of Beitou have been developed to generate energy from the steam and hot water reservoirs of Tatun Volcano Group. Large scale andesitic volcanic eruptions took place in north and northeast offshore islands of Taiwan during the Pleistocene. Both andesitic lavas and andesitic pyroclastics are presented. Acidic hot spring water has high arsenic, sulfate and lead concentrations. Previous studies revealed that As concentration in the hot spring water was up to 4.32 mg/L and overly exceeded the drinking water guideline of WHO, 0.01 mg/L (Wang, 2005; Chiang et al., 2010). The As-rich

spring water flows to Huang Gang Creek, discharging a high-As flux to the Guandu Plain. Long-term irrigation with high As concentration water has caused the high average As contents of 145 and 143 mg/kg in the upper (0–15 cm) and lower (15–30 cm) soils, respectively, in the Guandu Plain, markedly exceeds the soil contamination standard of 60 mg/kg (Chiang et al., 2010). Arsenic-rich spring water flows to the downstream wetland, and may alter aqueous and solid-phase compositions. As contents were as high as 1–5 g/kg in the coarse fraction (>0.25 mm) soil samples (Wu, 2008).

The Guandu wetland is near to the mouth of the Keelung and Tanshui Rivers, it has a semi-diurnal tidal regime with a tidal amplitude of approximately 1–2 m; and although it is only 10 km away from the Tanshui River estuary, the wetland area is widely affected by tidal fluctuations. Tidal seawater, which can intrude into the upper estuary approximately 25 km away from the river mouth, mixes with the river water during high tide, but only partially mixes during low tide (Liu et al., 2001). Seawater mixing with fresh water may provide excessive amount of competition ions such as Cl^- and SO_4^{2-} which can theoretically function as HCO_3^- and PO_4^{3-} . The effect of ionic competition against the adsorption site of As onto the surface of metal oxides is also assessed (Kim et al., 2000; Appelo et al., 2002). Hence, the variations of salinity, pH, and redox conditions may potentially affect the As releases and the retention reactions in wetland system.

2.2. Water, soil and plant sampling

Porewater and sediment samples of core were collected at the inner (S2 = 70 cm) and outer sites (S5 = 85 cm) of Guandu wetland in April, 2010 (Fig. 1). Porewater samples with an interval of 5 cm were extracted using a Rhizon sampler (microporous polymer, <0.2 μm pore size). The sediment samples with an interval of 5 cm were air-dried to facilitate the analyzing of chemical compounds. Porewater and sediment samples in both cores with an interval of 10 cm were extracted for isotopic analyses. Water samples were stored in polyethylene containers, maintained at 4 °C, and sent to the laboratory within 24 h. Sediment samples were stored in N_2 -purged plastic bags, dried at room temperature, and homogenized using 100-mesh sieves in an anaerobic glove box. The split samples were removed from the glove box and allowed to oxidize in an oven at 50 °C for 72 h. Chemical compositions, speciation of As and Fe, chemical sequential extraction, and isotopic compositions in aqueous phase and/or solid phase were analyzed.

2.3. Chemical compounds of water and soil analysis

The dissolved oxygen (DO), redox potential (Eh), electrical conductivity (EC) and pH of the porewater samples were measured at S2 and S5. Porewater samples were filtered through 0.45- μm glass fiber papers. Unacidified parameters (NO_3^- , Cl^- , and SO_4^{2-}) and acidified parameters (NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe and Mn) were used to measured by ion chromatography (by, DIONEX ICS-900). Bicarbonate was determined by acid titration. Porewater samples for metals and other ionic concentrations measurements were with 0.45 μm nylon filters and acidified with various acids for specific analysis (APHA, 1998). Ferrous (Fe^{2+}) concentrations of the samples were measured colorimetrically using the ferrozine method (Lovley and Phillips, 1987). Analytical method of As^{3+} , As^{5+} , MMA, and DMA followed closely from our previous study (Huang et al., 2003). The variances of duplicate measurements were less than 10%; recoveries of check and spike samples were between 85% and 115%, respectively. Moreover, chemical sequential extraction was conducted for the determination of As concentrations in the various mineral phases (Bauer et al., 2008). The extraction

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