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Natural attenuation process via microbial oxidation of arsenic in a high Andean watershed

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HIGHLIGHTS

- Dissolved As decreases in a stream from a hydrothermal source in Chilean Altiplano.
- As attenuation is governed by As(III) oxidation and a pH decrease.
- The oxidation of As(III) is mediated by As(III)-oxidizing microorganisms.
- Dissolved As attenuation is correlated with As immobilization on Fe-rich sediments.
- Biological oxidation coupled to sorption/coprecipitation limits the flux of As from hydrothermal waters.

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ABSTRACT

Rivers in northern Chile have arsenic (As) concentrations at levels that are toxic for humans and other organisms. Microorganism-mediated redox reactions have a crucial role in the As cycle; the microbial oxidation of As (As(III) to As(V)) is a critical transformation because it favors the immobilization of As in the solid phase. We studied the role of microbial As oxidation for controlling the mobility of As in the extreme environment found in the Chilean Altiplano (i.e., >4000 meters above sea level (masl) and <310 mm annual rainfall), which are conditions that have rarely been studied. Our model system was the upper Azufre River sub-basin, where the natural attenuation of As from hydrothermal discharge (pH 4–6) was observed. As(III) was actively oxidized by a microbial consortium, leading to a significant decrease in the dissolved As concentrations and a corresponding increase in the sediment's As concentration downstream of the hydrothermal source. In-situ oxidation experiments demonstrated that the As oxidation required biological activity, and microbiological molecular analysis confirmed the presence of As(III)-oxidizing groups (*aroA*-like genes) in the system. In addition, the pH measurements and solid phase analysis strongly suggested that the As removal mechanism involved adsorption or coprecipitation with Fe-oxyhydroxides. Taken together, these results indicate that the microorganism-mediated As oxidation contributed to the attenuation of As concentrations and the stabilization of As in the solid phase, therefore controlling the amount of As transported downstream. This study is the first to demonstrate the microbial oxidation of As in Altiplano basins and its relevance in the immobilization of As.

1. Introduction

Arsenic (As) is a toxic element widely distributed in natural environments (Cullen and Reimer, 1989; Smedley and Kinniburgh, 2002). The contamination of surface and groundwater by As is a serious environmental concern because such contamination limits the use of the water and has adverse effects on human health (Berg et al., 2001; Bhattacharya et al., 2002; Smedley and Kinniburgh, 2002). Although the behavior of As in nature has been widely studied in recent years (Berg et al., 2001; Manning et al., 1998; Nickson et al., 1998; Nordstrom, 2002; Oremland and Stolz, 2003; Roussel et al., 2000; Stollenwerk et al., 2007), the biogeochemical controls governing the mobilization, stabilization, and release of As into river systems are still unclear.

The mechanisms of As attenuation in natural environments include a combination of physical, chemical, and microbial factors (Wang and Mulligan, 2006). The sorption onto iron (Fe) oxyhydroxides is the major natural attenuation process for the removal and sequestration (stabilization) of As species (Drahota et al., 2012; Leblanc et al., 1996).

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Co-precipitation of As and Fe also contribute to the stabilization of As in solid phase (Fuller et al., 1993). However, changes in the As speciation, particularly the oxidation from As(III) to As(V), have a crucial role in the release and mobilization of As because As species differ in their solubility, toxicity, transport, and bioavailability (Aposhian and Aposhian, 2006; Casiot et al., 2005; Drahota et al., 2009; Masscheleyn et al., 1991; Smedley and Kinniburgh, 2002). Therefore, microorganisms can oxidize As and therefore increase its sorption onto mineral phases because As(V) binds more strongly to Fe oxyhydroxides than As(III) (Oremland and Stolz, 2003). The impact of As oxidation reactions catalyzed by microorganisms on As attenuation may vary according to the climatic and geochemical conditions of a particular system (Lin and Puls, 2003; Smedley and Kinniburgh, 2002).

The occurrence of As in arid environments is widespread due to geogenic or anthropogenic sources (Baker et al., 1998; Del Razo et al., 1990; Guo et al., 2003; Smedley et al., 2002). Northern Chile is seriously affected by high concentrations (>1 mg l^{-1}) of As in rivers (Alsina et al., in press; Caceres et al., 1992; Landrum et al., 2009; Pizarro et al., 2010; Queirolo et al., 2000; Romero et al., 2003; Sancha, 1999), which generates serious problems for the population reliant upon these waters in this arid region. The biogeochemical processes that control the fate of As in river systems are quite specific because the extreme conditions, which are high altitude (>4000 masl) and high aridity (<310 mm $year^{-1}$ of precipitation), impact the environment. In arid and semi-arid systems, metal enrichment processes may occur via capillary transport (Dold and Fontboté, 2001). The mobilized elements (e.g., As) are transported toward the surface of the soils and sediments where the presence of oxygen may facilitate oxidation (Bechtel et al., 2001; Dold and Fontboté, 2001; Smedley and Kinniburgh, 2002). Therefore, the As(III) oxidation and the As stabilization (especially as As(V) species) by adsorption processes occur predominantly under oxidizing conditions (Smedley and Kinniburgh, 2002). The role of biological reactions, particularly the reactions mediated by As-oxidizing microorganisms, in the biogeochemical cycling of As still is unknown for these types of systems.

The Chilean Altiplano is characterized by a scarcity of water and rich mining activity. Particularly, the Azufre River sub-basin contains a complex mixture of natural and anthropogenic contaminants from different sources, seriously affecting the quality of the surface water resources. We observed that in the upper section of this sub-basin, the As concentrations are high (1.0–3.5 mg l^{-1}); additionally, the hydrothermal waters and sediments exhibit naturally elevated concentrations of As (0.8 mg l^{-1} and >4 g kg^{-1} respectively). Interestingly, the total dissolved As (AsD) concentrations are attenuated ($\Delta - 70\%$ AsD), and a noticeable amount of As oxidation ($\Delta + 90\%$ As(V)/AsD) occurs in the hydrothermal springs (Leiva et al., 2011). Effective risk management and remediation efforts for such As-enriched fluvial systems as Azufre River sub-basin requires the understanding and quantification of the changes in chemical speciation, as well as the biogeochemical control of the mobilization/stabilization of As in the solid phase. In this regard, the Altiplano in northern Chile is an ideal site to study the processes that control As mobilization under extreme conditions.

2. General setting

2.1. Climatic and environmental characteristics of the model site

The Altiplano is an area in the central Andes (15°–34°S) covering the western part of Bolivia, northern Chile, southern Peru, and northern Argentina, with an average altitude of 3600 masl (Allmendinger et al., 1997). The Chilean Altiplano is an elevated plateau 4000 masl covered by numerous andesitic stratovolcanoes that can reach up 6500 masl (Muñoz and Charrier, 1996; Stern et al., 2007). Particularly, the geological formations include conglomerates of the Upper Pliocene–Pleistocene, sandstones, shales, and rhyolitic ignimbrites (Salas et al., 1966). This area has average temperatures of 0 °C, concentrated rainfall between 50 and 300 mm $year^{-1}$, and potential evaporation of approximately 600–1200 mm $year^{-1}$ (DGA, 1987). The climatic conditions on all timescales are closely related to changes in the upper-air circulation and by the amount of near-surface water vapor, impacting wet and dry conditions and inducing strong rainfall fluctuations (Garreaud et al., 2003).

The Azufre River sub-basin is located in the XV Region of Arica and Parinacota, in northern Chile (Fig. 1). This sub-basin is part of the Lluta River Watershed (LRW) and extends between 18° 00′–18° 30′ S and 70° 20′–69° 22′ W. The Azufre River originates in the upper section of the LRW in the Altiplano and has an average altitude of 4250 masl (Leiva et al., 2011). This area has a semi-arid climate: rainfall rarely exceeds an average of 310 mm annually and occurs as intense thunderstorms from late December to late February. This area is characterized by water scarcity caused by the limited rainfall, low humidity, strong solar radiation and high evaporation rates (4.9 ± 0.5 mm d^{-1}) overall. The Azufre River sub-basin is strongly influenced by the Tacora Volcano, which is the northernmost volcano in Chile and located at 17°43′S, 69°46′W with an altitude of 5980 masl. The Tacora volcano is a stratovolcano in the Central Volcanic Zone (CVZ) of the Andes (15°–28°S) (Stern et al., 2007; Clavero et al., 2005). The CVZ is a chain of quaternary stratovolcanoes and andesitic–rhyodacitic domes (Allmendinger et al., 1997 and Kay et al., 1999). The Tacora volcano has been active since at least the Middle Pleistocene and displays permanent fumarolic (CO_2 and SO_2 degassing) and hydrothermal features in the southwest flank of the volcano within a drainage area contributing to the Azufre River (Capaccioni et al., 2011; Clavero et al., 2005, 2006). Additionally, the legacy of sulfur mining is observed on the Tacora crater (~5500 masl) and the west flank, where tailings and waste rock deposits may be observed. Acid mine drainage (pH < 2.0; As < 0.4 mg l^{-1}, Fe < 10 mg l^{-1}) from uncontrolled exposure to water and atmospheric O_2 is observed at the foot of mine tailings. The mining legacy and the dry climate limit the growth of vegetation, but in the upper section of the watershed, there is a wetland where different biogeochemical processes can control the environmental fate of As and other contaminants.

The study site is located in this wetland, which runs along the middle reach of the Azufre River and receives a flow of several hydrothermal features; these hydrothermal features finally drain into the Azufre River as described in Fig. 1. Hydrothermal springs are characterized by elevated As content, causing the mobilization of high concentrations of dissolved As (>1 mg l^{-1}) and Fe (>1 mg l^{-1}) to the river flow (Leiva et al., 2011).

2.2. Microbiological context

Microbial processes have a significant impact on the mobility and speciation of As (Oremland and Stolz, 2003). The transformations mediated by microorganisms play an important role in their modulation of As behavior in soils, wetlands, groundwater, and surface waters, as well as in the toxicological characteristics of environmental As (Oremland and Stolz, 2003; Mukhopadhyay et al., 2002; Tsai et al., 2009). As(III) is more toxic and mobile than As(V) and its presence usually entails a comparatively larger environmental health risk and concern (Mondal et al., 2006; Pierce and Moore, 1982). Bacteria capable of oxidizing As(III) have been found in sediments, soils, mine tailings, hydrothermal sites, and natural waters (Donahoe-Christiansen et al., 2004; Gihring and Banfield, 2001; Gihring et al., 2001; Hamamura et al., 2009; Inskeep et al., 2007; Oremland et al., 2002; Oremland and Stolz, 2003; Santini et al., 2002). Both heterotrophic and autotrophic bacteria can oxidize As. Heterotrophic bacteria oxidize As(III) through a detoxification mechanism and do not obtain energy from the reaction (Anderson et al., 1992; Silver and Phung, 2005). In contrast, autotrophic bacteria oxidize As(III) as a chemolithoautotrophic growth strategy, where carbon fixation is