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Abiotic and biotic factors influencing the mobility of arsenic in groundwater of a through-flow island in the Okavango Delta, Botswana

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SUMMARY

The Okavango Delta of Botswana is a large arid-zone wetland comprising 20,000 km^2 of permanent and seasonal floodplains and over 100,000 islands. It has been shown that island groundwater can have very high dissolved arsenic (As) concentration, but the abiotic and biotic controls on As mobility are not well understood in this setting. At New Island, an island located in the seasonal swamp, dissolved As concentration increased from below detection limits in the surface water to 180 μg/L in groundwater, present as As(III) species. We investigated the relative importance of hydrologic, geochemical, and geomicrobial processes, as well as influences of recent extreme flooding events, in mobilizing and sequestering As in the shallow groundwater system under this island. Our results suggest that evapotranspiration and through-flow conditions control the location of the high arsenic zone. A combination of processes is hypothesized to control elevated As in the concentration zone of New Island: high evapotranspiration rates concentrate As and other solutes, more alkaline pH leads to desorption of arsenic or dissolution of arsenic sulfides, and formation of thioarsenic complexes acts to keep arsenic in solution. Evidence from X-ray absorption near-edge structure spectroscopy (XANES) and sulfate reducing bacteria (SRB) measurements further suggests that SRBs influence arsenic sequestration as orpiment (As_2S_3). Although dissolved organic matter (DOM) was not significantly correlated to dissolved As in the groundwater, our results suggest that DOM may serve as an electron donor for sulfate reduction or other microbial reactions that influence redox state and As mobility. These results have important implications for water management in the region and in other large wetland environments. The processes evaluated in this study are also relevant for arsenic removal in subsurface constructed wetland systems that may exhibit rapidly changing processes over small spatial scales.

1. Introduction

The occurrence of arsenic in groundwater of the Okavango Delta of Botswana is presently one of only several known cases of geogenic arsenic contamination on the African continent (Huntsman-Mapila et al., 2006, 2011; Ravenscroft et al., 2009). The Okavango Delta of Botswana is located in an arid zone that includes the Kalahari Desert to the south and Namibia to the west. This 20,000 km^2 wetland system includes over 100,000 islands, ranging in size from a few meters to over 50,000 ha (Gumbricht et al., 2004). Elevated arsenic concentrations have been measured in shallow groundwater underlying an island (Camp Island) in the Okavango Delta proper (Huntsman-Mapila et al., 2011) and in deep groundwater (>70 m) southeast of the Okavango Delta, near the town of Maun (Huntsman-Mapila et al., 2006). At Camp Island the highest total dissolved As (3.2 mg As L^{-1}) was measured in groundwater of the central part of the island where salinity and conductivity values were also highest (Huntsman-Mapila et al., 2011). Evaporative concentration of As and other solutes in the

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high concentration zone at the center of Camp Island was found to be a major driver of elevated As at this site, and the question of whether elevated As is associated with groundwater underlying the barren island centers of other islands has been raised.

The source of arsenic in the Okavango is geogenic but the exact origin has not been confirmed. Arsenic may derive from weathering of granitic bedrock in the headwaters in Angola, which has been proposed by Huntsman-Mapila et al. (2006) or potentially may be associated with rift tectonics. The tectonically-active Okavango Delta is the southwestern branch of the East African Rift Valley (Milzow et al., 2009). In the Main Ethiopian Rift sector of the East African Rift Valley, the rhyolitic rocks and their weathered and re-worked fluvio-lacustrine sediments have high content of As, as well as F, Mo, U, and V, and may be the source of these toxic elements elsewhere in the region (Rango et al., 2010).

The mobilization of geogenic arsenic from sediments in different parts of the world can be described by three main mechanisms. Arsenic can be mobilized under oxidizing conditions that lead to the dissolution of arsenopyrite or sulfidic minerals (Welch et al., 2000; Schreiber et al., 2000). In a second case, common in arid zones with alkaline, oxidizing groundwater and evapoconcentration of solutes, such as in the southwestern USA, La Pampa, Brazil and elsewhere in the Chaco-pampean aquifer, arsenate desorbs mainly from Fe oxyhydroxides and other mineral oxides at high pH (Ravenscroft et al., 2009). Finally, perhaps the most widely documented occurrence of groundwater arsenic pollution is in south and southeast Asia, where tens of millions of people have been exposed to arsenic concentrations above the World Health Organization recommended limit of $10\ \mu g\ As\ L^{-1}$ (Mukherjee and Bhattacharya, 2001; Ahmed et al., 2004; Fendorf et al., 2010). In southeast Asia, arsenic is mobilized from sediments mainly as a result of microbial reductive dissolution of Fe- and As-bearing minerals, for which labile dissolved organic matter is the electron donor (Mukherjee and Bhattacharya, 2001; McArthur et al., 2004; Smedley and Kinniburgh, 2002).

The Okavango Delta comprises two environments where elevated As concentrations are typically found in groundwater, specifically arid-zone closed basin environments and strongly reducing alluvial aquifers (Smedley and Kinniburgh, 2002; Nordstrom, 2002). The co-existence of both of these environments has been a challenge for identification of the triggers leading to high groundwater As concentration in the Okavango Delta. Huntsman-Mapila et al. (2011) postulated that elevated arsenic in the Okavango Delta may result from a combination of evapoconcentration of dissolved arsenic, possibly released by reductive dissolution earlier along the groundwater flowpath, and desorption of arsenic from sediments at higher pH. In addition, Huntsman-Mapila et al. (2011) identified that redox processes and the influence of DOM and iron on arsenic mobilization needed further investigation.

The presence of elevated arsenic concentrations where arid conditions and reducing sediments coexist is not unique to the Okavango Delta. Elevated arsenic concentrations have also been found in the San Joaquin Delta of California, USA (Belitz et al., 2003; Izbicki et al., 2008), which has alluvial and fluvial deposits. There, redox conditions are highly variable and elevated As may result from several mechanisms, including reductive dissolution of Fe minerals, evapoconcentration of As, and desorption of As from sediments at high pH (Belitz et al., 2003).

In wetlands, organic matter is typically a major reservoir for sulfur (Langner et al., 2011) and, in the event of sulfate depletion, the organic S pool also may be an important source of sulfate upon oxidation of organic material (Strickland et al., 1987). Under reducing conditions and in the presence of ample amounts of organic carbon as an electron donor, sulfate reducing bacteria (SRB) readily convert sulfate to hydrogen sulfide, which contributes to As(III) removal via the precipitation of As_2S_3 (orpiment) (Stumm and Morgan, 1996; Lizama et al., 2011). In evaporation basins of the San Joaquin Valley, California, which are used for the disposal of agricultural drainage, the sediments were a sink for As (Ryu et al., 2011) and chemical equilibrium modeling suggested that orpiment was formed (Ryu et al., 2002). In this environment Gao et al. (2007) identified that the potential role of DOM as a complexing agent with sulfide to maintain As in solution warranted further investigation. Indeed, the formation of thioarsenic species has been shown to keep As mobile in a variety of environments, such as sulfidic waters with orpiment dissolution (Suess and Planer-Friedrich, 2012), mine-impacted groundwater under sulfate-reducing conditions (Stucker et al., 2013), and geothermal waters (Planer-Friedrich et al., 2007).

To address some of the gaps in our knowledge regarding arsenic mobility in wetlands influenced by evaporation, the objectives of this study were (1) to characterize the chemical behavior of As along a groundwater flowpath with a natural evaporation gradient and (2) to evaluate the influence of redox processes, microorganisms, and hydrology on dissolved constituents, including DOM and arsenic. These goals also allowed us to test whether elevated As is widely associated with zones of evapoconcentration in groundwater of Okavango Delta islands. We evaluated groundwater solute and sediment chemistry along a west–east transect at New Island, a small island in the seasonal swamp of the Okavango Delta located approximately 20 km downstream of previously-studied Camp Island (Figs. 1 and 2). This study was conducted at the end of the annual flood season and after several years of intense flooding, which made it possible to also examine the influence of extreme flooding on groundwater biogeochemical processes and As mobility.

2. Methods

2.1. Study site and hydrogeologic setting

The Okavango Delta is located in the northwest of Botswana in southern Africa (Fig. 1). It is both an alluvial fan and an extensive wetland system that is annually flooded by approximately $10\ km^3$ of water originating in the Angolan Highlands and delivered via the Okavango River. In this region, evaporation exceeds precipitation by three to four times (McCarthy and Ellery, 1995; Ramberg and Wolski, 2008). Within the Okavango Delta, the Okavango River diverges into a series of distributary channels and floodplains that carry the water to its distal reaches (Fig. 1). The Boro River system (Fig. 1) conducts water through permanently-flooded and seasonally-flooded hydrotones, which have been described elsewhere (McCarthy and Ellery, 1995; Wolski and Savenije, 2006).

Islands are a characteristic landscape feature in the Okavango Delta. Islands initiate as termite mounds, scrollbars, and inverted channels, and grow as a result of calcite precipitation, dust accumulation, and sedimentation (Gumbricht et al., 2004). During the annual flood, surface water replenishes groundwater stores, including those of islands, and evapotranspiration drives the net groundwater flow toward island centers (McCarthy, 2006; Milzow et al., 2009). The groundwater flow, solute transport, and resulting solute accumulation in groundwater have been described and modeled extensively (Gieske, 1996; Wolski et al., 2005; McCarthy, 2006; Bauer et al., 2006; Wolski and Savenije, 2006; Bauer-Gottwein et al., 2007; Milzow et al., 2009). Zones of high solute concentration generally occur near the center of islands. Consequently, the ground surface above these zones of solute accumulation is typically barren or colonized only by salt-tolerant vegetation. At New Island, the zone of solute accumulation does not occur at the island center. Instead, a gradient formed by higher water table on the upstream side and lower water table elevation on the downstream side (Fig. 2) leads to a shifting of the concentration zone toward the eastern beach (Bauer-Gottwein et al., 2007). Interpolated electrical conductivity