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Peat formation concentrates arsenic within sediment deposits of the Mekong Delta

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Abstract

Mekong River Delta sediment bears arsenic that has been released to groundwater under anaerobic conditions over the past several thousand years. The oxidation state, speciation, and distribution of arsenic and the associated iron bearing phases are crucial determinants of As reactivity in sediments. Peat from buried mangrove swamps in particular may be an important host, source, or sink of arsenic in the Mekong Delta. The total concentration, speciation, and reactivity of arsenic and iron were examined in sediments in a Mekong Delta wetland by X-ray fluorescence spectrometry (XRF), X-ray absorption spectroscopy (XAS), and selective chemical extractions. Total solid-phase arsenic concentrations in a peat layer at a depth of 6 m below ground increased 10-fold relative to the overlying sediment. Extended X-ray absorption fine structure (EXAFS) spectroscopy revealed that arsenic in the peat was predominantly in the form of arsenian pyrite. Arsenic speciation in the peat was examined further at the micron-scale using μXRF and μX-ray absorption near-edge structure (XANES) spectroscopy coupled with principal component analysis. The multiple energy μXRF mapping and μXANES routine was repeated for both iron and sulfur phase analyses. Our μXRF/μXANES analyses confirm arsenic association with pyrite – a less reactive host phase than iron (hydr)oxides under anaerobic conditions. The arsenian pyrite likely formed upon deposition/formation of the peat in a past estuarine environment (~5.5 ka BP), a process that is not expected under current geochemical conditions. Presently, arsenian pyrite is neither a detectable source nor a sink for aqueous arsenic in our sediment profile, and under present geochemical conditions represents a stable host of As under the reducing aquifer conditions of the Mekong Delta. Furthermore, organic carbon within the peat is unable to fuel Fe(III) reduction, as noted by the persistence of goethite which can be reduced microbially with the addition of glucose.

1. INTRODUCTION

Human exposure to arsenic through domestic use of groundwater in South and Southeast Asia starts with the weathering of Himalayan As-bearing rock in basin headwaters, followed by riverine transport and deposition into Holocene aquifers (Saunders et al., 2005). Arsenic concentrations in basin groundwater commonly exceed the 10 μg As L^{-1} World Health Organization standard by more than 10-fold (Smedley and Kinniburgh, 2002). Consumption of arsenic-contaminated groundwater has led to the chronic poisoning of tens of millions of people in the

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Bengal Basin of West Bengal and Bangladesh (Chatterjee et al., 1995; Yu et al., 2003; Ahmed et al., 2006; Sambu and Wilson, 2008; Ravenscroft et al., 2009). The widespread use of tube wells for drinking water supply has put millions more at risk in the Red River (northern Vietnam) and Mekong Deltas (Cambodia and southern Vietnam) (Berg et al., 2007).

The biogeochemical cycling of iron, sulfur, and carbon (in natural organic matter) largely control the partitioning and speciation of arsenic in these deltaic sediments. Under anaerobic conditions, microbially driven oxidation of organic matter coupled to the dissimilatory reductive dissolution of As-bearing iron (hydr)oxides causes the transfer of arsenic from the solid to the aqueous phase (Nickson et al., 1998, 2000; McArthur et al., 2001; Akai et al., 2004; Islam et al., 2004; Van Geen et al., 2004). Reductive dissolution of As(V)-bearing Fe(III) (hydr)oxides is the dominant mechanism by which aqueous concentrations of arsenic, and its resulting transport, are increased (Smedley and Kinniburgh, 2002; Dixit and Hering, 2003; Postma et al., 2007; Kocar et al., 2008; Tufano et al., 2008; Fendorf and Kocar, 2009).

In addition to Fe(III), sulfate is an important electron acceptor linked to organic carbon oxidation in anaerobic microbial respiration, and sulfide precipitation may act as solid-phase sink for arsenic. In combination with pH, the mineralogical form of Fe(III) (hydr)oxides determines the relative favorability of iron and sulfate reduction, and the two terminal electron accepting processes often occur simultaneously (Postma and Jakobsen, 1996; Buschmann and Berg, 2009; Kocar and Fendorf, 2009). Stoichiometric iron and sulfate reduction can lead to the formation of $FeS_{(s)}$ (e.g., mackinawite) and subsequent adsorption of As or the co-precipitation of As-bearing iron sulfides (Postma and Jakobsen, 1996; Buschmann and Berg, 2009; Couture et al., 2010, 2013a). Iron monosulfides are often precursors to pyrite ($FeS_{2(s)}$) in low-temperature geochemical environments (Rickard, 1975, 1997; Rickard and Luther, 1997; Morse and Rickard, 2004), and may lead to arsenian pyrite ($Fe(S,As)_2$) (Savage et al., 2000; Lowers et al., 2007), or arsenopyrite (FeAsS) (Bostick and Fendorf, 2003). Alternatively, pyrite may form by heterogeneous nucleation without FeS precursors on iron-rich clay minerals (Lowers et al., 2007). Indeed, As-bearing iron sulfides, including arsenian pyrite, are present in Bengal Basin (Bangladesh) sediments (Polizzotto et al., 2005; Lowers et al., 2007). Adequate sediment sulfur (sulfate) supply and reaction time allow for authigenic arsenian pyrite formation with arsenic incorporation up to 1.3% (w/w) (Lowers et al., 2007). The extent to which pyrite incorporates structural arsenic increases with decreased pyrite growth rate, higher As:S ratios in solution, and/or a higher dissolved As concentration (Fleet et al., 1989; Bostick and Fendorf, 2003; Lowers et al., 2007). Non-Fe-bearing arsenic sulfides may scavenge As from solution as well. When arsenic reaches micro-molar levels under sulfate-reducing conditions, realgar (AsS) is the first As sulfide to precipitate in circumneutral pH environments with high Fe^{2+}, low HS^-/H_2S activities, whereas orpiment (As_2S_3) stability is predicted at low Fe^{2+}, high HS^-/H_2S conditions (O'Day et al., 2004). Thus, arsenic partitioning with sulfide minerals is a function of several environmental factors in sediment/soil systems including redox state, temperature, and activities of H^+, Fe^{2+}, and HS^-/H_2S.

Buried natural organic matter or peat is implicated as the fuel for reductive dissolution of arsenic-bearing iron (hydr)oxides, leading to As release in the Bengal Basin (McArthur et al., 2001, 2004, 2008, 2010, 2011). Peat may potentially drive arsenic release locally and/or produce dissolved organic carbon (DOC), which may stimulate As release down gradient in the aquifer (McArthur et al., 2008). However, peat often has sulfur-containing functional groups, particularly of marine or estuarine origin, with a strong affinity for arsenic (Langner et al., 2012). Peat also facilitates the formation of potentially stable arsenian pyrite in anoxic sediments through microbially mediated processes (Huertadiaz and Morse, 1992; Schoonen, 2004). Thus, the role of peat in regulating arsenic partitioning, reactivity, and mobility in sediments of the As-impacted deltas of S/SE Asia is complex and unresolved. Here we seek to (1) define the speciation of arsenic, iron, and sulfur in the peat found in near-surface sediments (upper 10 m) of the Mekong Delta, (2) determine the reactivity of the peat-associated arsenic, and (3) determine whether buried peat is a source or sink for arsenic relative to groundwater in deltaic sediments. We complement field measurement with laboratory incubation studies to define the processes controlling arsenic partitioning within the near-surface sediments.

2. MATERIALS AND METHODS

2.1. Field area

The Mekong River currently traces a 4600 km course from its headwaters in the Himalaya (Tibet) to the South China Sea (Hori, 2000). The modern Mekong Delta initiated at 8.4 ka following a period of rapid sea-level rise and aggradation of the fluvial system (Tamura et al., 2009). Sea-level rise decelerated for the subsequent ~2000 years, producing aggrading to prograding tidal flats and mangrove forests and resultant peat layers in the sediment profile of the present-day upper Mekong Delta (Tamura et al., 2009). Rapid progradation of the delta has occurred from 6.3 ka to the present, with the highest sediment accumulation rates ensuing in the past 0.6–1 ka (Tamura et al., 2009).

Our field area spans 50 km^2 of the upper Mekong Delta in Kandal Province, Cambodia, and is bracketed by the Mekong and Bassac rivers (Lat. 11 31 3.90 N, Long. 105 0 41.77E) (Polizzotto et al., 2008). Elevated levees along the riverbanks give way to native wetlands between the two rivers. The general stratigraphy of the field area is approximately 15 m of clays overlying >30 m of aquifer-forming sands (Benner et al., 2008). The annual monsoon causes the river stage to breach the levees, resulting in deposition of floodwater and arsenic-bearing sediments into the wetland basin. The hydraulic head of the interior surface wetlands exceeds that of the Mekong River throughout the year except for the latter part of the rainy season (roughly July through October) (Benner et al., 2008; Polizzotto et al.,