Mobilisation of arsenic following sea-water inundation of acid sulfate soils

Scott Johnston[A], Annabelle Keene[A], Richard Bush[A], Edward Burton[A] and Leigh Sullivan[A]

[A]Centre for Acid Sulfate Soil Research, Southern Cross GeoScience, Southern Cross University, Lismore, NSW 2480, Australia, Email scott.johnston@scu.edu.au

Abstract

Tidal seawater inundation of coastal acid sulfate soils can generate Fe- and SO_4-reducing conditions in previously oxic sediments. This creates potential for mobilisation of As during the redox transition. We investigate the hydrology, porewater geochemistry, solid-phase speciation and mineralogical partitioning of As across two tidal fringe toposequences and explore the consequences for As. Seawater inundation induced a tidally-controlled redox gradient. Maximum porewater As (~400 µg/L) occurred in the intertidal, redox transition zone between Fe-oxidizing and SO_4-reducing conditions. Mechanisms of As mobilisation include the reduction of solid-phase As(V) to As(III), reductive dissolution of As(V)-bearing secondary Fe(III) minerals and competitive anion desorption. There was attenuation of porewater As in the zone of contemporary pyrite reformation. Oscillating hydraulic gradients caused by tidal pumping promote upward advection of As and Fe^{2+}-enriched porewater in the intertidal zone, leading to accumulation of As(V)-enriched Fe(III) (hydr)oxides at the oxic sediment-water interface. This creates a natural reactive-Fe barrier, but does not completely retard the flux of porewater As to overtopping surface waters. The accumulated Fe minerals may be prone to future reductive dissolution. A conceptual model of As hydro-geochemical coupling is presented.

Key Words

Acid sulfate soil, iron, arsenic, sea-level rise, tidal marsh, East Trinity.

Introduction

Arsenic (As) in water supplies derived from coastal floodplain aquifers degrades the health of millions of people (Smedley and Kinniburgh 2002). It is increasingly recognized that redox transitions caused by inundation of oxic sediments can lead to mobilisation of As. As behaviour in this context is often intimately coupled with the geochemical cycling of Fe (hydr)oxides and sulfide minerals (Root *et al.* 2009). Coastal acid sulfate soils (CASS) often have elevated concentrations of As due to the tendency of As to accumulate in pyrite (Smedley and Kinniburgh 2002). Acid sulfate soils are also usually rich in secondary Fe(III) minerals such as goethite, ferrihydrite, jarosite and schwertmannite (Sullivan and Bush 2004). These Fe(III) minerals are important sorbents for As and can become enriched in As under oxic conditions in both acid sulfate soils and acid mine drainage (Smedley and Kinniburgh 2002).

Seawater inundation has been used as a technique to successfully ameliorate acidity within lowland CASS (Powell and Martens 2005). Seawater inundation initiates a large redox transition which leads to reductive dissolution of Fe(III) minerals and the reformation of sulfide-minerals, including pyrite (Johnston *et al.* 2009a, b). It also introduces tidal pumping to shallow groundwater, which can cause porewater exchange and solute redistribution within intertidal zone sediments. This study examines the potential for As mobilisation, attenuation and hydro-geochemical coupling with Fe and S across a seawater inundation-induced redox boundary in CASS.

Methods

Study site

The study site, East Trinity, is an ~800 ha Holocene sedimentary coastal plain dissected by several estuarine creeks (145°47’ E, 16°56’ S). A tide-excluding sea wall was constructed and the site was intensively drained in the 1970’s (Powell and Martens 2005). This caused the oxidation of iron-sulfides in former mangrove sediments and the widespread formation of severe acid sulfate soils across the site (Powell and Martens 2005). A remediation program began in 2001–02 that involved tidal inundation of acid sulfate soils up to an elevation of ~0.5 m AHD (AHD is Australian Height Datum, 0 m AHD approximates mean sea level). Tides regularly inundate most of the formerly acidified areas across the site. Two toposequence transects were established to bracket the fringe of the tide-imposed redox gradient (i.e. spanning the supratidal/intertidal zone; 0.6 to 0 m AHD; Figure 1). Both transects have similar stratigraphy, comprised of clay-textured former sulfuric horizons to about 0.7–1.0 m below ground level (bgl), underlain by un-oxidised, sulfidic estuarine muds.

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Hydrology

Groundwater levels along each transect were measured at 30 minute intervals (±0.01 m) using submersible pressure transducers vented to the atmosphere (Odyssey, ODYPS05) housed in a series of four 50 mm diameter PVC piezometers.

Solid-phase sampling

Replicate soil cores were obtained by gouge-auger from selected sampling locations. Cores were immediately sectioned and sub-samples sealed in air-tight polyethylene bags, completely filled with soil and frozen after collection until analysis. Near-total As [As_{Tot}] was extracted by hot aqua-regia digestion (APHA 1998) and measured by ICP-MS (Perkin-Elmer ELAN-DRCe). Duplicate analysis performed on twelve percent of samples had a precision within 8%. Fe-rich surficial sediment (0–0.01 m) was also sampled from across the study area and frozen. Jarosite pedofeatures from former sulfuric horizons were removed with a scalpel from air-dried bulk soil. Pyrite was enriched by density separation with *s*-tetrabromoethane from a bulk sample (~0.5 kg) of unoxidised sulfidic sediment. Arsenic K-edge X-ray absorption near-edge structure (XANES) spectra were collected on beamline 20B at the Photon Factory, Tsukuba Japan. Duplicate spectra were collected from selected natural samples and reference standards in fluorescence mode using a 32 element array Ge solid-state detector. The spectral background was subtracted using a polynomial fit and the edge jump height normalized to unity.

Porewater geochemistry

Porewaters were sampled during April 2008 via equilibration dialysis using 1.5 m long peepers. This is described in detail by Johnston *et al.* (2009c). Porewater filtrate (0.45 µm) was preserved with HNO_3 and stored in the dark at 4 °C for subsequent analysis of total As by ICP-MS (Perkin-Elmer ELAN-DRCe), operated in DRC mode to optimize interference removal. Five percent of samples were analysed in duplicate and had a precision within 6%.

Results and discussion

Tidal inundation frequency increased downslope and was accompanied by mostly sub-oxic Eh (<200 mV) in tidally inundated former sulfuric horizons. There was enrichment of As within key Fe mineral phases. Jarosite was enriched by a factor of ~4 (75 µg/g) compared to bulk soil (Table 1). The sulfidic sediment-derived dense mineral fraction (comprised mainly of pyrite and some marcasite), was enriched in As by more than an order of magnitude compared to bulk soil (Table 1). In addition, surface Fe-rich accumulations (0–0.01 m; 5 to 40% Fe w/w) also had elevated As contents (1–6x) (Table 1), with As_{Tot} positively correlated ($r^2 = 0.34$, α 0.05) with poorly crystalline Fe (data not shown).

Table 1. As in transect soils and key Fe fractions, mean (±standard deviation).

Location/soil fraction (*n*)	Near-Total extract (µg/g)
Transect 1 & 2 soils (*110*)	18.3 ±6.5
Jarosite (*4*)	75.7 ±14.7
Surface Fe(III)-rich accumulations (3*4*)	36.1 ±26.3
Pyrite (*2*)	279.0 ±24.9

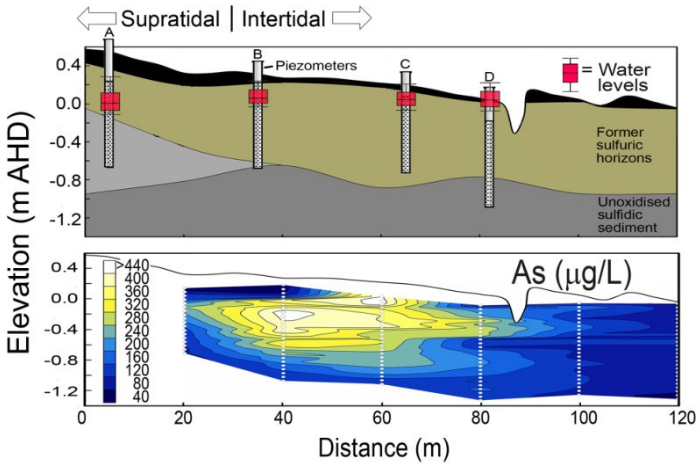

Figure 1. Transect 1 stratigraphy, hydrology and porewater As concentrations.

There was a distinct zone of As mobilisation in the porewaters at both transects, where concentrations exceeded 400 µg/L (Figure 1). The zone of maximum porewater As was spatially associated with former sulfuric horizons near the intertidal limit and most of this aqueous As (~80%) was As(III) (speciation data not shown). There were also very high concentrations of porewater Fe^{2+} (~2000 mg/L) in this same zone, consistent with reductive dissolution of secondary Fe(III) minerals. There was a significant positive relationship between As and Fe^{2+} in the zone of mobilisation ($r^2 = 0.71$, α 0.01, Figure 2). This is consistent with reductive dissolution of As-enriched Fe(III) minerals being a key process responsible for As mobilisation.

There was also a strong positive correlation between As and HCO_3^- at the same locations ($r^2 = 0.63$, α0.01, Figure 2). Bicarbonate competes with As for adsorption sites and this may be an additional mechanism responsible for elevated porewater As. Anaerobic carbon metabolism via Fe reduction also generates HCO_3^- and hence there is potential for coupling of both processes. Porewater As decreased towards the lower sections of both transects in the zone of contemporary pyrite reformation (~100 m). Dissolved As can be effectively sequestered by iron-sulfide minerals through surface complexation and co-precipitation and this is a likely mechanism of attenuation.

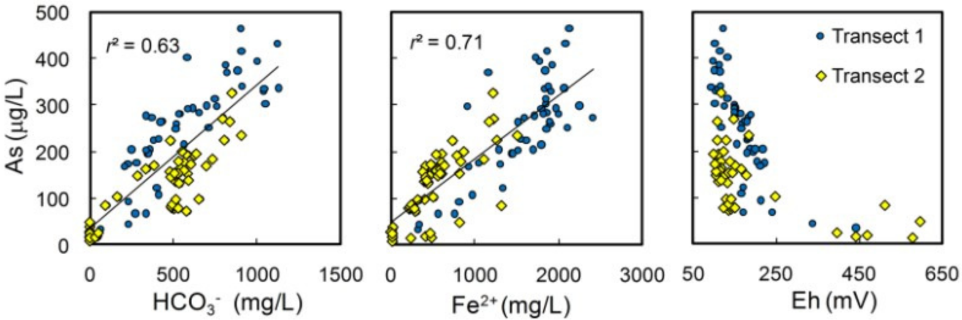

Figure 2. Relationships between porewater As and HCO_3^-, Fe^{2+}, and redox potential (SHE) from Transect 1 and 2 at 60 m distance.

The coupling of a redox transition triggering As mobilisation with physical forcing processes is an important feature of seawater inundation of CASS. Tidal forcing causes highly dynamic groundwater behaviour which generates oscillating horizontal hydraulic gradients (Figure 3). During the ebb-tide phase, the development of seaward hydraulic gradients promotes upward advection and seepage of As-and Fe^{2+}-rich porewater along the intertidal slope, followed by Fe oxidation and the precipitation of As(V)-enriched Fe(III) mineral phases.

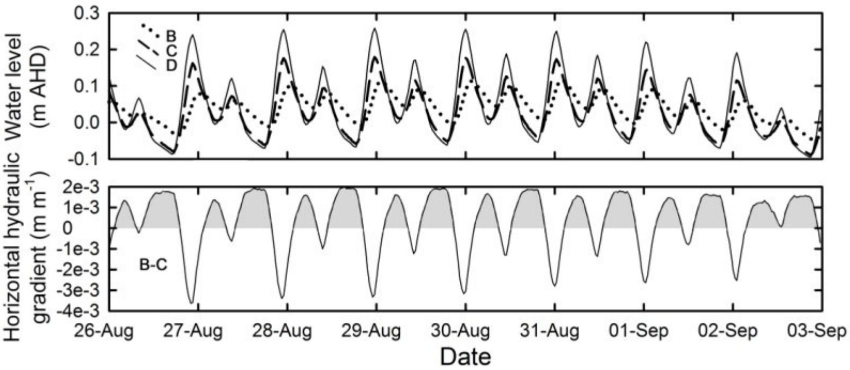

Figure 3. Transect 1 time-series groundwater levels and corresponding horizontal hydraulic gradients between piezometers B-C. Periods of effluent (seaward) horizontal hydraulic gradients are shaded grey.

Arsenic K-edge XANES analysis revealed distinct down-profile and downslope trends in solid-phase As speciation, consistent with the seawater-induced redox gradient (data not shown). The XANES spectra indicate that an FeAsS-like phase was an important reservoir for As in the original, un-drained parent material. Solid-phase As in both jarosite and surficial Fe(III)-rich material was mainly As(V). In former sulfuric horizons at 20 m and 60 m (Transect 1) the XANES data revealed a mixture of As(V) and As(III). In contrast, the XANES spectra for samples from the surface and in the former sulfuric horizon at 100 m, display edge positions consistent with As(III) or As sulfides. XANES data demonstrate that seawater inundation of CASS is leading to reduction of solid-phase As(V) to As(III), and the subsequent reformation of As sulfides within former sulfuric horizons.

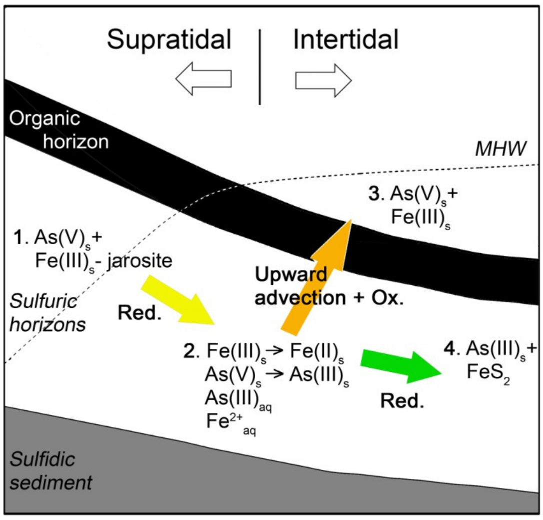

Figure 4. Conceptual model of As hydro-geochemistry across a tidal, seawater inundated CASS toposequence. MHW is mean high water.

Conclusion

Seawater inundation of a CASS toposequence has caused a major shift in the solid and aqueous-phase speciation, distribution and partitioning of As. While there is evidence of considerable As mobilisation, it appears to be spatially localized between two distinct geochemical regimes. As behaviour is intimately bound with the fate of Fe and S. Results are synthesised in a conceptual model which represents As hydro-geochemistry across the seawater inundation fringe (Figure 4). The oxidation of As-rich pyrite in the drained sulfidic parent material led to (1) the formation of acid sulfate conditions with preferential enrichment of As(V) in secondary Fe(III) minerals (e.g. jarosite). Seawater inundation (2) initiates reducing conditions stimulating As mobilisation by several processes including a) reductive dissolution of As-bearing secondary Fe(III) minerals, b) reduction of As(V) to As(III), and c) competitive anion desorption by HCO_3^-. Tidal pumping facilitates upward advection (3) of Fe^{2+} and As(III)-rich porewaters in the intertidal zone, where subsequent oxidation in surficial sediments results in the accumulation of tertiary Fe(III)-minerals enriched in As(V). Further downslope (4) there is attenuation of porewater As in the zone of contemporary pyrite re-formation, where solid phase As occurs predominantly in the form of As(III).

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