

# Mobility of arsenic and selected metals during re-flooding of iron- and organic-rich acid-sulfate soil

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## ABSTRACT

The drainage-induced oxidation of iron-sulfide minerals in acid-sulfate soils has adversely affected large areas of coastal floodplains. Re-flooding of these soils, via the re-establishment of more natural drainage regimes, is a potential remediation approach. Here we describe the mobility of Al, As, Fe, Mn, Ni and Zn during controlled re-flooding of an Fe- and organic-rich acid-sulfate soil material. Soil re-flooding caused the onset of microbially-mediated Fe(III)-reduction, which raised the pH of the initially acidic (pH 3.4) soil to pH 6.0 to 6.5, thereby immobilizing Al. The process of Fe(III)-reduction released high concentrations of Fe<sup>II</sup> and was associated with significant mobilization of As. During the early stages of re-flooding, Fe<sup>II</sup> mobility was controlled by dissolution of schwertmannite (Fe<sub>8</sub>O<sub>8</sub>(OH)<sub>6</sub>SO<sub>4</sub>) with an ion activity product (IAP) of 10<sup>19±2</sup>. The mobility of Fe<sup>II</sup> was subsequently controlled by the precipitation of siderite (FeCO<sub>3</sub>) with an IAP spanning 10<sup>-10</sup> to 10<sup>-7.5</sup>. The formation of acid-volatile sulfide (AVS), as a product of SO<sub>4</sub>-reduction, further retarded the mobility of Fe<sup>II</sup>. Interactions with AVS also strongly immobilized Mn, Ni and Zn, yet had little effect on As which remained relatively mobile in the re-flooded soil. This study shows that the mobilization of As and Fe during soil re-flooding should be considered when planning remediation approaches for acid-sulfate soils.

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## 1. Introduction

Many coastal plains around the world are underlain by soils that are, or may become hyper-acidic due to the oxidation of iron-sulfide minerals (Fanning et al., 2002). Iron-sulfide oxidation in these soils (termed Coastal Lowland Acid-Sulfate Soils; CLASS) occurs when the previously water-logged, sulfidic soils are allowed to drain (van Breeman, 1973; Fitzpatrick, 2003; Andriess and van Mensvoort, 2005). Drainage may occur naturally (e.g. due to isostatic uplift), but is mostly due to land management intervention (Dent and Pons, 1995; Astrom and Spiro, 2000). Iron-sulfide oxidation and associated acidification contributes to the release of iron, aluminium, arsenic and trace metals (Astrom, 1998; Appleyard et al., 2006; Burton et al., 2006a). Discharge of these elements from CLASS has caused widespread water quality degradation and is an important international problem (Astrom, 2001; Preda and Cox, 2001; Fanning et al., 2002; Macdonald et al., 2007).

Prior to the establishment of artificial soil drainage systems, CLASS landscapes typically supported seasonal to semi-permanent wetlands (Dent and Pons, 1995). The re-establishment of wetlands, achieved by reverting to more natural drainage regimes, has been proposed as an environmental remediation approach (Tulau, 2002). This approach has the potential advantage of promoting natural acidity-consuming processes, like Fe(III)- and SO<sub>4</sub>-reduction, which may cause the re-formation of iron-

sulfide minerals (Burton et al., 2007). For this reason, management efforts are increasingly being directed towards manipulating CLASS drainage in order to re-flood low-lying areas.

To date, studies of CLASS re-flooding have focused on changes in soil acidity and iron-sulfur geochemistry (Konsten et al., 1994; Ward et al., 2004; Johnston et al., 2005; Burton et al., 2007). Profound changes in the abundance of the major iron-sulfur phases have been observed, which may potentially influence As and metal mobility (Preda and Cox, 2004). In particular, reductive dissolution of Fe(III)-phases may release Fe as well as previously bound As and trace metals (Smedley and Kinniburgh, 2002; Burton et al., 2006b; Welch et al., 2007). Whilst a limited number of studies have documented Fe mobilization during CLASS re-flooding (Johnston et al., 2003, 2005; Burton et al., 2007), the corresponding behaviour of As and other metals has not been addressed.

Here we examine the mobility of As and selected metals (Al, Fe, Mn, Ni, and Zn) during re-flooding of an Fe- and organic-rich CLASS material. The results provide important new insights into processes controlling water quality in re-flooded CLASS landscapes.

## 2. Methods

### 2.1. General methods and reagents

All laboratory glass- and plastic-ware were cleaned by soaking in 5% (v/v) HNO<sub>3</sub> for at least 24 h, followed by repeated rinsing with deionised water. Reagents were analytical grade and all reagent

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solutions were prepared with deionised water (milliQ). Deoxygenated solutions were prepared by purging with N<sub>2</sub> for at least 2 h. All solid-phase results are presented on a dry weight basis (except where otherwise noted).

## 2.2. Sample collection

A sample of an Fe-rich O-horizon of a CLASS profile was collected from eastern Australia (29°26'29"S, 153°14'12"E). The sample site was typical of low-lying (<2 m above sea-level) CLASS landscapes (Sullivan and Bush, 2004; Burton et al., 2006c), with the soil classified as a Hydraquentic Sulfaquept according to soil taxonomy (Soil Survey Staff, 2006). The sample was ground to <2 mm and homogenized within 24 h of collection. The sample had a field moisture content of only 6% and, therefore, deionised water was added in order to achieve saturation (72% water w/w). Pore-water in this initial saturated soil was extracted (within 16 h) from duplicate sub-samples by centrifugation (4000 rpm, 10 min).

## 2.3. Soil re-flooding experiment

The saturated soil sample was added to a depth of 20 cm in upright Perspex columns (length 30 cm, internal diameter 6 cm, sealed at bottom end) (Fig. 1). A 5 cm depth of surface water, comprising 1 mM K, 1 mM Ca, 1 mM Mg, 30 mM Na, 15 mM SO<sub>4</sub> and 6 mM Cl at pH 3 (based on data presented by Burton et al., 2006c), was added to the columns. The re-flooded soil was then incubated in the dark at 25 ± 1 °C using a temperature-controlled water-bath. At twice weekly intervals, 100 mL of surface water was removed and replaced with fresh surface water. The replacement of surface water was performed in order to maintain a gradient in solute concentrations across the interface between the inundated soil and the surface water.

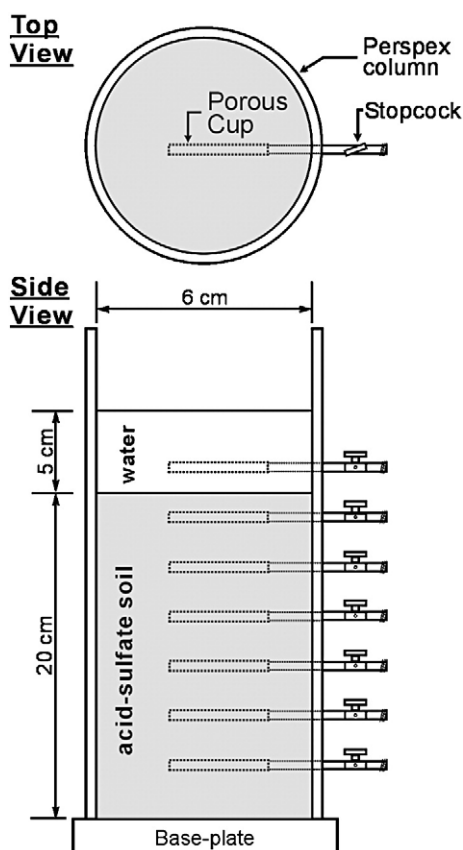


Fig. 1. Column design utilized for the re-flooding experiment. Pore-water samples were withdrawn into syringes via gas-tight stopcocks located at 7 depths within the column.

Surface- and pore-water samples (5 mL) were retrieved from duplicate columns (prior to surface water replacement) at 3, 7, 14, 28, 49, 70 and 91 days post-inundation. This was achieved via sampling ports located at +1.5, -1.5, -4.5, -7.5, -10.5, -13.5 and -16.5 cm above (+) or below (-) the interface between the soil and surface water (Fig. 1). The initial 1 mL of water collected from each sampling port was discarded, and the following 5 mL was filtered to <0.45 µm using an enclosed syringe-driven filter unit (to minimize atmospheric exposure). The pH and redox potential were determined using calibrated probes. Pore-water sulfide was preserved with ZnOAc prior to determination by the methylene blue method (APHA, 1998). Aliquots of filtrate were added to 1,10-phenanthroline solutions for total aqueous Fe and Fe<sup>II</sup> determination (APHA, 1998). Aqueous Fe<sup>III</sup> was determined by the difference between total Fe and Fe<sup>II</sup>. Aqueous concentrations of Al, As, Mn, Ni and Zn were determined by inductively coupled plasma-mass spectrometry (ICP-MS) using a Perkin-Elmer Optima 4000/30DV instrument. The As ICP-MS analytical data were corrected for interference from <sup>40</sup>Ar<sup>35</sup>Cl<sup>-</sup> using the isotope ratio approach. Detection limits for aqueous Al, As, Mn, Ni and Zn were <0.05 µM. Alkalinity was determined by Gran titration (Stumm and Morgan, 1996). Calcium, K, Mg and Na were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using a Perkin Elmer DV4300 instrument. Sulfate was determined by turbidimetric analysis (APHA, 1998). Chloride was determined by potentiometric titration (APHA, 1998). Activity coefficients for aqueous species were calculated by the Davies equation using PHREEQC 2.11 (Parkhurst and Appelo, 1999).

Replicate columns (without pore-water sampling ports) were sacrificed at 0, 7, 14, 28, 49, 70 and 91 days post-inundation for collection of solid-phase material. This involved removing the surface water, then incrementally extruding and collecting soil samples from the 0 to 3, 3 to 6, 6 to 9, 9 to 12, 12 to 15 and 15 to 18 cm depth intervals. Material from each depth interval was directly transferred into 50 mL polypropylene vials, which were completely filled with sample (zero headspace) and sealed with gas-tight screw-caps. The solid-phase soil samples were stored frozen under N<sub>2</sub> until analysed.

Total C and S content was determined using an Elementar combustion analyzer. The “near-total” concentrations of Al, As, Fe, Mn, Ni and Zn were determined by aqua-regia digestion (1:3 HNO<sub>3</sub>: HCl, 20 min, 1000 W microwave at 10% power) followed by ICP-AES analysis. Acid-volatile sulfide (AVS), which reflects the abundance of iron-monosulfide minerals, was analysed via the cold diffusion method described by Hsieh et al. (2002). Solid-phase Fe(II) was determined following the method of Phillips and Lovley (1987).

Solid-phase samples were dried at room temperature under a stream of high purity N<sub>2</sub> and examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). X-ray diffractograms were obtained for randomly oriented powders using a Phillips PW 1050/70 diffractometer with a Cu X-ray tube. Samples were step scanned from 10 °2θ to 65 °2θ using a 0.05 °2θ step and a 3 s count time. Samples for SEM examination were mounted on aluminium stubs, coated with carbon, and the elemental composition and morphology of selected specimens determined using a Leica 440 SEM with an ISIS energy dispersive X-ray (EDX) microanalysis system. A quantitative peak-to-background EDX method for rough-surfaced specimens was used (Sullivan and Bush, 1997).

Iron K-edge X-ray absorption near-edge structure (XANES) spectroscopy was undertaken on bending magnet beamline 20B at the Australian National Beamline Facility (ANBF) in the Photon Factory, Tsukuba City, Japan. Mineral standards and soil samples for XANES were transported frozen under N<sub>2</sub>. The specimens were analysed wet with a Kapton tape cover to prevent atmospheric exposure. The X-ray energy resolution was maintained by a Si(III) channel-cut monochromator and energy calibration was achieved via an in-line Fe(0) standard (first inflection point assigned to 7112 eV). Spectra were collected in fluorescence mode using a 32 element array Ge solid-state

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