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

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1. Introduction

Many coastal plains around the world are underlain by soils that are, or may become, highly-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 waterlogged, surficial soils are allowed to drain (van Breeman, 1973; Fitzpatrick, 2003; Anicereesi and van Mensvoort, 2005). Drainage may occur naturally (e.g., due to isotatic uplift), but is mostly due to land management intervention (Dent and Pons, 1995; Astrom and Spinu, 2000). Iron-sulfide oxidation and associated acidification contributes to the release of iron, aluminium, arsenic and trace metals (Astrom, 1988; Appleyard et al., 2005; Burton et al., 2006a). Discharge of these elements from CLASS has caused widespread water quality degradation and is an important international problem (Astrom, 2001; Peda 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 reversing 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 SO₄ 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 CASS 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 (Kronstien 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 (Peda 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-rich 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 plasticware were cleaned by soaking in 5% (v/v) HNO₃ for at least 24 h, followed by repeated rinsing with deionized water. Reagents were analytical grade and all reagents...
solutions were prepared with deionised water (milliQ). Deoxygenated solutions were prepared by purging with N₂ 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′29.5″S, 153°14′12.4″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 Hydromorphic Sulfurate 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 is 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 surfacewater, comprising 1 mM K, 1 mM Ca, 1 mM Mg, 30 mM Na, 15 mM SO₄ and 6 mM Cl at pH 3 (based on data presented by Burnet 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.

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 sulfate was preserved with ZnOAc prior to determination by the methylene blue method (APHA, 1998). Aliquots of filtrate were added to 1.0-phenanthroline solutions for total aqueous Fe and Fe(III) determination (APHA, 1998). Aqueous Fe(II) was determined by the difference between total Fe and Fe(III). Aqueous concentrations of Al, As, Mn, Ni and Zn were determined by inductively coupled plasma-mass spectrometry (ICP-MS) using a Perkin-Elmer Optima 4300DV instrument. The As ICP-MS analytical data were corrected for interference from 40K 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, Mg and Na were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using a Perkin Elmer D4030 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 PREDICT 2.11 (Parhant and Appelo, 1999). Replicate columns (without pre-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 N₂ until analysed.

Total C and S content was determined using an Elemental combustion analyser. The “near-total” concentrations of Al, As, Fe, Mn, Ni and Zn were determined by aqua-regia digestion (1:3 HNO₃: HCl, 20 min, 1000 W microwave at 10% power) followed by ICP-AES analysis. Acid-volatile sulfide (AVS), which reflects the abundance of iron-monomonsulfide 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 Lorbey (1987).

Solid-phase samples were dried at room temperature under a stream of high purity N₂ 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° 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-JEM with an EDS 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) spec troscopy 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 N₂. The specimens were analysed wet with a Kapton tape cover to prevent atmospheric exposure. The X-ray energy resolution was maintained by a Si(111) 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
detector. The pre-edge background was subtracted and the edge jump was normalized to 1 using the PySpline software package (Tenderholt et al., 2006). Quantitative Fe speciation was determined by linear combination fitting of the sample spectrum with contributions from selected Fe minerals (O'Fly et al., 2004). The choice of minerals for linear combination fitting was based on XRD, SEM and EDX data and included synthetic goethite, nano-particle scale mackinawite, schwertmannite and siderite (see results and discussion section). The mineral standards were synthesized following Cornell and Schwertmann (2003) for goethite (Fe(3+)O(OH)), Wolthers et al. (2005) for nanoparticle scale mackinawite (FeS), Regensberg et al. (2004) for schwertmannite (Fe(2+)O(OH)SO4) and Jensen et al. (2002) for siderite (FeCO3). Linear combination fitting was performed with the WinXAS software package (Ressler, 1998), with no energy shifts allowed during fitting.

In the present study, total aqueous concentrations are presented without valence (e.g., Fe), individual aqueous species are shown with a charge (e.g., Fe2+) and the sum of aqueous species for components with a specific redox state are indicated by superscripted Roman numerals (e.g., FeVI). The sum of solid-phase species for components with a specific redox state are indicated by upper-case Roman numerals (e.g., Fe(III)).

3 Results and discussion

3.1. Properties of the initial soil sample

The initial, saturated soil sample was pH 3.4 with an Eh of 520 mV; indicating acidic/oxic conditions. The sample was relatively saline, with high concentrations of pore-water Cl (428 mM) and Na (353 mM). The molar ratio of pore-water Cl to pore-water SO4 (31 mM) was 13.8, which is substantially lower than the corresponding ratio in average seawater (Cl:SO4 = 18.3). This relatively low Cl:SO4 ratio reflects an enrichment in SO4 due to pyrite (FeS2) oxidation in the underlying sulfidic soils. The initial pore-water also contained a relatively high concentration of FeII (7.1 mM), which is consistent with Fe release associated with pyrite oxidation.

The initial sample was dark yellow-brown in colour (Munsell 10YR 4/4; moist sample) and contained 26% organic C, 1.5% total S, 23% total Fe and 17% FeII. The soil mineralogy was dominated by schwertmannite (Fe(2+)O(OH)SO4) (Fig 2a), which is a poorly ordered Fe(II)-oxhydroxysulfate (Bigham et al., 1990). The molar ratio of total FeII to S was 7.9:1, which is very close to the ideal schwertmannite stoichiometric ratio of 8:1. This indicates that schwertmannite was the predominant source of both Fe and S in the initial soil sample. Schwertmannite has a unique “pin-cushion” morphology (Fig 2b) and generally precipitates from Fe- and SO4-rich solutions at pH 3 to 4 (Bigham et al., 1996). Sullivan and Bush (2004) have demonstrated that schwertmannite is abundant in CLASS landscapes, where it commonly occurs in surface soil horizons in low-lying areas.

The initial soil contained low “near-total” concentrations (aquarregia digestion) of Al (38 μmol g−1), As (88 nmol g−1), Mn (548 nmol g−1), Ni (73 nmol g−1) and Zn (188 nmol g−1) compared, for example, to world-average shale (Al 3,360,000 μmol g−1, As 170 nmol g−1, Mn 1,590,000 nmol g−1, Ni 850 nmol g−1, Zn 1,450 nmol g−1; Li, 2000). However, the corresponding initial pore-water concentrations were high with 202 μM for Al, 1.0 μM for As, 218 μM for Mn, 10.2 μM for Ni and 27.5 μM for Zn. These concentrations greatly exceed the respective Australian water quality trigger values for protection of 95% of aquatic species (Al 0.03 μM, As3+ 0.32 μM, AsV 0.17 μM, Mn 35 μM, Ni 0.2 μM and Zn 0.13 μM; ANZECC/ARMCANZ, 2000). Such elevated pore-water Al, As, Mn, Ni and Zn concentrations are not attributed to anthropogenic pollution, but rather can be attributed to the enhanced solubility of these elements under highly acidic soil conditions (Astrom, 1998, 2001; Freda and Cox, 2001; Appleby et al., 2006; Macdonald et al., 2007).

![Fig. 2. X-ray diffractogram showing the presence of schwertmannite (a), scanning electron photomicrograph of schwertmannite particles (b) and energy dispersive X-ray spectrum for the schwertmannite composition (c) in the initial Fe- and organic-rich acid-sulfate soil. Note: Schwertmannite is denoted in (a) by "Sc".]

3.2. General trends in pH, Eh and major ions during soil re-flooding

Re-flooding of CLASS involves manipulating surface drainage in order to retain freshwater in low-lying areas (Tait et al., 2002). This approach facilitates wetland re-establishment and is likely to create strong gradients in geochemical properties. In particular, the initial ionic composition will differ considerably between the submerged soil and the overlying surface water. For example, relatively saline surface soils are likely to be covered initially by less saline surface water. This situation was simulated in a controlled, re-flooding experiment using a natural iron-rich CLASS material.

Re-flooding caused an increase in pH to between 60 and 65, with a corresponding Eh decrease to ~100 mV during the initial 28 day period (Fig. 3). The pH/Eh data reflect a shift from acidic/oxic to near-neutral/oxic conditions in response to soil re-flooding. The trend in pore-water Cl concentrations was consistent with the upwards diffusive flux of this conservative solute from the pore-water to the surface-water (Fig. 3). Accordingly, in the material at lower depth within the columns (i.e. ~10.5, ~13.5 and ~16.5 cm), pore-water Cl decreased steadily from 428 mM initially to between 150 and 200 mM at 91 days (Fig. 3). Contrast pore-water Cl in the near-surface material (i.e. ~1.5 and ~4.5 cm) decreased rapidly to ~150 mM during the initial 7 days. The concentrations of pore-water Na, K, Ca and Mg varied in a similar way to pore-water Cl, thereby suggesting that upwards diffusive transport was also important for these elements (Fig. 3).

3.3. Iron behaviour during soil re-flooding

During the experiment described here, pore-water FeII comprised >95% of total pore-water Fe concentrations, thereby preventing the
accurate determination of pore-water Fe$^{II}$. The relatively low concentration of pore-water Fe$^{II}$ (i.e. $<$5% of total Fe) compared to the high concentration of Fe$^{III}$ (7.1 mM) in the initial pore-water reflects the relatively low solubility of Fe(III)- versus Fe(II)-phases. The dominance of schwertmannite in the initial soil suggests that this phase may control Fe$^{III}$ solubility during the early stages of re-flooding, according to:

$$\text{Fe}_2\text{O}_3(\text{OH})_2\text{SO}_4 + 22\text{H}^+ + 8e^- = 8\text{Fe}^{II} + \text{SO}_4^{2-} + 14\text{H}_2\text{O}$$  \hspace{1cm} (1)

The importance of this reaction is supported qualitatively by the pH-Eh data (Fig. 4), which follow the schwertmannite-Fe$^{III}$ boundary during the initial stages of the experiment.

A more quantitative description of apparent schwertmannite solubility can be determined by calculation of the ion activity product (IAP) for schwertmannite:

$$\text{IAP}_{\text{Schwertmannite}} = \frac{[\text{Fe}^{II}]^3 [\text{SO}_4^{2-}]}{[\text{H}^+]^{12}}$$  \hspace{1cm} (2)

Note that at equilibrium the IAP value equals the solubility product constant ($K_{sp}$). The IAP values for schwertmannite were calculated by modeling the Fe$^{II}$ and SO$_4^{2-}$ activities using the PHREEQC code with pH, Eh and total aqueous components (including total Fe) as input variables. The observed IAP for schwertmannite was $10^{10.12}$ for samples within the pH range of 3 to 4 (i.e. shaded area presented in Fig. 4). The observed IAP compares well with a schwertmannite $K_{sp}$ value of $10^{19.25}$ as presented by Bigham et al. (1996). Agreement with Bigham et al. (1996) is significant as there is considerable disagreement in the literature regarding schwertmannite $K_{sp}$ values. For example, a number of schwertmannite solubility studies have recommended the use of much lower values spanning $10^7$ to $10^9$ (Tu et al., 1999; Kawano and Tomita, 2001; Majdan et al., 2004). These lower $K_{sp}$ values contrast significantly with Regenspurg et al. (2004) who, like Bigham et al. (1996), found that schwertmannite solubility was best described by a $K_{sp}$ value close to $10^{19}$. The IAP values determined here support the use of a schwertmannite $K_{sp}$ value of $10^{19.25}$ for predicting Fe mobility in re-flooded CLASS with pH spanning 3 to 4.

Soil re-flooding caused substantial increases in pore-water Fe$^{III}$ during the initial 14 to 28 day period (Fig. 3). For example, the pore-water Fe$^{III}$ concentration at = 16.5 cm increased from 7.1 mM initially to 167 mM at 28 days (Fig. 3). The increase in pore-water Fe$^{III}$ is consistent with the reductive dissolution of schwertmannite (Eq. (1)). This process, which is mediated by Fe-reducing bacteria, usually involves the generation of alkalinity through the oxidation of simple organic species such as acetate (Appelo and Postma, 2005). Hence, the observed increase during the initial 28 days in pH and alkalinity (Fig. 3) can be attributed to the microbially-mediated reductive dissolution of schwertmannite.

The congruent dissolution of schwertmannite, via bacterial Fe$^{III}$-reduction, is expected to release Fe$^{II}$ and SO$_4^{2-}$ in a ratio of 8:1 (Eq. (1)). However, the observed ratio of Fe$^{III}$ to SO$_4^{2-}$ released to the pore-water at all depth intervals during the initial 28 days of waterfoggaging was best described by a ratio of ~1:1 (i.e. linear regression yielded: SO$_4^{2-}$=1.1·Fe$^{III}$, r$^2$=0.94; F=0.05). The XRD data, SEM-EDX observations and total Fe(III) to S ratio in the initial soil demonstrate that schwertmannite was the only considerable source of additional pore-water Fe and SO$_4^{2-}$ during the re-flooding experiment. Therefore, the significant non-stoichiometric release of SO$_4^{2-}$ and Fe$^{III}$ may be due to either preferential dissolution of schwertmannite-derived SO$_4^{2-}$ (compared with Fe$^{III}$), or the precipitation of secondary Fe minerals. In either case, such incongruent dissolution reflects a major shift in the mineralogy of the remaining solid-phase Fe.

This shift in mineralogy may be due to the formation of solid-phase Fe(II) minerals as products of schwertmannite reduction. Solid-phase Fe(II), when expressed on a pore-water volumetric basis, increased at...
a rate equivalent to 4.6 mmol day\(^{-1}\) during the initial 28 days in the 15 to 18 cm depth interval (based on linear regression of data presented in Fig. 5). Comparable data on solid-phase Fe(II) (data not presented) was obtained for the other depth intervals. The 15 to 18 cm depth interval is used here as an example because at this depth pore-waters were only minimally affected by diffusive loss during the initial 28 days as evidenced by the relatively stable Cl concentrations (i.e. at the \(\sim 16.5\) cm depth; Fig. 3). Hence, the changes in pore-water SO\(_4\) and Fe\(^{III}\) at this depth during the initial 28 days are due mainly to geochemical reactions, rather than to diffusive transport (as in the near-surface depth intervals).

Coincident with the increase in solid-phase Fe(II) at 4.6 mmol day\(^{-1}\), the pore-water Fe\(^{III}\) concentration at the \(\sim 16.5\) cm depth increased at a rate of 6.0 mmol day\(^{-1}\) (Fig. 5). Together this data implies a rate of reduction of schwertmannite-derived Fe(III) equating 10.6 mmol day\(^{-1}\). If the increase in pore-water SO\(_4\) at the \(\sim 16.5\) cm depth during the initial 28 days was due to the reductive dissolution of schwertmannite alone, then pore-water SO\(_4\) would have increased at a rate of 3.3 mmol day\(^{-1}\). This rate is based on the calculated rate of reduction of schwertmannite-derived Fe(III), combined with a stoichiometric Fe:SO\(_4\) ratio in the dissolving schwertmannite of 8:1. However, the pore-water SO\(_4\) concentration actually increased at a rate of 5.9 mmol day\(^{-1}\) (Fig. 5), which is almost 2-fold faster than estimated for reductive dissolution of schwertmannite. This indicates that only a minor proportion of the increase in pore-water SO\(_4\) during the initial 28 day period was due to reduction dissolution of schwertmannite.

An additional potential mechanism of SO\(_4\) dissolution is the transformation of schwertmannite to goethite (Bigham et al., 1998):

\[
\text{Fe}_2\text{O}_3(\text{OH})_2\cdot\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow 8\text{FeOOH} + 6\text{SO}_4^{2-} + 2\text{H}^+ \tag{3}\]

The rate of this reaction can be estimated by the difference between the actual rate of SO\(_4\) dissolution (5.9 mmol day\(^{-1}\)) and the calculated rate of SO\(_4\) dissolution due to Eq. \((\ref{eq:1})\) \(1.3\) mmol day\(^{-1}\), based on pore-water Fe\(^{II}\) and solid-phase Fe(II). This calculation indicates that the rate of transformation of schwertmannite to goethite in the 15 to 18 cm depth interval over the initial 28 days was 4.5 mmol day\(^{-1}\) (as SO\(_4\)). At this rate, complete transformation of schwertmannite to goethite would be expected over approximately 40 days (using total 5 as a measure of the initial schwertmannite content, and considering the soil water content and density).

![Fig. 5. Variations in solid-phase Fe(II), pore-water Fe\(^{II}\) and pore-water SO\(_4\), during the initial 28 days of re-flooding in the 15 to 18 cm depth interval. The lines represent best fits from linear regression analysis. The solid-phase Fe(II) data was converted from gravimetric to volumetric units by considering the soil water content and density. Data points are means of duplicate experiments.](image)

Although the rate calculations described above apply to the 15 to 18 cm depth interval, goethite formation is expected to be an important process at all depths within the soil column. This expectation is confirmed by the XRD data for the 0 to 3 cm depth interval at 91 days, which show that goethite was a major solid-phase product of soil re-flooding (Fig. 6a). Linear combination fitting of the Fe-K-edge XANES spectrum for the 0 to 3 cm depth interval revealed that goethite comprised 58% of total Fe at 91 days (Fig. 7). The XRD and XANES data support the rate calculations, which indicate transformation of schwertmannite to goethite during the early stages of the re-flooding experiment.

Following the initial increase in pore-water Fe\(^{III}\), there was a subsequent decrease over days 28 to 91 for all depths (Fig. 3). The observed decreases in pore-water Fe\(^{III}\) corresponded to a change from the initial yellowish-brown colour to a strong black. The XRD data for the 0 to 3 cm depth interval shows that the soil at 91 days contained both siderite (FeCO\(_3\)) and nano-particle goethite (Fe\(_2\)O\(_3\)) (Fig. 6a). This suggests that the colour change and decrease in pore-water Fe\(^{III}\) are due to the formation of these Fe(II)-containing minerals. Linear combination fitting of the Fe XANES spectrum for the 0 to 3 cm, 91 day sample revealed that 33% of total Fe was present in siderite and 9% in nano-particle goethite (Fig. 7).
The co-occurrence of siderite and nano-particle mackinawite is interesting as this situation has been found only rarely in the natural environment (Burton et al., 2006c). Siderite commonly occurs in anoxic, Fe(III)-reducing systems where SO\(_4\) is absent or present at low concentrations. In contrast, iron-sulfides (such as nano-particle mackinawite) form in SO\(_4\)-rich systems, where Fe reacts with H\(_2\)S produced by dissimilatory SO\(_4\)-reduction. The formation of nano-particle mackinawite is clear evidence that SO\(_4\)-reduction occurred in response to soil re-flooding. Although SO\(_4\)-reduction releases H\(_2\)S, the pore-water H\(_2\)S concentrations were below detection (<1 μM). This is consistent with very low H\(_2\)S solubility in the presence of abundant pore-water Fe\(^{0}\) (Burton et al., 2006d).

Siderite was present as globules with a diameter of ~<1 μm (Fig. 6b and c). Energy-dispersive X-ray microanalysis (EDX) showed that the siderite aggregates contained a Ca content of 3% to 5%. The inclusion of some Ca within siderite probably explains the decrease in pore-water Ca relative to pore-water Cl towards the end of the re-flooding experiment (Fig. 3). The pore-waters within the re-flooded soil exhibited siderite IAP values of 10\(^{-10}\) to 10\(^{-12}\) from day 3 onwards (Fig. 8). This represents a 10- to 1000-fold supersaturation with regard to the siderite K\(_s\) value of 10\(^{-10.4}\) (Jensen et al., 2002). Such supersaturation is consistent with Jensen et al. (2002), who found comparable IAP values due to sluggish equilibration kinetics when siderite was precipitated from Fe\(^{6+}\) and HCO\(_3\)-rich synthetic solutions (Fig. 8). The present study demonstrates that the siderite K\(_s\) value of 10\(^{-10.4}\) may significantly underestimate Fe\(^{0}\) mobility in re-flooded Fe-rich soils. The results suggest that siderite IAP values between 10\(^{-10}\) and 10\(^{-12}\) may be more appropriate for predicting Fe\(^{0}\) mobility in near-neutral, re-flooded CLASS settings (Fig. 8).

The sulfide within nano-particle mackinawite is recovered as AVS (Burton et al., 2007). The AVS content therefore provides a quantitative measure of the concentration of nano-particle mackinawite. Fig. 9 shows that AVS was present in the re-flooded soil columns from day 49 onwards. In the 0 to 3 cm depth interval, the AVS content increased linearly over this period, reaching a concentration of 237 μmol g\(^{-1}\) at 91 days. This AVS content indicates that ∼6% of total Fe was bound within nano-particle mackinawite, which agrees well with the corresponding Fe XANES data presented in Fig. 7. The 0 to 3 cm depth interval contained the highest AVS content, probably due to continual re-supply of SO\(_4\) by the twice weekly surface water replacements. This hypothesis is consistent with the very low pore-water SO\(_4\) concentrations at 70 to 91 in the lower depths (i.e., ∼4.5 to ∼16.5 cm) (Fig. 3), suggesting that AVS formation at depth was limited by SO\(_4\) supply.

The results show that AVS was an important product of SO\(_4\)-reduction during soil re-flooding (Fig. 9). The Fe stability field diagram presented in Fig. 4 suggests that Fe(III)-reduction will occur at higher Eh than SO\(_4\)-reduction. However, SO\(_4\)-reduction may occur concurrently with, or preferentially to Fe(III)-reduction under some conditions (Appelo and Postma, 2005). These conditions can be evaluated on the basis of predominance fields for SO\(_4\)-versus Fe(III)-reduction (Postma and Jakobsen, 1996). Fig. 10 shows that SO\(_4\)-reduction (and thus, in these situations, AVS formation) is not expected when Fe(III) is supplied by schwertmannite (i.e. all data points are to the right of the schwertmannite line in Fig. 10). Clearly, this is inconsistent with the observed presence of AVS from day 49 onwards (Fig. 9). In contrast, the presence of AVS exhibits excellent agreement with the goethite line (Fig. 10). In particular, AVS was only present when the pH-Fe\(^{2+}\) data in Fig. 10 are to the right of the goethite line (i.e. indicating SO\(_4\)-reduction). Good agreement between the occurrence of AVS and the theoretical predominance fields for reduction of SO\(_4\) versus reduction of goethite-derived Fe(III) implies that complete schwertmannite transformation to goethite is a requisite condition for AVS formation. This is further supported by agreement between the onset of AVS formation (i.e. re-flooding duration of 35 to 49 days) and the time calculated above for complete transformation of schwertmannite to goethite (i.e. approximately 40 days). Overall, the results indicate that Fe(III) availability to Fe-reducing bacteria was greatly decreased by the transformation of schwertmannite to goethite. In turn, this decreased availability of Fe(III) to Fe-reducing bacteria allowed SO\(_4\)-reducing bacteria an energetic advantage (in competing for organic electron donors), which resulted in subsequent AVS formation.
3.4. Aluminium, manganese, nickel and zinc behaviour during soil re-flooding

The pore-water concentrations of Al, Mn, Ni and Zn decreased during the soil re-flooding experiment (Fig. 3). Pore-water Al decreased relatively rapidly from 202 μM initially to below detection (<0.05 μM) at a re-flooding duration of 14 days (Fig. 3). For pore-water samples with pH < 5, the Al solubility was pH-dependent, following the relationship: log[A] = −1.3pH−1.8 (r² = 0.97). Pore-water Al was below detection (<0.05 μM) at pH > 5, which is consistent with the first hydrolysis constant for Al (pKₐ = 5.0). Thus, as the pore-waters within the soil columns increased towards pH > 5 (due to acidity consumption via schwertmannite re-reaction), hydrolysis caused the Al to become insoluble and precipitate most likely as an Al-oxyhydroxide phase.

The pore-water Mn, Ni and Zn concentrations decreased more slowly in response to soil re-flooding than the corresponding pore-water Al concentrations (Fig. 3). Pore-water Mn spanned 2 μM to 5 μM from day 49 onwards, whereas pore-water Zn and Ni were below detection (i.e. <0.05 μM) during this period. The very low pore-water Mn concentrations and undetectable pore-water Ni and Zn present at days 45 to 91 coincide with AVS formation in the soil columns (Figs. 3 and 9). The results suggest that interactions with AVS may have constrained Mn, Ni and Zn solubility. This is consistent with trace metal behaviour in sulfidic sediments, where AVS is known to be a key factor controlling metal mobility (Morse and Luther, 1993; Simpson et al., 2002; Burton et al., 2005, 2006e).

Interaction of Mn, Ni and Zn with AVS can involve sorption to, or co-precipitation with, the dominant Fe-nanosulfide (e.g. nanoparticulate mackinawite) or can involve the precipitation of discrete non-ferrous sulfides (Morse and Luther, 1993). NiS (millerite) and ZnS (spalerite and wurtzite) are less soluble than nanoparticulate mackinawite. Hence, pore-water Ni and Zn can precipitate with sulfide in preference over Fe and thereby be sequestered as millerite and spalerite/wurtzite, respectively. In contrast, alabandite (MnS) is much more soluble than nanoparticulate mackinawite, and therefore cannot control Mn solubility under Fe-rich pore-water conditions. The relatively high solubility of alabandite means that Mn also has negligible tendency to co-precipitate with nanoparticulate mackinawite (Arakaki and Morse, 1993).

Whilst the precipitation of discrete sulfide minerals is possible for N and Zn, the precipitation of a carbonate phase may be more important for Mn. Speciation calculations using PHREEQC reveal that the pore-waters were supersaturated with regard to rhodochrosite (MnCO₃) at 24 to 49 days in the lower depth intervals (i.e. −10.5 cm to −6.5 cm). However, pore-water Mn was undersaturated with regard to rhodochrosite at all depths following day 46. This indicates that although precipitation of rhodochrosite may have occurred in the lower depths at 24 to 49 days, rhodochrosite precipitation cannot account for the very low pore-water Mn concentrations from day 49 onwards. The very low Mn concentrations towards the end of the re-flooding experiment are therefore probably due to Mn sorption to reactive surfaces. Arakaki and Morse (1993) show that Mn sorbs strongly to nanoparticulate mackinawite, which provides an explanation for the significant drop in pore-water Mn in the presence of AVS.

3.5. Arsenic behaviour during soil re-flooding

During the initial 7 days following soil re-flooding the pore-water As concentration either decreased from the initial concentration of 1.3 μM or remained relatively constant (Fig. 3). The decrease in pore-water As during this period was most pronounced towards the interface between the surface water and the re-flooded soil. Fig. 11a shows that the pore-water As:Cl ratio remained relatively constant at between 2 × 10⁻⁶ to 3 × 10⁻⁶ during the 0 to 7 day period. This indicates that, in the 7 days following re-flooding, As behaved as a relatively conservative solute. Therefore, the initial decrease in pore-water As within the near-surface depths can be attributed to upwards diffusive flux of As from the pore-water to the overlying surface water.

The pore-water As concentrations peaked at between 14 to 28 days following re-flooding (Fig. 3). At the lower depths (~7.5 to ~16.5 cm), the peak pore-water As concentrations represent a substantial increase above the initial concentration. For the ~1.5 cm and ~4.5 cm depths, the peak at 14 days represents pore-water As concentrations that are comparable to, or less than the respective initial concentration (Fig. 3). However, examination of the pore-water As:Cl ratios reveals that all
depths experienced a major increase in pore-water As relative to pore-water Cl between 7 and 28 days (Fig. 11a). Furthermore, although the absolute pore-water As concentrations decreased towards 91 days (Fig. 3), the pore-water As:Cl ratios remained well above the corresponding ratio in the initial pore-water (Fig. 11a).

The results demonstrate clearly that As was significantly mobilized in response to soil re-flooding (Figs. 3 and 11a). During the re-flooding experiment, pore-water As was positively correlated with pore-water Fe(II) (r = 0.75, P < 0.05). The significant positive correlation indicates that As behaviour was strongly linked to Fe geochemistry. Although pore-water As and Fe(II) were correlated overall, the pore-water As:Fe(II) ratios indicate substantial decoupling during the initial 14 days (Fig. 11b). In particular, there was a 14 day lag in the mobilization of As relative to Fe(II) (Fig. 11b). Such decoupling of As and Fe is increasingly being recognized as an important aspect of As behaviour (Issam et al., 2004; van Geen et al., 2004; Burnol et al., 2007).

In a recent study, Burnol et al. (2007) found that As mobilization was delayed in comparison to Fe(II) when As-spiked ferricydrate underwent reductive dissolution. They showed that As was mobilized via desorption of AsO4, following microbial reduction of more strongly sorbed As(V) (Burnol et al., 2007). The results presented in Fig. 12a indicate that reductant of As(III) may also be important in the present study. Fig. 12a shows that samples with relatively low pore-water As:Cl ratios (i.e., during the initial stages of re-flooding) lay within the H2AsO4 stability field. In contrast, the pore-water As:Cl ratios increase considerably for samples within the H2AsO4 stability field (Fig. 12a). The enrichment in pore-water As within the H2AsO4 field is reasonable, given that As(III) is only weakly retained by soil solid-phases compared with As(V) (Smoley and Kinneir, 2002). Overall, the results suggest that reduction of As(V) to As(III) may have been a key cause of the significant As mobilization observed in the present study. This also helps to explain the lag in As release relative to Fe(II), as reduction of schwertmannite-derived Fe(III) occurs at higher Eh than reduction of As(V) to As(III).

Several other processes are likely to have exacerbated the effect of As(III)-reduction in increasing pore-water As during the 7 to 28 day period. Reductive dissolution of schwertmannite would have decreased the number of reactive surface sites available for As retention. Microbially-mediated schwertmannite reduction releases SO4 and HCO3 when coupled to oxidation of simple organics, which may have further enhanced As desorption via an anion exchange mechanism. The increase in pH due to schwertmannite reduction would have decreased the schwertmannite anion exchange capacity, thereby causing desorption of As bound via outer-sphere surface complexes. Transformation of schwertmannite to goethite may have also increased As partitioning to the pore-water, due to As having a lesser sorption affinity for goethite compared to schwertmannite (Acero et al., 2006). Additionally, the very high concentrations of SO4 released to the pore-water as a result of schwertmannite transformation to goethite would have competed with As for anion exchange sites. It is clear that a range of processes may have contributed to the observed As mobilization. Resolving the relative importance of these inter-related As desorption processes is an area requiring further research.

Fig. 11b shows an increase in the pore-water As:Fe(II) ratio from days 28 to 49. This period corresponds with the onset of solid-phase sulfide formation, as evident from the AVS data (Fig. 9). In sulfidic systems, As may be sequestered via the formation of As-sulfide minerals such as dispersed sorption (AsS2 (Smoley and Kinneir, 2002; Bostick et al., 2004). Competition for solid-phase sulfide between As and Fe can be evaluated by the following equilibrium reaction between nanoparticulate mackinawite and dispersed op- riment (Wilford and Ford, 2006):

\[ 3\text{FeS}_2 + 2\text{H}_2\text{AsS}_2\text{O}_7 + 6\text{H}_2\text{O} = \text{AsS}_3\text{S}_8 + 3\text{Fe}^{3+} + 6\text{H}_2\text{O} \] (4)

Boundaries for this reaction are presented in Fig. 12b, and were calculated from ΔG° values of dispersed op- riment (−87.7 kJ mol⁻¹). Nordstrom and Archer, 2003) nanoparticulate mackinawite (−98.2 kJ mol⁻¹; Rickard, 2006), H2AsS2O7 (−640 kJ mol⁻¹; Nordstrom and Archer, 2003), Fe(II) (−90.5 kJ mol⁻¹; Parker and Kharolokvsi, 1995) and H2O (−237.18 kJ mol⁻¹; Stumm and Morgan, 1996). Fig. 12b shows that permanganate formation in sulfidic systems is favoured over nanoparticulate mackinawite as H3AsO4 increases, pH decreases and Fe(II) decreases. The Fe-rich conditions and near-neutral pH in the re-flooding experiment (see shaded area in Fig. 12b) indicate that nanoparticulate mackinawite would have outcompeted dispersed op- riment for the available sulfide. This is consistent with the preferential removal of pore-water Fe(II) compared with As between days 28 to 49 (evident by the increase in pore-water As:Fe(II), Fig. 11b).

Several studies have hypothesized that sorption of As to iron-monosulfide minerals, such as nanoparticulate mackinawite, may retard As mobility under SO4-reducing conditions (Smoley and Kinneir, 2002; Wolthers et al., 2005; Wilford and Ford, 2006). Fig. 12b suggests that As sorption to nanoparticulate mackinawite would have been more important in the re-flooding experiment than the precipitation of dispersed op- riment. Sorption of As to nanoparticulate mackinawite occurs via the formation of relatively weak outer-sphere complexes (Tarquhar et al., 2002; Wolthers et al., 2005). Such complexes would be subject to significant competition from the high concentrations of pore-water HCO3 produced during soil re-flooding. This would have depressed As retention by nanoparticulate mackinawite, thereby enhancing As mobility in the re-flooding soil despite the presence of abundant AVS from days 49 to 91. This is consistent with Zheng et al. (2004) who found that As in Bangladesh groundwater remained highly mobile under SO4-reducing conditions. Overall the results of the present study show that, unlike Mn, Ni and Zn, the formation of AVS did not greatly decrease pore-water As concentrations in the re-flooding soil.
4. Conclusions

An understanding of the factors that govern the mobility of arsenic and metals is essential to assess possible risks to water quality in acid-sulfate soil landscapes. Such understanding is needed at severely acidified sites, for example, in order to select appropriate remediation strategies, design long-term monitoring approaches and to prepare contingency plans in the event that geochemical conditions change. In the present study, we examined the partitioning of Al, As, Fe, Mn, Ni and Zn between the solid-phase and pore-water after re-flooding of an active acid-sulfate soil material.

Re-flooding triggered acidity consumption by the microbially-mediated redox-dissolution of schwertmannite. This raised the pH of the initially acidic soil and subsequently decreased pore-water Al concentrations. Reductive dissolution of schwertmannite also leads to very high concentrations of pore-water Fe. In natural environments, pore-water Fe may be transported away from its anoxic site of formation, where it may re-oxidize and hydrolyse thereby releasing the previously consumed acidity. The results suggest that formation of Fe(II) (via SO4-reduction) can retard this Fe3+ mobility. Likewise, the results clearly show that Fe(III) formation also strongly immobilizes Mn, Ni and Zn in re-flooded acid-sulfate soil.

Soil re-flooding and the resulting redox-dissolution of schwertmannite caused significant As mobilization. Speciation calculations, along with some decomposing of the observed Fe and As behaviour, suggest that reduction of Fe(III) to Fe(II) had a key role in As desorption. However, it is likely that a number of additional mechanisms (related to Fe-S transformations) also affected As mobility. Further research into the effect of Fe-S transformations on As desorption is required to be able to predict As behaviour in re-flooded acid-sulfate soils.

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