Is bacterial sulfate reduction a dominant process for the removal of iron in Reducing and Alkalinity Producing Systems?[1]

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ABSTRACT

Bacterial sulfate reduction (BSR) and the resultant reaction of H_2S with dissolved iron or iron oxides is often assumed to be a key control on the removal of iron in passive, anaerobic treatment systems. Here, we show that in two Reducing and Alkalinity Producing Systems (RAPS) in Northeast England, most iron is actually removed as ox(yhydrox)ide, with a secondary role for sulfide. The RAPS treat net acidic coal mine water with average pH = 4.5, iron = 15-65 mg L^{-1} and sulfate = 360-1100 mg L^{-1}. Between 35-74% of influent iron and 8-26% influent sulfate are removed in the RAPS sediment. Concentrations of iron and sulfur species have been determined on sediment cores of both RAPS, along with influent and effluent water chemistries and $\delta^{34}S\text{-}SO_4^{2-}$ and $\delta^{34}S\text{-}HS^-$. The occurrence of BSR is evidenced by $\Delta^{34}S_{SO4\text{-}HS}$ around 40‰ in the effluent and influent waters, detectable concentrations of reduced inorganic sulfide in the effluents and the occurrence of ferrous sulfide mineral species in the sediments. However, only 3-9% of the sedimentary iron occurs as sulfides; the remainder occurs as ox(yhydrox)ide or in adsorbed form. The existence of significant amounts of elemental sulfur (7-22% of sedimentary sulfur) indicates an important oxidative pathway for H_2S, probably through reaction with Fe oxides. These findings question the assumption that BSR is a controlling mechanism for the removal of iron in anaerobic passive treatment systems.

Additional Key Words: passive mine water treatment, coal mine drainage, sulfur stable isotopes, bacterial sulfate reduction, RAPS

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INTRODUCTION

Passive treatment of mine water relies on "naturally-available energy sources" and requires only infrequent maintenance to operate effectively (PIRAMID Consortium, 2003). For treatment of metalliferous net-acidic water, anaerobic treatment systems, such as Reducing and Alkalinity-Producing Systems (RAPS), are recommended (Younger et al., 2002) Intuitively, the effectiveness of these systems is governed by two principles: (i) raise alkalinity via limestone dissolution, and (ii) encourage dissimilatory bacterial sulfate reduction to increase alkalinity and remove iron in the form of sulfide minerals (e.g. pyrite, iron mono-sulfides). Some of the key chemical reactions are shown in equations 1-4.

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \quad (1)$$
$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \quad (2)$$
$$H_2S + Fe^{2+} \rightarrow FeS + 2H^+ \quad (3)$$
$$2FeOOH + H_2S + 4H^+ \rightarrow 2FeS + 4H_2O \quad (4)$$

The RAPS at Bowden Close, County Durham, UK, are the most closely monitored systems of this sort in the UK. The treatment system combines two parallel RAPS, followed by an aerobic reed wetland for removal of residual iron (Figure 1). The treatment system, commissioned in 2003, treats two net-acidic, metal laden discharges; one arising from a closed underground coal mine (discharge 1, RAPS 1 inf; Q_{avg}=29 L min^{-1}), the other originating from a spoil heap (discharge 2, RAPS 2 inf; Q_{avg}=88 L min^{-1}). Discharge 1 is directed into RAPS 1, whereas discharge 2 enters RAPS 2. Underdrains and overflows of both systems are discharged via underground aeration pipes into the aerobic reed bed from where the water is released into a local stream. The reactive substrate of the RAPS consists of a horse manure-spent straw compost-limestone layer of 80 cm thickness through which the mine water is forced by gravity.

The overall objectives of the treatment system are to lower total concentrations of iron and aluminium, and to raise pH and alkalinity of the mine drainage (Table 1).

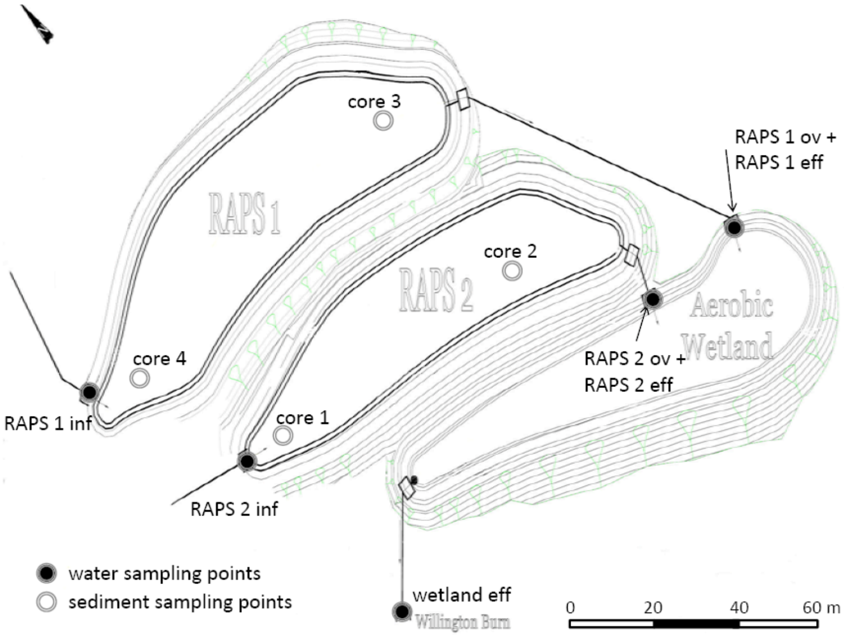

Figure 1. Bowden Close mine water treatment system and sampling points for surface water and sediments

Table 1. Averages, minima and maxima of acid mine discharges 1 and 2

	discharge 1	discharge 2
iron	15.8 (1.0-36.4)	63.8 (12.1-355.0)
aluminium	5.1 (1.2-13.3)	31.9 (1.1-66.0)
pH	4.5 (3.2-6.9)	4.7 (4.2-6.2)
alkalinity	24 (0-110)	10 (0-75)

average (minimum-maximum) = mg L^{-1} except pH, alkalinity = mg $CaCO_3$ eq L^{-1}

The treatment performance of the whole treatment scheme at Bowden Close including the removal behavior of other metals is discussed elsewhere (e.g. Jarvis et al., 2005).

Total effluent iron concentrations from the RAPS, monitored over a four year period, averaged 4.2 mg L^{-1} (range: 0.1-16.7 mg L^{-1}) and 5.1 mg L^{-1} (range = 0.7-16.5 mg L^{-1}) for RAPS 1 and RAPS 2, respectively. The results showed that 74% and 35% of total iron was retained in RAPS 1 and 2 before entering the aerobic reed bed. This equates to removal rates for iron of 0.4 g $m^{-2}d^{-1}$ and 2.7 g $m^{-2}d^{-1}$ for RAPS 1 and 2, respectively. The pH values of both mine waters were raised by more than two units to 7.4 (RAPS 1, range = 6.4-8.2) and 7.0 (RAPS 2, range: 6.4-7.3). Effluent alkalinity concentrations averaged 273 mg L^{-1} $CaCO_3$eq (RAPS 1) and 211 mg L^{-1} $CaCO_3$eq (RAPS 2). Net alkalinities (NetAlk = Alkalinity – nonMn-Acidity; after Hedin et al., (1994) and Jage et al., (2001)) showed positive values throughout the period of monitoring. Redox potentials of effluents were typically 20 mV (RAPS 1_{avg}) and -50 mV (RAPS 2_{avg}).

METHODOLOGY

Since April 2008 surface water samples from influents and effluents were taken for the determination of sulfur stable isotope ratios in aqueous sulfate and sulfide and analysed using a modification of the method of Mayer and Krouse (2004) by precipitating sulfate as barium sulfate and sulfide as zinc sulfide and later conversion to silver sulfide. The samples were then analysed by standard conventional techniques (sulfates after Coleman and Moore (1978); sulfides after Robinson and Kusakabe (1975)). In November 2004 four sediment cores were taken (two per RAPS) at locations shown in Figure 1. After extrusion and partitioning into 3 cm sections, sediments were centrifuged (3000 rpm, 10 minutes) to separate pore waters. These were analysed for all major and minor cation and anion species, pH, Eh, alkalinity and dissolved ferrous iron.

Sediment samples were multi-acid digested (Hossner, 2005; US EPA 3050B, 1996) and analysed for their total carbon (TC), total sulfur (TS) and total organic carbon (TOC) concentrations. Solid phase iron was sequentially extracted using the method of Poulton and Canfield (2005). The sequential extraction of sulfur was carried out using a modified method of Mayer and Krouse (2004) and Duan et al., (1997) to differentiate between seven sulfur phases: 1) WSS – water soluble sulfate, 2) ES – elemental sulfur, 3) AVS – acid volatile sulfur, 4) ASS – acid soluble sulfate, 5) CRS – chromium reducible sulfur, 6) AS – adsorbed sulfate and 7) OrgS – organically bound sulfur. The reduced inorganic sulfur (RIS) fractions were recovered for stable isotope analysis.

RESULTS

Evidence for Bacterial Sulfate Reduction

The determination of sulfur concentrations in influents and effluents of the RAPS indicated a mean removal in sulfate concentration of 26% (removal rate: 3.3 g $m^{-2}d^{-1}$) in RAPS1 and 8% in RAPS 2 (removal rate: 2.7 g $m^{-2}d^{-1}$). The occurrence of bacterial sulfate reduction (BSR) within the reactive substrate was demonstrated by the distinct H_2S smell and sulfide concentrations reaching 0.5 mg L^{-1} during summer months in effluent waters. During BSR, preferential reduction of $^{32}SO_4^{2-}$ results in isotopically light (^{32}S-enriched) sulfide and leaves residual sulfate enriched in ^{34}S. This was observed in both RAPS, with $\delta^{34}S$ values of effluent sulfate +4.5‰ and +2.8‰ greater than influent values in RAPS 1 and RAPS 2, respectively. Isotope ratios of dissolved sulfide in the effluents showed typical isotope fractionation for open, well mixed, systems (Canfield, 2001) with $\Delta^{34}S_{SO4-HS}$ ranging between 39.1‰ and 45.8‰ in both RAPS systems.

BSR was also evidenced by the presence of pyrite (FeS_2), elemental sulfur and small amounts of meta-stable iron mono-sulfides which were found throughout the sediment column (Figure 2). Concentrations of RIS ranged between 0.6-4.0 g kg^{-1} in RAPS 1 and 1.0-8.3 g kg^{-1} in RAPS 2. On average, 29% to 52% of the total sediment sulfur occurred as reduced inorganic sulfur (RIS; i.e.: CRS, AVS or ES) considered to be a direct or indirect product of microbial sulfate reduction. Maximum reduced sulfur concentrations were detected in near surface horizons in all cores except core 3 in RAPS 1, where highest reduced sulfur concentrations were detected at depths of 35 cm.

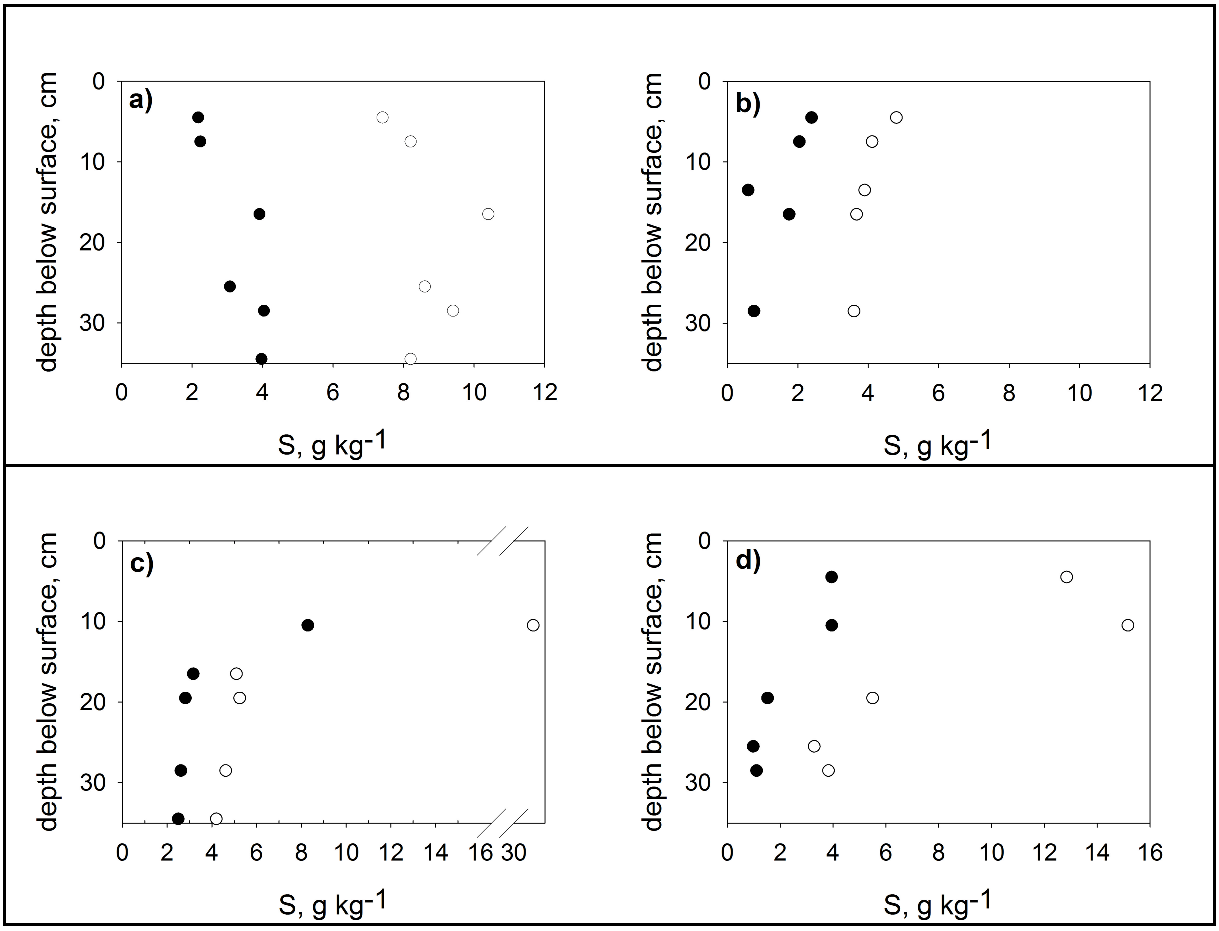

Figure 2. Concentrations of reduced inorganic sulfur (RIS, closed circle) and total sulfur concentrations (TS, open circle) in the reactive substrate of Bowden Close RAPSystems, a) RAPS 1, core 3, b) RAPS 1, core 4, c) RAPS 2, core 1, d) RAPS 2, core 2

Solid Phase Iron

Results of the sequential extraction of iron in the substrate are summarized in Figure 3. Despite the evidence of high levels of BSR, more than 92 % of all iron was non-sulfidic. This was most frequently in the form of oxyhydroxide iron phases in the upper sediment horizons, with iron oxide species increasingly important at greater depths (results not presented here). In contrast, iron sulfides comprised only 4.1-7.9% of total iron in RAPS 1 and 2.3-5.5% in RAPS 2, and amounts of ferrous mono-sulfide species were negligible. This suggests that BSR is, in fact, a rather minor process in the overall immobilisation of iron within the RAPS.

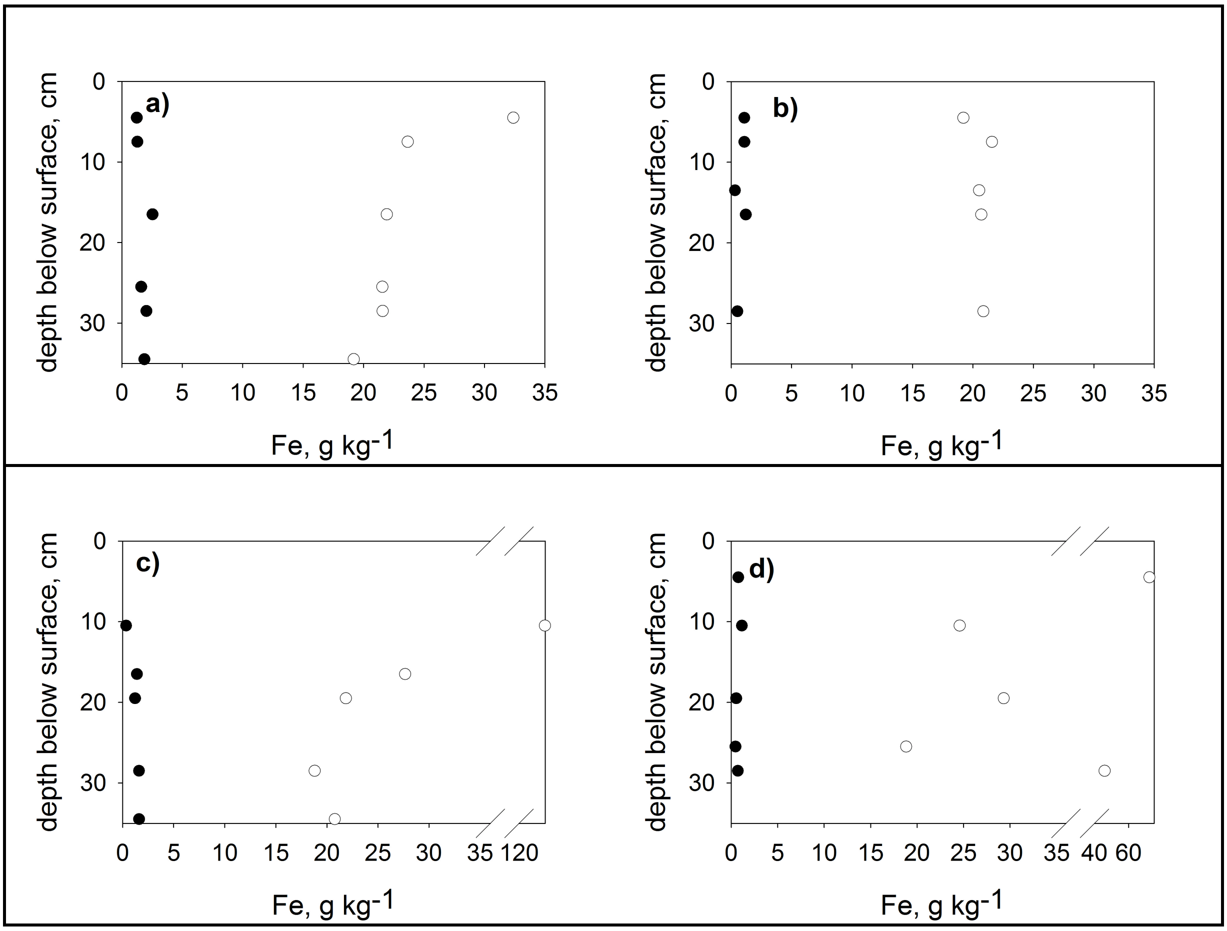

Figure 3 Concentrations of reduced inorganic sulfur bound iron (RSFe, closed circle) and total iron concentrations (TFe, open circle) in the reactive substrate of Bowden Close RAPSystems, a) RAPS 1, core 3, b) RAPS 1, core 4, c) RAPS 2, core 1, d) RAPS 2, core 2

DISCUSSION AND CONCLUSIONS

Whilst it has hitherto been assumed that BSR is a controlling mechanism for the removal of iron in anaerobic passive treatment systems, such as the RAPS discussed in this paper, our data indicate that BSR is a rather minor process in the overall immobilization of iron within the RAPS. There are three principal factors that generally appear to limit the formation of reduced inorganic sulfur species in marine and lacustrine environments. These are (after Berner et al. 1985):

i. The availability of free ionic sulfate species as electron acceptors for BSR in the interstitial water

ii. The quantity of dissolved ferrous iron and reactive iron mineral species (e.g. hydroxides and oxides) to react with hydrogen sulfide, the principal product of BSR, and

iii. The quantity and quality of electron donors (organic molecules and H_2) metabolizable for dissimilatory sulfate reducers.

The results presented here suggest that none of these factors are likely to be responsible for the low pyrite concentrations observed in the Bowden Close RAPS, for the following reasons:

i. Sulfate concentrations are high in both influents *and* effluents (average effluent concentrations: 200 mg L^{-1} RAPS 1, 800 mg L^{-1} RAPS 2), and sulfate is present at all depths in the interstitial water, with average concentrations in the range of 82 mg L^{-1} (core 4, RAPS 1) to 753 mg L^{-1} (core 1, RAPS 2).
ii. Despite significant spatial variability, iron in the filtered fraction of the interstitial water was detected in all sediment cores. Average concentrations ranged from 0.02 mg L^{-1} in RAPS 1 to 105 mg L^{-1} in RAPS 2. In addition, reduced iron is present in the effluent waters of both RAPS (average for 8 months monitoring: 1.9 mg L^{-1} RAPS 1, 4.1 mg L^{-1} RAPS 2). Furthermore, reactive iron species (i.e. ox(yhydrox)ides) have been observed at all depths of the sediment cores.
iii. Concentrations of total organic carbon ranged from 7.5%-18.7% of the dry matter at all depths, although the precise nature of this carbon source, and in particular its biological availability for metabolisation, is not yet clear (this is the subject of future research). Notwithstanding the latter proviso, BSR is a clearly established and significant process in both RAPS.

It seems more likely that other parameters such as limited hydraulic retention time of the mine water within the sediment (Wolkersdorfer et al., 2005), relatively low ambient temperatures, and high iron loads (Fe) in the influent waters may be limiting the extent of iron removal as a sulfide.

Although redox potentials in interstitial water indicate reducing conditions, and BSR is occurring, iron is largely removed as an oxide or hydroxide, with only minor amounts of iron permanently retained in the sediment in the form of sulfide minerals. Oxidative removal of iron far exceeds reductive removal. Furthermore, reoxidation of hydrogen sulfide and metastable iron mono-sulfides may be occurring, perhaps by iron oxides. Reoxidation is suggested by the near absence of AVS and the fact that elemental sulfur (a direct oxidation product of H_2S or AVS) comprises 7% - 22% of total sulfur at all sediment depths.

In conclusion, this study suggests that in the Bowden Close RAPS system bacterial sulfate reduction is not a significant process for the removal of iron, although it may still play an important role in the generation of alkalinity, in addition to that generated by $CaCO_3$ dissolution. The relative importance of BSR and $CaCO_3$ dissolution for alkalinity generation is currently being investigated using stable carbon isotopes.

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