

## Biogeochemical interactions in a compost wetland for spoil heap leachate remediation at Quaking Houses, County Durham, UK.

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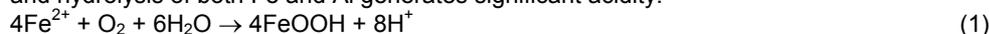
**Keywords:** Wetlands, Sulphate reduction, iron reduction, rates, alkalinity generation.

### ABSTRACT

The linked redox geochemistry of carbon, sulphur and iron is at the heart of remediation of acidic waters within passive, anaerobic wetland sediments. Sediment cores were extracted from the Quaking Houses constructed wetland in County Durham, England. Pore water profiles show concomitant reduction of both sulphate and iron oxide. Solid phase analyses show that iron sulphides are precipitated. The build up of dissolved iron in sediment pore waters indicates that the net rate of iron reduction (FeR) exceeds that of bacterial sulphate reduction (BSR). Incubation data also supports this, in that FeR (chemical plus microbial) proceeds at a faster rate than BSR. BSR was found to generate alkalinity at around 6 times the rate of microbial FeR. Despite high rates of BSR, only 10 – 15% of Fe is present as sulphide precipitates. Around 80 – 90% of solid phase iron is sequestered into the sediment as oxides/oxyhydroxides of unknown composition.

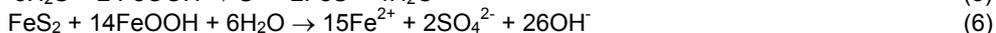
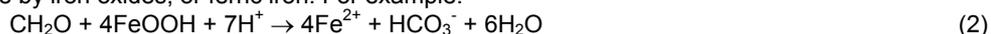
### INTRODUCTION

The effective treatment of AMD discharges through passive techniques is not only a function of engineering design, but also biogeochemistry. Passive treatment systems for acidic drainage are designed to exploit the linked biogeochemical redox cycles of carbon, sulphur, and iron with the dual aims of raising pH and alkalinity, and removing metal pollutants such as iron, aluminium, manganese, and zinc. Both aerobic and anaerobic passive treatment systems have been deployed. At least for net acidic waters, aerobic systems are of limited use. Although iron can be successfully removed by oxidation and hydrolysis, and trace metals can be subsequently removed from solution by adsorption onto the surface of oxyhydroxides (Johnson & Thornton, 1987) the oxidation and hydrolysis of both Fe and Al generates significant acidity:



For this reason anaerobic systems provide a much higher potential for successful remediation.

Successful remediation of AMD using anaerobic systems depends on the balance of reactions (chemical and abiotic) within the C-Fe-S cycles. There is an immense literature on the C-Fe-S geochemistry of marine and freshwater sediments (e.g. Berner, 1985; Holmer & Storkholm, 2001; Kostka & Luther, 1994; Lin & Morse, 1991; Thamdrup, 2000) which reveals a diverse suite of potential reactions. Some of the key reactions include the microbially mediated dissimilatory reduction of sulphate and iron oxide, the formation of iron sulphides, and the reoxidation of sulphide by iron oxides, or ferric iron. For example:



Most of these reactions involve the generation or consumption of protons and/or the generation of alkalinity. It is clear therefore that the overall balance of the C-S-Fe cycles dictate the remediation potential of an anaerobic treatment system.

Design of anaerobic constructed wetlands has focussed on microbial sulphate reduction as being the key process for alkalinity generation (Fortin *et al.*, 2000; Hedin *et al.*, 1988; McIntyre *et al.*, 1990; Younger *et al.*, 2002) though literature regarding the geochemistry of constructed anaerobic wetlands is sparse.

The general aim of this project was to study C-S-Fe cycling to test this assumption, using a range of geochemical methods. A temporal geochemical study and incubation experiments were employed to this end. Specific aims were to quantify the rates of key reactions within a passive treatment system i.e. bacterial sulphate reduction and iron reduction, and to use that information to estimate carbon turnover and alkalinity generation. This paper shows results of a biogeochemical study of the Quaking Houses constructed wetland in County Durham, England (Morrison, 2005).

### STUDY AREA

Quaking Houses Wetland can be located on Ordnance Survey map, Landranger series 88, Tyneside & Co. Durham Area, at grid reference NZ 185 506. It lies alongside the Stanley Burn, a small tributary of the River Wear in Co. Durham, England. The artificial wetland was commissioned in November 1997 to treat acidic colliery spoil leachate, which was draining into the Stanley Burn. Prior to treatment the leachate was characterized by high

loadings of iron and aluminium ( $\sim 0.4$  mM for both), and low pH ( $\sim 4$ ) (Jarvis, 2000). In 1998 the spoil heap responsible for the discharge was capped, resulting in raised pH and lower metal concentrations, although still net acidic. The design of the wetland, constrained by hydrogeological factors, consists of two ponds (Figure 1). Both ponds contain a substrate composed of horse and cow manure, and composted municipal waste in a ratio of 30:40:30. Water from the influent pipe enters the first cell with a mean flow rate of  $80 \text{ L min}^{-1}$ , then decants over a weir into the second cell where it is dispersed by vegetation and baffles. This is primarily a surface-flow system with nominal average water retention time of  $\sim 24$  hours (Younger *et al.*, 2002).

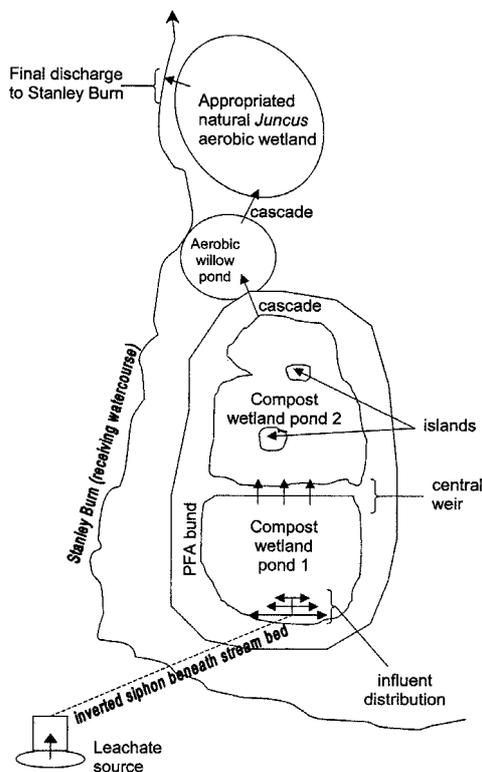


Figure 1. A schematic of Quaking Houses Wetland.

Over a period of 16 months, field data, surface waters and four sediment cores were sampled for analysis. Porewaters were extracted under anaerobic conditions from each core at depth intervals of 1 cm. Porewaters and sediments then underwent a series of extractions and analyses to determine concentrations, enabling concentration with depth profiles to be plotted, for redox sensitive Fe and S species. Following the geochemical characterization of the sediment and waters, a series of incubation experiments were carried out to determine the rates of sulphate and iron reduction.

## RESULTS

Porewater and solid phase data for iron and sulfur species are shown in Figures 2-5, respectively. Superficially, the porewater data resemble trends which have been reported previously in natural, marine sediments (Canfield *et al.*, 1993; Thamdrup *et al.*, 2000; Wijsman *et al.*, 2001). Reduction of iron oxides in the top few centimeters of the wetland sediments results in increasing abundances of dissolved iron, below which concentrations of dissolved Fe decline steadily. Microbial sulfate reduction occurs in the surficial sediments resulting in steadily declining concentrations of sulfate. Figure 2 illustrates this trend clearly, but also highlights a temporal effect where there is a net diffusion of sulphate out of the sediment over the top 2 cm in the November and January cores. Careful appraisal of the porewater profiles reveal that in fact they differ from those reported in natural sediments in several important ways. Most obviously, porewater Fe increases to the very high concentration of  $\sim 1.3$  mM (Figure 3), despite the rapid generation of sulfide via sulfate reduction. In the top few centimeters of the sediment, rapid reduction of iron occurs concomitantly with rapid reduction of sulfate, with net production of reduced iron being greater than net production of reduced sulfur.

Solid phase sulfide data (Figure 4) show that the reduced iron and sulfur precipitate as pyrite ( $\text{FeS}_2$ ) and acid volatile sulfide ( $\text{FeS}$  and similar compounds). Pathways of iron sulfide formation in these sediments are not yet defined but could include direct precipitation from the end products of bacterial sulphate reduction (BSR) and microbial iron reduction (MFeR), and the abiotic reaction of dissolved sulfide with solid phase iron oxides; the detection of significant concentrations of elemental sulphur (up to  $225 \mu\text{mol g}^{-1}$ ) support abiotic reaction between Fe(III) and sulphide.

Figure 5 shows the exceptionally high concentration of amorphous iron oxide in the sediment (mean value for all cores is  $500 \mu\text{mol g}^{-1}$  over top 2cm). This was a surprising find given the very high organic carbon contents (10 – 35%) of these sediments, although ascorbate-extractable Fe(III) (Fe-asc) has been measured in natural sediments (Kostka & Luther, 1994; Luther *et al.*, 2003; Rutten & De Lange, 2003).

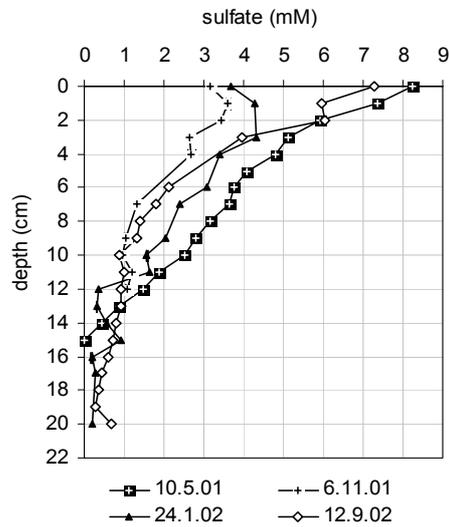


Figure 2: Pore water sulphate depth profiles illustrating temporal differences between winter months and summer months. In all cases  $\text{SO}_4^{2-}$  concentrations reach a minimum after 12 cm.

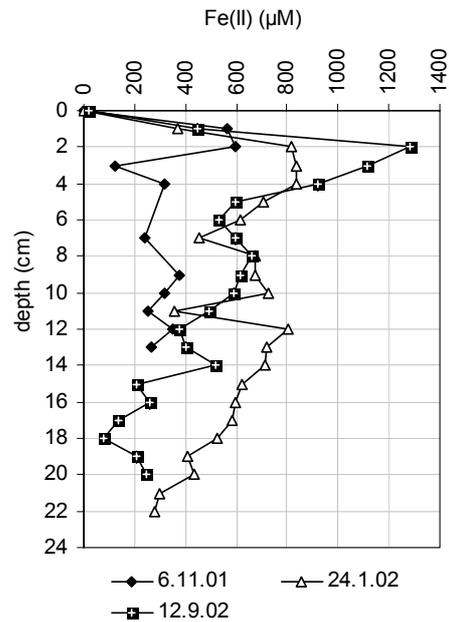


Figure 3: Pore water Fe(II) depth profiles. Net production of Fe(II) is greater than production of sulphide. High concentrations of dissolved Fe(II) occur throughout the cores.

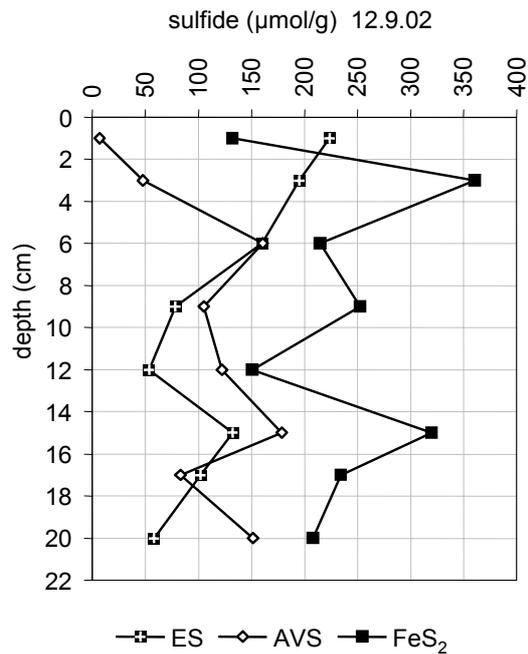


Figure 4: Solid phase sulphide data for September. High concentrations of elemental S at the surface are consistent with chemical reduction of FeOOH by H<sub>2</sub>S.

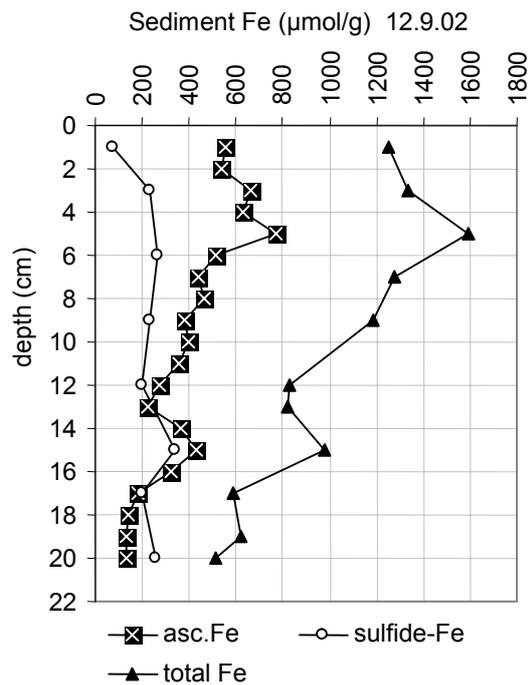


Figure 5: Solid phase Fe data for September. Approximately 9% of the sediment is present as Fe, but only 1-2% is present as sulphides, with ~ 4% as ascorbate soluble amorphous iron oxide.

Total Fe (TFe) extracted from the sediment was present to very high concentrations, particularly the surficial sediments (Figure 5); 7 - 13% of sediment dry weight. These values are substantially greater than the mean value quoted for a saltmarsh (2.74%) (Kostka & Luther, 1994), and also for a fresh water lake (0.1 – 2.3%) (Luther *et al.*, 2003). Figure 5 also shows the contributions made to the TFe by both Fe-asc and sulphide-bearing Fe (S-Fe). There are three important observations to be made;

1. TFe >> Fe-asc + S-Fe
2. S-Fe represents only 7 – 12% of TFe in these sediments.
3. Fe-asc is approximately 20-45% of the TFe in the top half of the cores.

Some of the rates of reaction results from the incubation experiments are shown in Table 1, together with examples of diffusion rates for sulphate and iron.

**Table 1: Diffusion and reaction rates for BSR and FeR determined during this project. Diffusional and depositional rates expressed in  $\mu\text{mol cm}^{-2}\text{d}^{-1}$ , reaction rates in  $\mu\text{mol cm}^{-3}\text{d}^{-1}$ .**

Sample Date	Determinand	Value	Experiment
November 2001	SO <sub>4</sub> <sup>2-</sup> out of	0.141	Diffusion rates from pore water profiles
	Fe <sup>2+</sup> out of	0.173	
September 2002	SO <sub>4</sub> <sup>2-</sup> into	-0.430	Inflow/outflow data
	Fe <sup>2+</sup> out of	0.194	
Jan'00 – Feb'05	Fe deposition	1.22	Microcosm experiments
September 2003	<i>net</i> BSR rate	0.14 – 2.00	
	<i>net</i> FeR rate	0.37	<sup>35</sup> S-radiotracer experiments
April 2004	Total BSR rate	0.075 – 0.660	
	Total FeR rate	0.97	CFeR+MFeR

## DISCUSSION

There is broad agreement between geochemical and incubation experimental data, in that both sets demonstrate concomitant reduction of both sulphate and iron in the surface sediments. Comparison of diffusional fluxes with reaction rates show reasonably close agreement, given the inherent uncertainties in the calculations. The diffusional rate of SO<sub>4</sub><sup>2-</sup> into the sediment during the summer falls within the reduction rate range determined from the incubation experiments. This is what we would expect since diffusion of SO<sub>4</sub><sup>2-</sup> into the sediment is driven by BSR. The *net* FeR rate is actually a *net* accumulation rate of Fe<sup>2+</sup> in the pore water, this is over and above any precipitation; this “free” Fe<sup>2+</sup> if not precipitated or adsorbed, would diffuse out of the sediment. Comparison of diffusional and reaction rates for Fe show that Fe diffuses out of the sediment at rates which are comparable to the *net* FeR rate. Although FeR as a whole proceeds at a faster rate than BSR (as evidenced by the accumulation of Fe<sup>2+</sup>) calculation of the contribution made by BSR and MFeR to bicarbonate alkalinity using the stoichiometry of the reactions between SO<sub>4</sub><sup>2-</sup> and organic matter, and FeOOH with organic matter, show that BSR generates bicarbonate at around 6 times the rate of MFeR in this study. BSR is therefore very important as a process for elevating and buffering pH in this system. Its value as a method of sequestering Fe<sup>2+</sup> is less significant, as only 7 – 12% of the TFe is present as sulphide precipitates; the remainder is present as amorphous FeOOH, and other poorly defined Fe-oxides.

We hypothesize that the oxide forms as a direct result of oxidation of dissolved pore water iron by oxygen supplied to the sediments through plant roots, or through the action of iron-oxidising bacteria present on the root surface (Emerson *et al.*, 1999); although the sphere of influence of radial oxygen loss from roots is confined to the root surface (Colmer, 2003), root density may counteract this. The formation of iron sulphides, the generation of S<sup>0</sup>, and the presence of very high concentrations of reactive Fe-oxyhydroxides in the surface sediments indicate an extremely dynamic environment where oxidation and reduction reactions occur simultaneously, over small distances. A study by Weiss *et al.* (2003) detected a significant presence of FeOB and FeRB associated with the roots of *Typha*, and suggested that the FeR rate was actually enhanced in the rhizosphere.

The occurrence of iron oxide in surface sediments clearly reflects deposition from surface waters and the fact that the rate of addition of oxidized iron must be greater than the rate at which it can be reduced either by dissimilatory microbial reduction (Lovley & Phillips, 1988; Nealson & Saffarini, 1994) or by abiotic reaction with dissolved sulphide.

Degree of pyritisation (DOP) values for the wetland were found to be low, indicating that pyritisation was limited by the concentration of sulphide in the pore waters. However, sulphate is not limiting in the surface waters, and BSR generates sulphide in the sediment. The rate of BSR i.e. sulphide production may be affected by the retention time of the water in the wetland. When this treatment system was designed, the main focus of the remediation was to remove as much of the iron (and other metals) as possible, and to elevate the pH; the removal of sulphate itself was not a priority. Design criteria (Jarvis, 2000) was based on work carried out in the USA, and involved the use of first-order kinetics to model potential contaminant loads and removal rates for specified treatment areas and retention times (Hedin *et al.*, 1994; Tarutis *et al.*, 1999). In light of BSR and FeR reduction rates determined in this study, is the nominal retention time in the wetland of 20 hours sufficiently long enough? Using mean influent SO<sub>4</sub><sup>2-</sup> and Fe<sup>2+</sup> concentration data, plus mean flow rate for the wetland, together with maximum reduction rates determined for BSR ( $2 \mu\text{mol cm}^{-3}\text{d}^{-1}$ ) and total FeR ( $1 \mu\text{mol cm}^{-3}\text{d}^{-1}$ ), the retention time in the wetland required for 100% removal was found to be two days for Fe, and 88 days for SO<sub>4</sub><sup>2-</sup>. The removal of sulphate is important only as a means of generating alkalinity, and providing a sulphide-sink for Fe<sup>2+</sup>. However, had the design of the wetland permitted a retention time of two days instead of one, there would be increased removal of both Fe and SO<sub>4</sub><sup>2-</sup>. This also has implications for contaminant loads in that a sudden “flush” or increase in Fe load to the wetland would result in a greater proportion of Fe exiting at the effluent untreated. Engineering constraints have probably dictated that this particular wetland treatment system operates at less than 100% efficiency.

## CONCLUSIONS

1. The temporal study has shown there to be seasonally affected changes in the biogeochemistry of Quaking Houses wetland. During the summer months there is a trend towards greater accumulation of  $\text{Fe}^{2+}$  in the top 2 cm (1200 – 1400  $\mu\text{M}$ ) as compared with the winter months (800 – 900  $\mu\text{M}$ ). Diffusion rates of sulphate into the sediment during the summer months (0.18 – 0.43  $\mu\text{mol cm}^{-3}\text{d}^{-1}$ ) fall within the range determined through microcosm experiments (0.075 – 2.03  $\mu\text{mol cm}^{-3}\text{d}^{-1}$ ), in this study. During the winter months sulphate diffuses out of the sediments into the overlying water. Reasons for this could include pore water re-equilibration with lower surface water  $\text{SO}_4$  concentrations, net sulphide oxidation, and/or desorption of  $\text{SO}_4$  from secondary mineral phases.
2. Precipitation of Fe as sulphides is not a major sink for Fe. Sulphide-bearing Fe accounts for only 7 – 12 % of the total Fe in the cores. The degree of pyritization is low, between 3 and 10%, given the high percentage of OC in these sediments (15 – 30%). Production of sulphide is the limiting factor. Instead Fe is stored in the sediment mainly as potentially reactive phases of oxides and/or hydroxides.
3. There is intense cycling of Fe and S in the surface sediments and in the rhizosphere. In this heavily vegetated wetland system, the contribution of ROL to the biogeochemistry of the rhizosphere must be significant. There is no direct evidence of this; however photos of Fe-plaques on roots, and the identification of high concentrations of amorphous  $\text{FeOOH}$  (200 – 800  $\mu\text{mol/g}$  dry weight) in the sediments would lead us to conclude that the effect of ROL is important. Even though the sediments are reducing, microenvironments exist where oxidative processes can occur along side reduction reactions.
4. Sulphate reduction rates fall within the range measured in some natural sediments, tending to be faster than marine rates, but in the scope determined for salt marsh and some oligotrophic lake sediments. Ranges measured for Quaking Houses were; *net* BSR rate between 0.14 and 2.00  $\mu\text{mol cm}^{-3}\text{d}^{-1}$ . Iron reduction rates determined by the microcosm method for marine and acid mine lake sediments, gave values of 0.1 – 2.4  $\mu\text{mol cm}^{-3}\text{d}^{-1}$ . Following microcosm experiments on Quaking Houses sediments, three rates for FeR have been determined – CFeR (0.20  $\mu\text{mol cm}^{-3}\text{d}^{-1}$ ), MFeR (0.77  $\mu\text{mol cm}^{-3}\text{d}^{-1}$ ), and  $\text{FeR}_T$  (total  $\approx 1 \mu\text{mol cm}^{-3}\text{d}^{-1}$ ). These FeR rates are at the upper limit of what was determined in this study, but fall within the range of those determined in acid mine lakes and marine sediments. Rates for CFeR are dependent on BSR rates, and the supply of sulphide to the sediment, as well as the reactivity of the Fe oxide phase.
5. BSR was found to generate significantly more alkalinity than MFeR, in this study. Thus reinforcing the assumption that BSR is a key process in the successful treatment of net acidic coal mine drainage. However, BSR seems to be less important as a pathway for sequestering Fe into the sediment, in this well vegetated wetland.

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