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STABLE ISOTOPIC MODELLING OF THE LONGEVITY OF TREATMENT PROCESSES OPERATING IN A CONSTRUCTED WETLAND FOR THE AMELIORATION OF ACID MINE DRAINAGE

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ABSTRACT

Artificial wetlands are cited as low cost, low maintenance, long-term treatment options for the amelioration of Acid Mine Drainage (AMD). However, little published work to date has attempted to quantify their expected longevity. Two of the treatment processes identified to be operating within anaerobic wetlands are bacterial sulfate reduction (BSR) and alkalinity supplementation. As BSR utilises the geochemical cycling of S and C, and alkalinity supplementation C, an understanding of wetland stable isotopic systematics ($\delta^{34}S$ and $\delta^{13}C$) allows each method to be identified and quantified. Within anaerobic wetlands alkalinity supplementation is predominantly derived from two sources - a by product of bacterial activity and limestone dissolution. Consequently, a mass balance calculation of the type

$$\delta^{13}C_{GEN.}Alk_{GEN} = \delta^{13}C_{BACT.}Alk_{1-X} + \delta^{13}C_{LST.}Alk_{X}$$

allows quantification of the relevant proportions from each source due to their distinctly different isotopic signatures.

Within this framework, this paper presents the results from a study of an artificial wetland at Pelenna, South Wales, U.K. The wetland comprises four individual cells which have been receiving AMD from the Whitworth No.1 discharge since October 1995. Mean influent chemistry is characterised by Fe 22 mg/l, SO_4^{2-} 3.6 mM (345 mg/l) and pH 6. The study indicated BSR is most productive in cells containing mushroom compost. However, the efficiency of BSR decreases with time as precipitated sulfides become oxidized. Alkalinity supplementation from limestone dissolution has an expected treatment lifetime of 9 years.

INTRODUCTION

Anaerobic wetlands are aimed at raising the pH and alkalinity and lowering the Fe content of influent water. In many situations, both in the laboratory and in the field, these aims are being fulfilled (Wieder, 1990; Dvorak, 1992; Rees, 1998). However, few attempts (Poulton, 1994; Wieder, 1990,) have been made to quantify the longevity of the processes responsible. As a result, this has lead to a cautious attitude taken by parties funding construction due to potential hidden future costs. In the U.K., until the introduction of the Mine (Notice of Abandonment Act) 1998, the bodies invariably involved with construction were local authorities. As a result, such organisations sought cost effective solutions which constructed wetlands are believed to offer (Brodie et al.; Wieder, et al., 1990).

Removal Processes

A number of removal processes have been identified to be operating within constructed wetlands:

Aerobic ferrous iron (Fe^{2+}) oxidation and hydrolysis (ferrolysis)

This is the dominant Fe removal mechanism where Fe is removed as sparingly soluble iron oxyhydroxides. Their formation simplistically summarised as:

$Fe^{2+} + 1/4\ O_2 + H^+ \longrightarrow Fe^{3+} + 1/2\ H_20$ (**oxidation**)

$Fe^{3+} + 3\ H_20 \longrightarrow Fe(OH)_3 + 3\ H^+$ (**hydrolysis**)

Overall, the combination of oxidation and hydrolysis results in the generation of proton acidity:

$Fe^{2+} + 2\ H_2O + O_2 \longrightarrow Fe(OH)_3 + 2\ H^+$ (**ferrolysis**)

Bacterial Sulfate Reduction (BSR) and metal sulfide precipitation

BSR is an anaerobic microbial process where simple, short chain organic molecules (represented by CH_2O) are oxidised as part of the metabolic cycle of the bacteria. Overall, the process results in the generation of dissolved sulfide and alkalinity:

$SO_4^{2-} + 2\ CH_2O \longrightarrow H_2S + 2\ HCO_3^-$

The dissolved sulfide produced can undergo a number of processes beneficial to treatment including degassing of hydrogen sulfide (H_2S) gas, formation of insoluble organic sulfur species and reaction with heavy metals to form metal sulfides. The most common secondary sulfide mineral formed is pyrite (FeS_2) along with its intermediary iron sulfide compounds, as Fe is often the dominant metal cation found in AMD.

Limestone Dissolution

Although not directly a metal removal process, limestone dissolution is integral to the longevity of constructed wetlands. Limestone is often added to spent mushroom compost, frequently used as a wetland substrate. This produces alkalinity which buffers pH to circumneutral levels thereby allowing bacterial processes to occur at appreciable rates. This process summarised as:

$CaCO_3 + H^+ \longrightarrow Ca^{2+} + HCO_3^-$

Scope of Paper

This paper is based upon research undertaken as part of an MSc thesis which utilised stable isotopes, coupled with major and trace element chemistry to assess the longevity of anaerobic wetlands (Rees, 1998). Only the isotopic data is presented here.

STUDY SITE

Davies et al. (1997) identified 60 km of river in Wales, suffering from the deleterious environmental affects associated with AMD. The river Pelenna, Tonmawr, South Wales was one of the more extensive, which prompted the Environment Agency (EA) and local authority to treat the five major discharges affecting the Pelenna (Whitworth No.1, Garth Tonmawr, Gwenffrwd, Whitworth A and Whitworth B) using constructed wetlands. SRK (UK) Consulting were approached to provide initial designs and consultations.

The Whitworth No.1 wetland (Figure 1) was the first in the River Pelenna Project treatment programme (started in 1993) to be constructed. The wetland occupies a total combined areal extent of 900 m^2. Each cell is made from pre-cast concrete lined with bentonite and overlain by sand and ~70 cm of substrate. Different combinations of plant (Typha and Juncus), substrate (bark mulch and mushroom compost) and flow regime are incorporated into the design to assess their relative efficiency. Influent water is directed through pipes to each cell whereas effluent waters feed directly into outlet chambers containing water quality monitoring facilities.

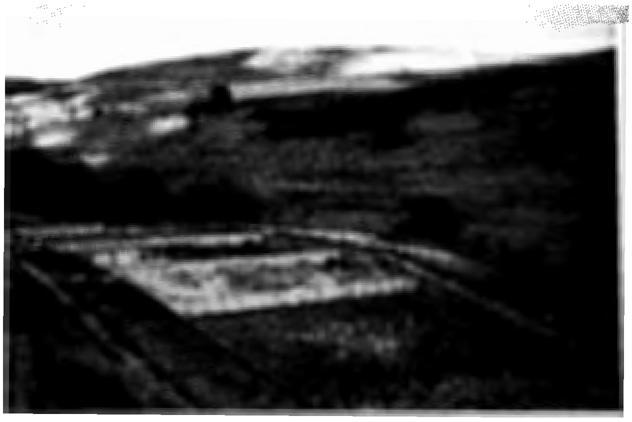

Figure 1. View looking north over the Whitworth No.1 wetlands.

Cell 1 is in the foreground. The mine adit is out of view on the left (April 1998).

The inlet pipes intermittently block due to precipitation and accumulation of ochre. This leads to unequal flow distribution between the respective cells. Also, the construction of the outlet chambers prevents effective flow monitoring and it has been necessary to assume flow is equally distributed at 0.75 L/sec to each cell.

SAMPLING METHODOLOGY AND ANALYTICAL TECHNIQUES

Substrate

Cores were sampled on 6/6/98 using 100 mm aluminium tubes. Sample oxidation was minimised by freezing each core with dry ice within 2 minutes of extraction. Cores were returned to the laboratory for storage in a freezer within 36 hours. Cores were sectioned relative to visible Redox zones and then halved frozen using a dry (no lubrication) rotary band saw. The frozen samples were then freeze dried. Finally, the dried samples were homogenised using a Moulinex food processor. The resultant powder was used for all substrate analysis and stored in a deep freeze between analysis. These samples were analysed for

- Inorganic and organic C content and $\delta^{13}C$ - all isotope results reported as delta (δ) notation relative to the PDB international standard as:
  $\delta^{13}C_{sample}$ /per mil (‰) = $R_{sample} - R_{PDB} / R_{PDB} \times 1000$
  where R is the $^{13}C/^{12}C$ ratio of the sample or standard (PDB).
- Pyrite content, as described by Newton (1995).

Waters

Waters were collected by directing flow into PTFE containers. Measurement of pH was made in the field using a HI 9024 model pH meter. Separate samples were filtered through 0.45 µm Whatman cellulose nitrate filters for analysis of metals, anions, alkalinity and stable C and S isotopes. Samples for cation analysis (only Fe is reported here) were acidified with conc. HNO_3 and analysed via ICP - OES within 2 weeks of collection. Anions (only SO_4 is reported here) were analysed using a Dionex DX100 Ion Chromatograph. Alkalinity was quantified through titration against a 5 mM HCL solution with the end point (pH 4.5) monitored using a pH meter.

Samples for isotopic analysis were placed into airtight plastic bottles containing 50 ml of $SrCl_2$. The $SrCl_2$ (in excess) acted as a fixing agent for HCO_3 and CO_2 as solid $SrCO_3$. Consequently, sample collection was done as rapidly as possible to prevent atmospheric CO_2 from precipitating. Approximately 30 mg of each sample was run on the C vacuum line at the University of Leeds, where phosphoric acid was added which liberated CO_2. The isotopic ratio of the evolved CO_2 was measured using a VG SIRA 10 mass spectrometer with the results quoted in the same notation as summarised for substrate $\delta^{13}C$.

RESULTS

Influent - Effluent Waters

The monitoring of influent and effluent chemistry conducted as part of the MSc study between 30/4/98 and 1/7/98 supplements data collected by the EA as summarized in Figure 2 for a number of parameters.

Effluent pH and alkalinity are generally greater than the corresponding influent values, whereas the reverse is true for SO_4^{2-} and Fe. The results are those expected from a wetland within which ferrolysis, BSR and limestone dissolution processes are operating. Monitoring of individual cells has been severely hampered due to wetland construction. However, without such data each cell can not be effectively assessed. Table 1 summarizes the mean chemistry that does exist for each cell relative to mean total influent and effluent chemistry. Values for mean $\delta^{13}C$ are those collected during this study.

	SO_4 mM	pH	Fe (total)	Alkalinity meq/l	$\delta^{13}C$ ‰
Influent	3.69	6.26	22.66	0.75	-8
Cell 1	3.62	7.09	6.04	1.12	-1.02
Cell 2	3.59	7.01	5.66	1.28	-7.19
Cell 3	3.38	6.85	5.64	0.97	-6.37
Cell 4	3.72	7.17	1.6	1.38	-7.17
Effluent	3.02	7.16	3.5	1.27	-5.02

Table 1 Mean influent, individual cell effluent and total effluent chemistry.

Substrate carbon and pyrite

Results for inorganic C and organic C are reported as dry wt % (Figure 2). Depth values used are the central points of each core section analysed. Inorganic C is subordinate to organic C because of the bark and compost substrates used. Organic C contents increase initially with depth but decline below approximately 20 cm. The reduction in organic C at the base of each core is due to sampling the sand / gravel which directly underlies the organic substrate. Cell 3 (mushroom compost) has a slightly higher inorganic C content than cell 4 (bark mulch) due to the addition of limestone.

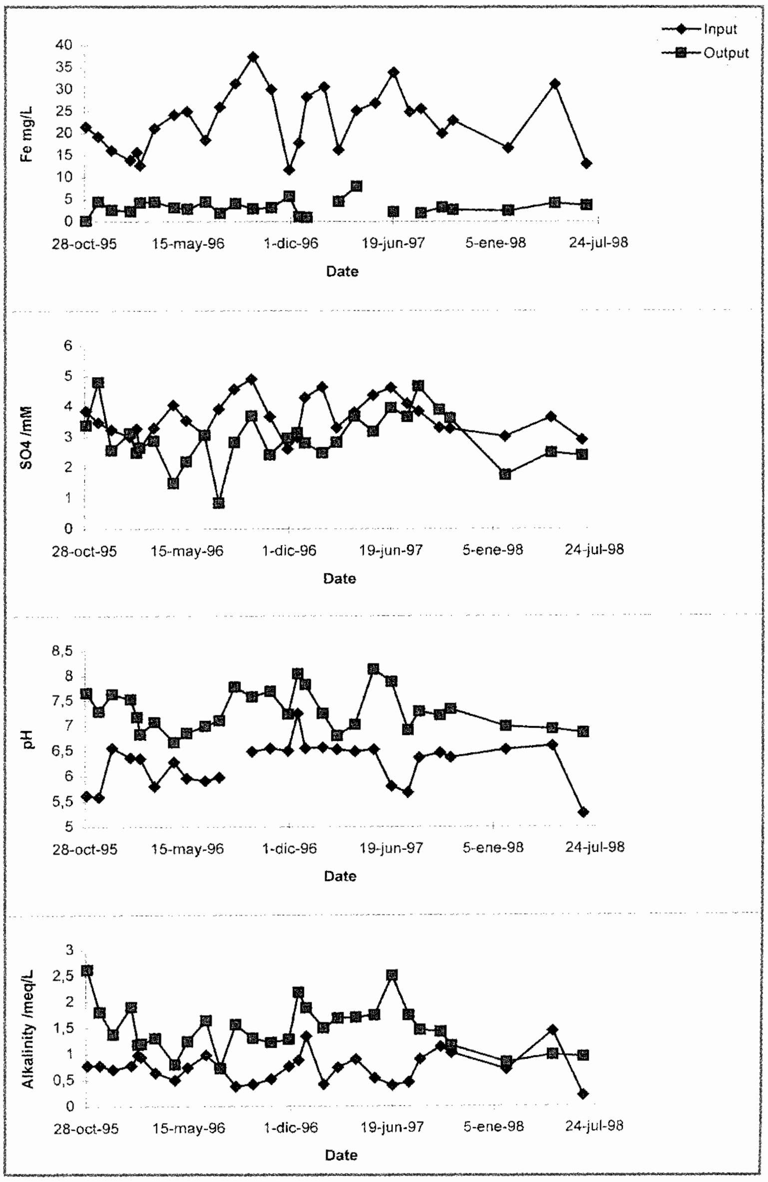

Figure 2. Temporal variation of selected determinants.

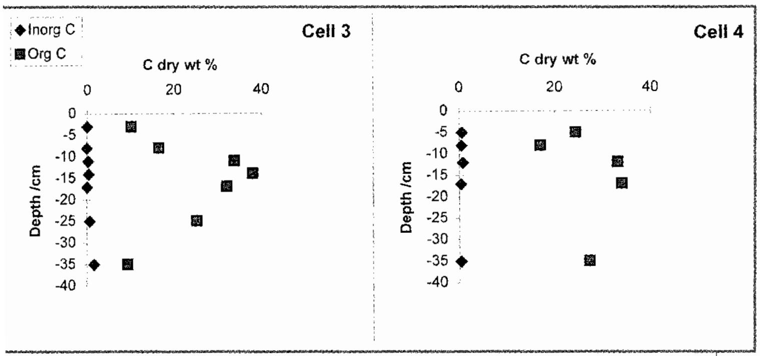

Figure 3 Substrate carbon profiles.

Pyrite contents in cell 3 and 4 are distinctly different, with cell 3 containing the greatest amount (Figure 4). This indicates conditions within cell 3 (which contains a mushroom compost) are suited to BSR and pyrite accumulation whereas in cell 4 (which contains bark mulch) they are less suited. These results are in exact agreement with those reported by Wiseman (1997) where cell 4 waters at depth had redox (Eh) values between +11 and + 41 mV, indicative of an oxidising environment unable to support BSR and facilitate pyrite accumulation. In comparison, cell 3 had reducing conditions with Eh ranging between -39 and -169 mV facilitate BSR and allow pyrite accumulation due to the anoxic conditions.

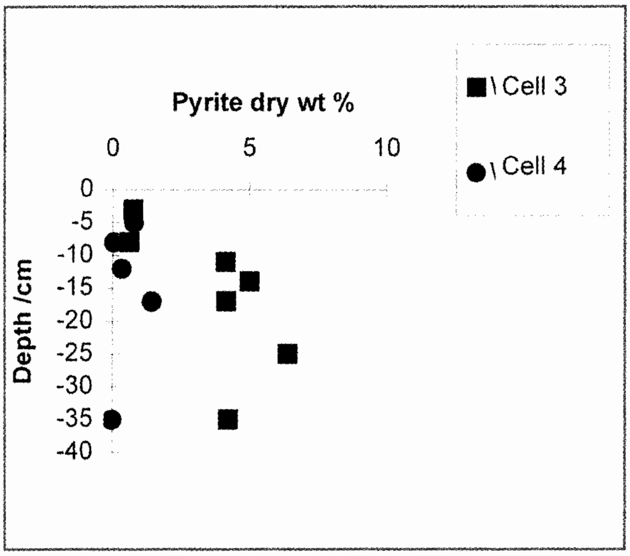

Figure 4. Pyrite content variation with depth for cells 3 and 4.

DISCUSSION

Isotopic Model

Two end member processes operating within the wetland control the net isotopic signature of the alkaline wetland effluent water:

- Bacterial activity
- Limestone dissolution

Therefore, the wetland can be treated as a steady state box model where the net alkalinity and $\delta^{13}C$ values generated are the difference between effluent and influent values. This can be summarised as:

$$\delta^{13}C_{GEN}.Alk_{GEN} = \delta^{13}C_{EFF}.Alk_{EFF} - \delta^{13}C_{INF}.\ Alk_{INF}$$

Isotopic values are multiplied by the respective alkalinity as the alkalinity effectively represents the fraction of C atoms contributing to the $\delta^{13}C$ ratio. Therefore, to differentiate between the two sources of alkalinity using the isotopic signatures a simultaneous equation was derived:

$$\delta^{13}C_{GEN}.Alk_{GEN} = \delta^{13}C_{BACT}.\ Alk_{Y} + \delta^{13}C_{LST}.Alk_{X} \text{ (where x+y=1)}$$

GEN - generated; BACT - bacterial isotopic composition; LST - limestone; Y - fraction of alkalinity from bacterial processes and X - fraction of alkalinity from limestone dissolution.

Isotopic signatures for the limestone ($\delta^{13}C_{LST}$) and organic matter were constrained through analyses of fresh bark much, freeze dried wetland sediment and acid washed core samples from cells 3 and 4. (The isotopic signature of organic matter is the same as $\delta^{13}C_{BACT}$ as there is no isotopic fractionation during oxidation). Unfortunately, the analysis of the freeze-dried sample to determine the limestone isotopic signature did not run on the vacuum line. This was likely due to the high sulfur content of the sample. However, the $\delta^{13}C_{BACT}$ were more important to constrain as they potentially could be highly varied. However, the results suggest such variation was not evident (Table 2) and the mean $\delta^{13}C_{BACT}$ obtained was -26.8%.

Sample	$\delta^{13}C$ / $^{0}/_{00}$
Bark mulch	-25.0
WT3 core	-28.7
WT4 core	-26.7
Mean	-26.8

Table 2 Summary of substrate isotopic analyses.

A $\delta_{13}C$ value of +2% was used for the limestone based on previous data for the Whitworth wetland.

Solvation of the simultaneous equation using the above figures and those given in Table 1 indicates limestone dissolution was the dominant source of alkalinity in the Whitworth wetlands (Table 3). (The isotopic signatures of the organic matter and limestone were assumed not to vary between cells).

The results for cell 1 are dubious due to the isotopic signature of the output water (-$^{0}/_{00}$) being highly anomalous relative to the other waters, likely due to contamination during sampling or analysis.

Limestone dissolution flux and longevity

Only cells 2 and 3 contain added limestone. Therefore, an averaged value of 78.5% is used for the percentage alkalinity derived from limestone dissolution. However, cell 3 was the only cell

Cell	% Alkalinity from bacterial processes	% Alkalinity from limestone dissolution
1	5	95
2	23	77
3	20	80
4	25	75
Total system	16	84

Table 3. Partitioning of alkalinity using C isotopes.

where the amount of inorganic C was determined. Consequently, the following discussion is limited to cell 3, an anaerobic wetland.

Total alkalinity in cell 3 effluent water was 0.64 meq/L, of which 78.5% (0.50 meq/L) is derived from limestone dissolution. Based on these figures and assuming the flow rate of 0.75 l/sec, the alkalinity flux derived from limestone dissolution was 30 eq/day or (1.5 kg/day $CaCO_3$). Using this value, and assuming the average inorganic C content from cell 3 (1.5 dry wt%) is applicable to the whole of cell 3 the longevity of the contained limestone can be derived. Therefore, assuming the dissolution rate (alkalinity flux) is constant, the limestone currently contained in cell 3, will potentially last for a further 9 years.

In addition to the assumptions outlined, above there are two further major caveats in the calculation:

- Limestone in all areas of the wetland is consumed at the same rate;
- Rate of consumption does not change with time.

An assessment of limestone grainsize distribution and spatial homogeneity was not possible in this study. Therefore, the above factors are essentially governed by variations in influent and pore water pH. The pH of influent waters has remained approximately constant at pH 6, and is unlikely to become more acid in the future. Therefore, the longevity of the limestone is governed by internal wetland processes which have the potential to affect pH.

Pyrite oxidation

Such processes would include oxidation of pyrite contained within the wetland substrate. This could occur either aerobically or anaerobically, both processes mediated by bacteria. If this were occurring, shifts in the $\delta^{34}S$ signature of influent - effluent SO_4 could potentially offer a method for monitoring such a process. This method is based on the fact that during BSR and pyrite formation, kinetic fractionations result in the formation of isotopically light (enriched in ^{32}S) pyrite. Consequently, subsequent oxidation of the isotopically light sulfide results in the generation of isotopically light SO_4. If oxidation were occurring the $\delta^{34}S$ -SO_4 would become increasingly negative.

In order to assess the occurrence of the above process, cell 3 influent and effluent waters were sampled for $\delta^{34}S$-SO_4. Influent waters had a $\delta^{34}S$ of -6.3 whereas the cell output values had a value of $-7.5^{0}/_{00}$. Therefore, based on this data it appears pyrite oxidation is occurring in cell 3, approximately 3 years since initial operation, consequently, the longevity calculated for limestone dissolution is an overestimate. This is due to significant quantities of acidity being generated during pyrite oxidation - as demonstrated by the existence of AMD.

SUMMARY

The observations made and conclusions drawn are in close agreement with those of Wieder (1992) for a compost wetland receiving influent water with pH 2.89, dissolved Fe 119 mg/L and SO_4^{2-} 32 mM (3132 mg/L). This chemistry distinctly different to that found at Pelenna. Wieder concluded compost wetlands receiving similar waters reach a point of minimal effective treatment. However, based on the presented isotopic study it appears anaerobic wetlands reach a point of minimal effectiveness, irrespective of influent chemistry. This point being where the rate of pyrite oxidation exceeds that of pyrite formation (Rees, 1998).

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The views expressed in this paper are entirely those of the authors and not SRK (UK) Consulting. Wetlands are effective for the treatment of AMD, particularly if ferrolysis is the principle chemical removal process. This has been demonstrated by a number of wetlands designed by SRK at a number of sites world-wide, including a number in the UK under similar climatic conditions to that at Pelenna.

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