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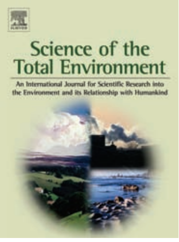

Iron and manganese removal in wetland treatment systems: Rates, processes and implications for management

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ABSTRACT

Mine water drainage is a significant environmental problem throughout the world and constructed wetlands are being increasingly used to treat such contaminating discharges. Iron and manganese removal within a wetland treatment system at Whittle Colliery, UK which receives alkaline waters, was monitored to determine rates and processes within the different components of the system. In addition hourly samples were taken for a period of 24 h to determine the effect of photosynthetic organisms on metal removal. Significant iron removal occurred, with removal rates of 98% at Whittle. Oxidation of iron to form iron hydroxide precipitates was the dominant removal process in the proximal sections of the treatment system (i.e. oxidation ponds and initial reaches of the wetland), whereas biotic removal processes appeared to become more important in distal parts of the systems, where iron concentrations were much lower. Significant manganese removal was also observed, although this did not become substantial until iron concentrations had fallen below 5 mg/L. The process by which manganese was removed is not clear, but bacterially-mediated oxidation may be involved. Further elucidation of the relative importance of abiotic and biotic removal processes within treatment systems is important in the design and long-term management of constructed systems.

1. Introduction

In common with many others parts of the world the UK has a long history of mining activity, estimated to exceed 4000 years (Goudie, 1993). These activities have historically produced mining contamination of soils, sediments and waters but the nature of the processes involved mean that the generation of pollution will continue for many years into the future. The contamination of water bodies is particularly important as it has a significant effect on the population due to the extensive use of boreholes, dams and rivers for potable water. It is difficult to accurately measure the extent to which water bodies are directly impacted by mine waters, but estimates have suggested that in the UK around 700 km of watercourses are affected (Jarvis and Younger, 2000), and Neymeyer et al. (2007) have recently documented migration of a major plume of polluted mine water in a public supply aquifer. In addition to the effect that mine discharges have on water bodies as a potential resource, they have been shown to have a significant effect upon riverine ecosystems, causing changes in communities and a reduction in diversity (Armitage and Blackburn, 1985; Malmqvist and Hoffsten, 1999). This impact on the ecological component of the landscape has become a high priority for many governments since the implementation of the EU Water Framework Directive (2000/60/EC) which requires member states to ensure that water bodies achieve good chemical and ecological status by the year 2015. In addition the proposed EU Mine Wastes Directive also requires member states to 'ensure that operators take all measures necessary to prevent or reduce…adverse effects on the

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environment and human health' by the year 2014 (2006/21/EC). This increased protection of habitats and water supplies means that mine water will have to meet acceptable standards for discharge agreed between the regulator and principal polluter. However many of the sites that currently pollute or pose an immediate threat are 'orphan' sites having no owner directly responsible, leaving governments with the responsibility of remediation.

As a result of this situation there has been significant effort over recent years to develop low-cost technologies for the remediation of mine waters. Prior to this, mine discharges have typically been treated with the addition of oxidative chemicals, liming agents and flocculants (Batty and Younger, 2004) but the need for more sustainable, cost effective solutions has led to the development of constructed wetlands as an alternative. This technology has been widely used in the UK and the Coal Authority alone has completed 35 full scale systems as of 2006.

Although the use of wetlands to treat mine water has proved largely successful, there have been cases where they have either over- or under-performed with respect to metal removal (David Laine pers comm.). Some authors advocate using a formula based upon first-order kinetics to calculate the size of wetland required to treat mine waters (Tarutis et al., 1999), though this approach has been challenged on the grounds that far more processes than iron oxidation affect overall removal rates (Batty and Younger 2002; Younger et al. 2002). Furthermore, it is unlikely that the transformation of metals within wetlands is completely abiotic and the actions of microorganisms and plants need to be accounted for. Previous research has suggested that biological activity in the root zones of wetland plants may be more important where iron concentrations are lower (Batty and Younger, 2002). It has also been suggested that some metal removal processes in aquatic environments will vary with changes in light intensity linked to photosynthetic or other biological activity (Butler, 2006; Hallberg and Johnson, 2005; Robbins and Corley, 2005). This suggests that in passive treatment systems, particularly those that incorporate different cells (e.g. oxidation ponds, wetlands) removal processes and rates will vary through the system which has important implications for the design and management of such schemes.

The aim of this investigation was to determine whether removal of iron and manganese in terms of rates and processes varied diurnally, and spatially within a wetland treatment system receiving waters with alkaline pH, by using physicochemical measurement on time scales of days and hours.

2. Materials and methods

2.1. Site description

Whittle Colliery is 3 miles south of the nearby Shilbottle Colliery (Fig. 1) and closed in 1997. In 1999/2000 it was identified that water rising in the mine workings was at risk of polluting the Hazon Burn, which flows into the River Coquet (Parker, 2000). The waters were net alkaline (pH ~ 7) and contained elevated concentrations of Fe and Mn (~45 and 2 mg/L respectively) together with around 3000 mg/L of sulphate. A suitable site was obtained by the Coal Authority to construct a lagoon and wetland system to remediate the water. A pumping station was put in place to transfer the water to a series of three wetlands, via two oxidation lagoons. A small slipway is present between the output from the pumping station and the oxidation lagoons. The wetlands (each 3000 m^2 in size) were planted with *Typha latifolia* (wetlands 1 and 3), and *Phragmites australis* (wetland 2). Each wetland is linked to the next by a slipway which facilitates oxygenation of the waters. The full system was completed in 2001 and fully commissioned in 2002 (Nuttall, 2003).

2.2. Field sampling

Water samples were collected every 2–3 days for a total period of 28 days (May–June 2004). Samples were collected at approximately the same time each day in order to minimise diurnal variations. Two water samples were collected at each sample point in the treatment system (Fig. 2). One sample was filtered through a standard filter paper (Whatman no.1; particle retention is 8–12 μm) in the field and the other half left unfiltered to determine the relative contributions of coarse particulate and dissolved fractions of metals. Both samples were acidified in the field with 10 M nitric acid within a few minutes of collection. These were stored at 4 °C until laboratory analysis for Fe and Mn concentrations.

In-situ measurements of pH, conductivity, oxidation–reduction potential and temperature were made using a field multiparameter instrument (Camlab Ultrameter 6P). Dissolved oxygen measurements were also made in-situ (YSI95 DO meter). Flow rates into the systems were determined using a simple bucket and stopwatch method (timed volume method). This was repeated three times at each site in order to ensure repeatability.

In addition to the main sampling campaign, a 24-hour period of hourly sampling was also undertaken to determine diurnal fluctuations in removal of metals. For logistical reasons it was not possible to carry out sampling for 24 h at all 8 sample points. Therefore, representative sites were selected and are illustrated in Fig. 3. In addition time constraints also prevented replicate samples being taken. Measurements and samples were taken as detailed for the main sampling campaign.

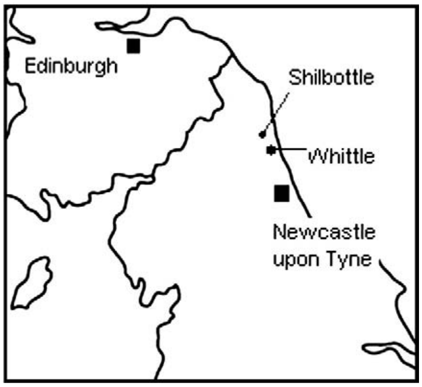

Fig. 1 – Location map of Whittle system in the UK.

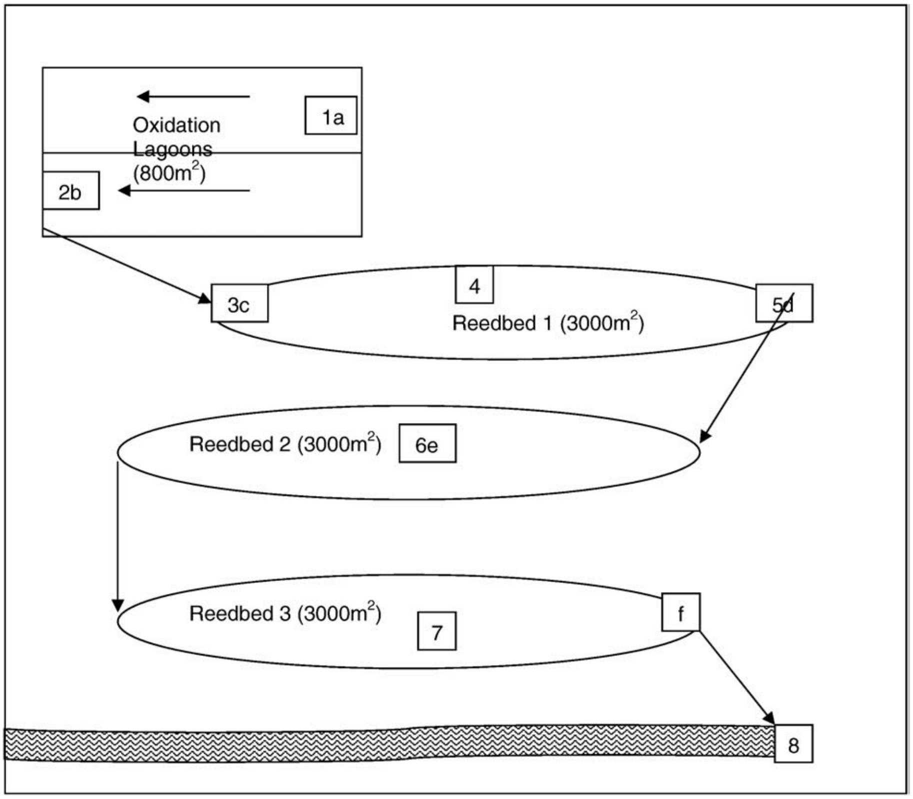

Fig. 2 – Plan of Whittle treatment system. Numbers indicated sampling points for the 3 week sampling period and letters indicate sampling points for the 24 h sampling period.

2.3. *Analytical techniques*

All iron and manganese concentrations were determined using Atomic Absorption Spectrometry (Unicam 929 flame spectrometer). Standards derived from analytical grade chemicals were used to calibrate the AAS and standards were analysed every 20 samples to ensure maintenance of accuracy. Where samples were outside the range of detection, samples were diluted using deionised water. Analytical and sample blanks were used for quality assurance and control. Detection limits for Fe and Mn were 0.003 mg L^{-1}.

2.4. *Calculations*

In order to assess the performance of the treatment system it was necessary to calculate the removal rates for Fe and Mn. This was done for individual components of the system (e.g. lagoons and wetlands) and the whole system. Three measures of removal were calculated; (1) treatment efficiency (Wieder, 1989), (2) area-adjusted removal (Hedin and Nairn, 1993) and (3) first-order removal (Tarutis et al., 1999).

$$\text{Treatment Efficiency}(\%) = (C_{\text{in}} - C_{\text{out}})/C_{\text{in}} \times 100 \tag{1}$$

$$\text{Area-adjusted removal}\left(\text{g m}^{-2}\,\text{day}^{-1}\right) = (C_{\text{in}} - C_{\text{out}})Q/A \tag{2}$$

$$\text{First-order removal}\left(\text{m day}^{-1}\right) = Q/A \;\; \ln\,(C_{\text{in}} - C_{\text{out}}). \tag{3}$$

Where C_{in} is inflow metal concentration, C_{out} is outflow metal concentration, Q is flow rate (m^3 d^{-1}) and A is area (m^2). The area of the different sections of the treatment system are indicated in Fig. 2.

2.5. *Statistics*

Differences between Fe and Mn concentrations at sampling points within the wetlands were analysed using a one-way ANOVA followed by a Tukey HSD test. Where data did not fit

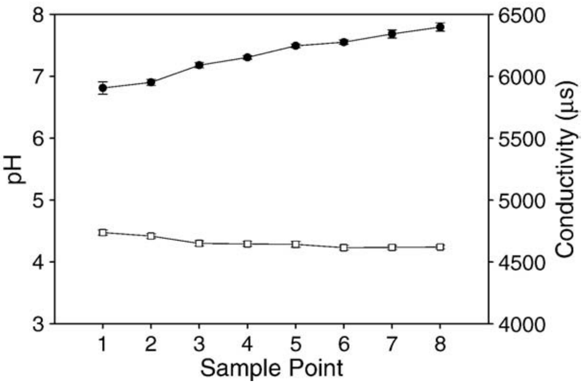

Fig. 3 – pH and conductivity of surface waters from Whittle treatment system. Error bars are mean ± SE (*n* = 12).

Table 1 – Metal removal in terms of treatment efficiency, area-adjusted removal (AAR) and first-order removal (FOR) in different components of the Whittle treatment system in the UK figures are means ± SE, $n = 12$

	Treatment efficiency (%)		AAR (g m^{-2} day)		FOR (m day^{-1})	
	Fe	Mn	Fe	Mn	Fe	Mn
Lagoons	15.4 (10.2)	6.5 (3.3)	11.5 (7.7)	0.2 (0.1)	0.53 (0.26)	0.16 (0.09)
Wetland 1	92.2 (1.2)	38.1 (8.5)	14.3 (2.3)	0.3 (0)	1.52 (0.07)	0.28 (0.12)
Wetlands 2 and 3	70 (7.4)	64.5 (15.7)	0.4 (0.1)	0.5 (0.1)	0.43 (0.07)	0.47 (0.09)
Whole system	98.4 (0.3)	76.8 (9.6)	5.6 (0.4)	0.2 (0.1)	0.77 (0.03)	0.35 (0.05)

the assumptions of the test, data transformations were carried out.

3. Results

3.1. *Overall performance*

The flow rate of influent water at Whittle was maintained at 1200 L/min. The influent pH had a mean of 6.82 (±0.097) with an effluent pH mean 7.79 (±0.065), giving an increase of almost 1 pH unit across the system (Fig. 3). Conductivity was not highly variable, remaining at around 4600 μs throughout the system (Fig. 3).

There was a significant difference in Fe concentrations between sampling points in the Whittle system (ANOVA $p < 0.001$). Fe concentrations were significantly higher in points 1–3 than all other points indicating that most of the iron removal occurred by point 4 (Fig. 4). Points 7 and 8 also had lower concentrations than points 1–5. Fe concentrations at the exit point (sample point 8) are consistently ≤1 mg/L. Iron removal in percentage terms was 98% for the whole system (Table 1). Wetland 1 showed the highest percentage removal (92%) of the system components followed by wetlands 2 and 3 and the lagoons. Area-adjusted removal rates show that wetland 1 had the greatest removal rate followed by the lagoons and finally wetlands 2 and 3.

Manganese concentrations were also significantly different between sampling points in Whittle. The differences followed the same pattern as that for Fe, with higher concentrations in points 1–4 than points 6–8 (Fig. 4). Manganese concentration in the effluent was consistently lower than ≤0.4 mg/L. Manganese removal rates as a percentage were around 78% for the whole system, with the greatest removal found in wetlands 2 and 3, and the least in the lagoons (Table 1). Area-adjusted removal rates showed that wetlands 2 and 3 had the greatest value of 0.5 g m^{-2} day followed by wetland 1 and the lagoons, a pattern also seen for first-order removal.

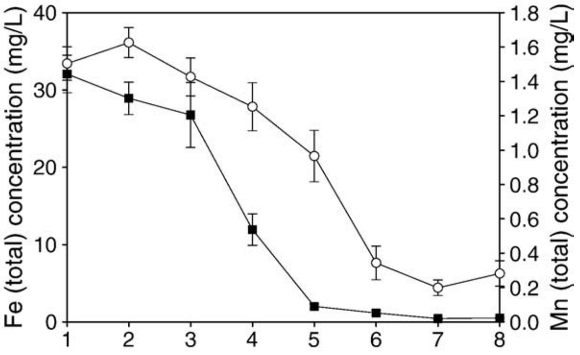

Fig. 4 – Iron –■– and manganese –○– concentrations of surface waters from Whittle treatment system. Error bars are mean ± SE ($n = 12$).

3.2. *Diurnal variations in removal of Fe and Mn*

Removal of iron in the Whittle system was consistent throughout the 24 h period with most of the iron being removed by the end of the first wetland (Fig. 5A), which is consistent with the longer term sampling (Fig. 4). Concentrations of iron were

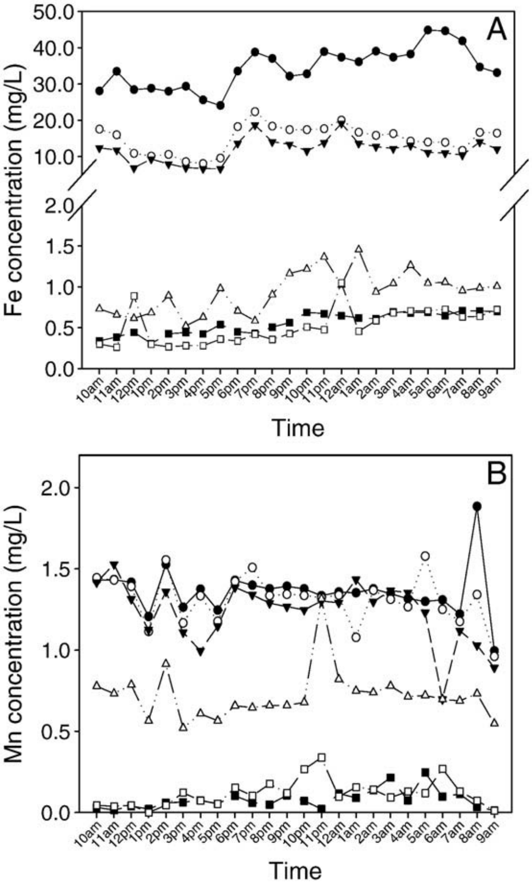

Fig. 5 – Fe (A) and Mn (B) concentrations in water samples from points a –●–, b ····○····, c —▼—, d ··–▽··–, e –■–, f ··–□··– at Whittle treatment system during 24 h sampling on the 7/06/2004. Sunrise was 4:30 am and sunset 9:45 pm.

consistently <1 mg/L by the end of the third wetland. The first three sampling points show very similar patterns in Fe concentration throughout the 24 h period with only some discrepancies in the early hours of the morning (5–8am). However points d, e and f did not show similar patterns to the other sampling points.

Removal of manganese was also consistent throughout the 24 h period at Whittle (Fig. 5B). However, in comparison to iron, manganese removal was negligible within the oxidation lagoons and the first wetland. Significant removal of manganese did not occur until point d in the second wetland.

pH measurements showed that there was a consistent increase in pH across the treatment system throughout the 24 h period (Fig. 6A), which is likely due to degassing of excess dissolved CO_2 (cf Younger et al. 2002). Between points a and b (within the oxidation lagoons) there was some decrease in pH at times during the 24 h period. However during the hours of 11 pm and 3 am there was an increase in pH between points a and b.

Dissolved oxygen concentrations also increased though the course of the treatment system, up to point e reaching levels of around 80% (Fig. 6B). However, point f showed a very different pattern through the 24 h period. Oxygen levels continued to increase between points e and f in the hours 9 am to 7 pm. However during the rest of the 24 h period oxygen levels fell between points e and f.

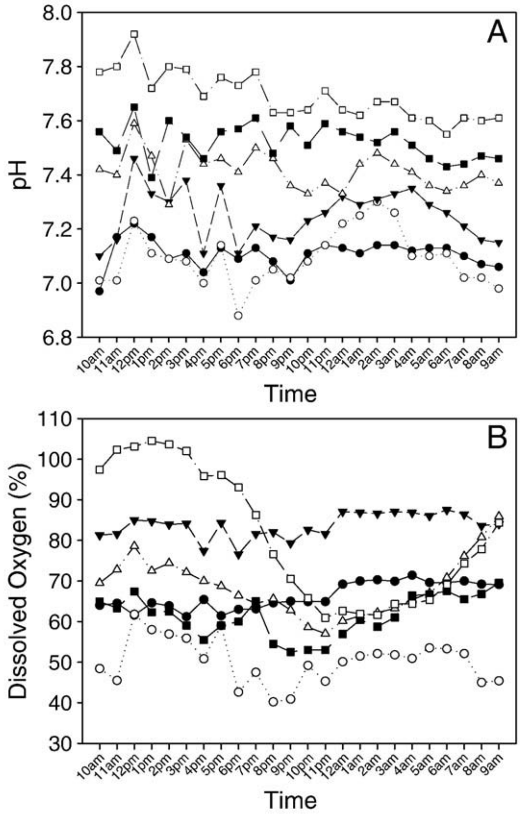

Fig. 6 – Field measurements of pH (A) and dissolved oxygen (B) from points a –•–, b ····○····, c —▼—, d··–▽··–, e –▪–, f ··–□··– at Whittle treatment system during 24 h period sampling on the 7/06/2004. Sunrise was 4:30 am and sunset 9:45 pm.

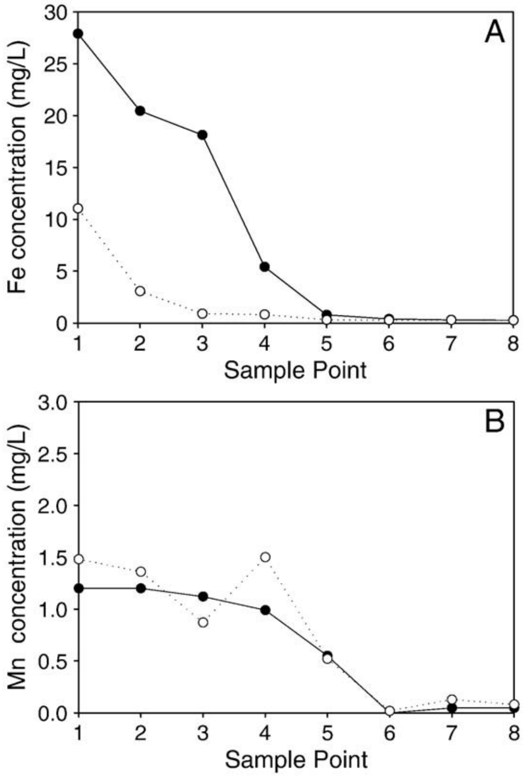

Fig. 7 – Effect of filtration on (A) iron concentrations and (B) manganese concentrations in water samples from Whittle treatment system. Unfiltered –•–, filtered ····○····.

3.3. *Effect of filtration upon iron and manganese concentrations*

Differences in iron concentrations were found between filtered and unfiltered samples (Fig. 7). Unfiltered samples contained higher concentrations of Fe up to sample point 5. This suggests that some of the iron was present as coarse particulates. Filtered iron was at concentrations of <1 mg/L by sample point 3.

Manganese concentrations were low and showed only small differences between filtered and unfiltered samples (Fig. 7). In a small number of cases it appears that manganese concentrations are higher in filtered samples than unfiltered samples. Equivalent iron concentrations did not show this pattern which indicates that this is not a contamination problem. Fig. 4 shows that Mn concentration between samples can be very high therefore we propose that it is more likely due to high variability in manganese concentrations within the samples, but further work is required to test this hypothesis.

4. Discussion

Aerobic wetlands are considered to be a 'proven' technology for the treatment of net-alkaline ferruginous waters (e.g. Younger et al., 2002). The data from the present study support this view point as the aerobic treatment system at Whittle Colliery consistently removed iron down to effluent levels of <1 mg/L and in most cases below 0.5 mg/L. In terms of overall performance the Whittle system showed similar percentage removal rates for iron to that reported for other wetland treatment systems (e.g. Tarutis et al. 1999; Wiseman and Edwards 2004). The removal rates have also improved since the first tests undertaken at Whittle in early 2002 (Nuttall, 2003) when 97% Fe removal was reported, demonstrating a continuing function of the wetland past the first 'honeymoon' period when sorption to organic matter is at a maximum. The area-adjusted removal rates however, were found to be significantly lower than those reported by Hedin et al. (1994) where rates in wetland systems treating alkaline drainage were on average 23 g m^{-2} day, as opposed to 5.6 g m^{-2} day for Whittle. This is most likely due to the large area of the wetland system which was deliberately over-engineered, giving a lower removal figure for the whole system. In addition, the wetlands used in Hedin et al. (1994) were supplemented with limestone and/or spent mushroom compost which will affect the chemical reactions and removal processes taking place. No such additions were used in the Whittle system. The use of a passive treatment system following pumping of a discharge is unusual, as pumped waters are usually associated with chemical treatment. However, the combination of the two at Whittle is extremely successful and provides a low-cost alternative to chemical treatment. The isolated location of the system together with the land available for the construction of a large system made this particularly appropriate, but may not be suitable where land is limited.

Closer examination of the figures shows that the majority of the iron is removed in the early part of the system and removal rates for the first wetland are at 14 g m^{-2} day, closer to, but still lower than those rates quoted by Hedin et al. (1994). First-order removal rates for Whittle show much greater removal of iron than the majority of schemes studied by Tarutis et al. (1999). First-order removal rates are thought to be a much better way of assessing wetland performance for sewage treatment wetlands (Kadlec and Knight, 1996) but the application to mine waters, has been questioned due to the lack of knowledge surrounding the chemical reactions that occur (Younger et al 2002).

Aerobic wetlands are often sized according to the suggested removal rate of 20 g m^2 day (Kalin, 2001; PIRAMID Consortium, 2003). It is clear that the Whittle system does not reach this figure overall, albeit it approaches this value within wetland 1. This supports the suggestion that most of the metal removal within passive systems may occur in a small area of the system (Johnson and Hallberg, 2002). The removal of iron at Whittle appeared to take place in the proximal parts of the system, i.e. in the oxidation lagoons and the first wetland cell. Concentrations of iron decreased from an average influent level of 32 mg/L to an average level of 2 mg/L at the end of the first wetland. The final two wetlands act to 'polish' the remaining iron which is critical in meeting targets for effluents which can be 0.5 mg/L. This supports previous suggestions that the size of the wetland system required to remove a unit of iron contamination (1 g day^{-1}) gets larger as inflow concentrations get lower (Hedin et al. 1994). Previous work in aerobic wetland cells also showed that rapid removal of iron occurred within the first 30 m of a 100 m cell (Hall and Puhlmann, 2005). The results from the filtration experiment show that in the oxidation lagoons and the first wetland the majority of the iron was present as coarse particulates that are removed by filtration. The better removal rate seen in the first wetland in comparison to the oxidation lagoons suggests that the presence of plants and substrate increases the effective removal even when dominated by chemical precipitation of iron hydroxides. This is possibly due to baffling of flow, the presence of adsorption surfaces and the release of oxygen from roots as previously suggested (Francour and Semroud, 1992; Batty, 2003). In the final two wetlands the filtered and unfiltered iron concentrations were very similar suggesting that the iron is in the dissolved and possibly colloidal fraction. The processes of iron removal may therefore be different in the early and later parts of the wetland. In the oxidation lagoons and first wetland it appears that oxidative processes and the formation of iron hydroxides was the dominant process of removal which has previously been suggested to be the dominant removal process in wetlands treating coal mine drainage (Wiseman and Edwards 2004). In the latter parts of the wetland however, it is unclear what the dominant process was. It is interesting to note that despite the oxidation of iron within the wetland there was no large drop in pH. Ferric iron hydrolysis produces hydrogen ions which can cause a reduction in pH, however it is evident there is buffering capacity within the environment related to the carbonate chemistry of the waters that prevented this drop in pH.

The 24 h sampling programme shows that patterns of iron concentration between the main input and the input to the first wetland were very similar. This suggests that the removal process was at a consistent rate, possibly indicating a purely abiotic process. However, within the wetlands iron concentrations fluctuate and there is no discernable link between input and output patterns. This is partly explained by the time taken for the waters to flow through the wetland. However it also suggests that biotic processes may be involved in the removal of iron, which would explain the variations seen during the 24 h period. There were no distinct patterns in iron concentrations during the 24 h period within the three wetlands although there is some indication that iron concentrations were slightly higher between the hours of 10 pm and 4 am (hours of darkness). Previous research has shown that strong diel changes in iron concentrations within treatment systems were related to oxygen and pH (Goulet and Pick, 2001). This was attributed to the effects of plant photosynthesis. The rise in iron concentrations during hours of darkness in the present study could have its origins in the same process. However, pH values did not show any correlation with iron removal and in most cases dissolved oxygen did not show any significant difference during the 24 h period. The final wetland did show a dramatic decrease in oxygen levels during hours of darkness which indicates that photosynthesis may be the controlling factor on oxygen levels in this wetland only. As this pattern did not show up in the first two wetlands, it indicates that there was another controlling factor which affected oxygen concentrations, possibly the oxidation of iron. Plant activity therefore, may become an important factor in the distal regions of wetland treatment systems, where iron is at lower concentrations which supports previous research demonstrating the critical role of macrophytes at iron concentrations of <2 mg/L (Batty and Younger, 2002). Bacterial communities are also able to mediate the oxidation of iron, although biological oxidation of iron proceeds more slowly than abiotic oxidation at higher pH values (Kirby et al., 1999). However the role of these organisms in this system is unclear. It is possible that iron removal is facilitated by bacteria throughout the system but further investigations need to be undertaken.

Previous work by the author (Batty et al., 2005) demonstrated that macroinvertebrate communities within the Whittle system improved with distance from the input. This was true for the number of taxa, Biological Monitoring Working Party score and Average Score per Taxon. The improvement in community structure may be due to the removal of iron precipitates in the early parts of the wetland which can smother habitat niches in wetlands and also directly smother the invertebrates themselves. This process is much more likely to affect macroinvertebrate communities than direct toxicity of metals. The presence of invertebrates within wetlands is of significance as not only do they contribute to biodiversity (an ancillary benefit of wetlands) but they are also involved in the decomposition of plant litter which provides a food source (carbon) for bacterial communities possibly involved in bacterially-mediated removal of metals.

The passive removal of manganese from mine waters is generally considered to be a much more difficult task than removal of iron. Previous estimations have suggested that in order to remove manganese a wetland of between 20 and 40 times the size of that required for removal of iron under similar conditions would be required (Hedin et al 1994; Hedin and Nairn, 1993). This is based upon the observation that Mn removal is between 20 and 40 times slower than that for Fe in a range of treatment systems (Hedin et al 1994) and is largely due to the conditions required for the oxidation of manganese. The abiotic oxidation of manganese requires a pH above 8, and even then is very slow at $\text{pH} < 9.0$ (Stumm and Morgan, 1996), which is clearly not achievable within wetland treatment systems. However, the results from Whittle show that manganese was removed by this treatment system from an average influent concentration of 1.5 mg/L to an average effluent concentration of 0.3 mg/L. The percentage removal rates are high with an average of 76.8% significantly greater than the first recorded removal of 34% in 2002, despite similar flow rates and influent concentrations (Nuttall, 2003). The pH within the treatment system where manganese removal occurred was between 7 and 7.5. Where manganese oxidation occurs below pH 8 it is generally considered to be microbially-mediated (Lind and Hem, 1993). Manganese concentrations decreased through the wetland, although a significant drop in manganese concentration did not occur until wetland 2. This corresponds to the point where iron concentrations have dropped to below 1 mg/L. The presence of iron has previously been shown to have an inhibitory effect upon the removal of manganese and the formation of manganese oxides (e.g. Gouzinis et al., 1998), and furthermore soluble Fe (II) can also reductively dissolve manganese oxides (Villinski et al., 2001). It is not evident how the manganese is being removed in the Whittle system. Filtration of water samples did not remove a significant amount of Mn suggesting that it was not present in the form of coarse particulates which is consistent with previous investigations (Gammons et al., 2000). Mn oxides typically occur as dark coloured precipitates (e.g. Katsoyiannis and Zouboulis, 2004), but these were not evident upon the filter papers following filtration supporting this interpretation. However, it is possible that Mn oxides were present as colloids which would not be removed by filtration as used in this investigation. Previous work has suggested that removal of Mn may be related to rates of oxygenic photosynthesis giving higher removal of Mn during summer months (Hallberg and Johnson, 2005). However no significant variations in manganese removal were evident during the hours of darkness at Whittle in any of the treatment components. This suggests that photosynthetic organisms were not responsible for the removal of manganese, and further research into this area needs to be undertaken.

5. Conclusion

The removal of iron from mine waters can be successfully achieved by the installation of passive treatment systems that include oxidation ponds and wetlands. Results suggest that most of the iron removal will occur in the early parts of the system, however in order to achieve very low effluent concentrations it is necessary to include wetlands of a sufficient size to remove the last few mg/L of iron. Oxidation of iron appears to be the dominant removal process in the early parts of the system, but once iron concentrations are sufficiently low, biotic removal processes may become more important. Further work is required to determine the relative importance of different biota in the removal of iron in wetlands. Manganese removal can also be achieved using wetland systems, however it is clear that iron needs to be removed before manganese removal is able to take place.

This research has shown the importance of location within treatment systems in terms of metal removal. Further detailed monitoring and investigations into the relative importance of biotic and abiotic removal processes occurring spatially and temporally within wetlands will allow engineering and management decisions to maximise and ensure the continuing removal efficiency of the systems.

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