

An appraisal of iron and manganese removal at Shilbottle and Whittle wetland sites in Northumberland, UK.

Batty Lesley*, Hooley Daniel

School of Civil Engineering and Geosciences, University of Newcastle, Newcastle upon Tyne, NE1 7RU, UK

* Current Affiliation: School of Geography, Earth and Environmental Science

University of Birmingham

Edgbaston, B15 2TT

E-mail: L.C.Batty@bham.ac.uk

Keywords: mine water, iron, manganese, removal rates, wetlands

ABSTRACT

The removal of iron and manganese at two passive treatment systems for the treatment of mine water in the North East of England was compared over a period of three weeks. In addition, 24 hour sampling was undertaken to determine the effect of diurnal variations in metal removal. Removal of iron was found to occur at both sites though effluent concentrations were much lower at Whittle. Oxidation of iron was the dominant removal process in the early parts of the systems (in the oxidation ponds and early parts of the wetlands) whereas biotic removal processes appeared to become more important in the distal parts of the system where iron concentrations were much lower. Manganese was also removed at Whittle but this was not achieved until iron was at concentrations below 5 mg.L⁻¹. Iron concentrations did not fall low enough in the Shilbottle system to allow manganese removal. The process of manganese removal was not evident but bacterially-mediated oxidation is likely to be involved. Further elucidation of the relative importance of abiotic and biotic removal processes within treatment systems is important in the design and management of constructed systems.

INTRODUCTION

The UK, in common with many others parts of the world, has a long history of mining activity which have caused pollution of soils, sediments and waters. The contamination of water sources has a significant effect upon the UK population due to the extensive use of water resources for potable water, including boreholes, dams and rivers. Mine waters have been shown to have a significant effect upon riverine ecosystems, causing changes in communities and a reduction in diversity (e.g. Armitage & Blackburn 1985; Malmqvist & Hoffsten 1999). Although mining and its operators have not been covered by environmental legislation in the past, the EC Water Framework Directive (2000/60/EC) will require member states to address mine water issues. Increased protection of habitats and drinking water supplies and achieving "good status" for waters means that mine water will have to meet acceptable standards for discharge agreed between the regulator and principal polluter. However many of the sites likely to pollute are 'orphan' sites leaving governments with the responsibility of remediation. Mine waters have typically been treated with the addition of oxidative chemicals, liming agents and flocculants (e.g. Younger *et al* 2002) 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 30 full scale systems.

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.). The formulae used to calculate the size of wetland required to treat the mine water in question is based upon first order kinetics (e.g. Tarutis *et al* 1999). However, 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 form of plants may be more important where iron concentrations are lower (Batty & Younger 2002). This suggests that in passive treatment systems, particularly those that incorporate different cells (e.g. oxidation ponds, wetlands) removal processes will vary through the system which has important implications for the design and management of such schemes.

The objective of this investigation was to assess the removal rates of iron and manganese in two different passive treatment systems, one receiving net acidic metalliferous waters and the other net alkaline ferruginous waters.

MATERIALS AND METHODS

Site Descriptions

Shilbottle

Shilbottle Colliery is an abandoned mine situated in Northumberland, UK. Large pyritic spoil heaps remain on the site and previously water percolating through the heaps fed into the Tyelaw Burn, a tributary of the River Coquet (a Site of Special Scientific Interest (SSSI)). The waters were net acidic (pH ~ 3.0) with elevated concentrations of Fe, Mn, Al, Zn and sulphate. Early remediation involved the construction of a series of three aerobic wetlands, planted with *Phragmites australis*, in 1996 (Batty and Younger, 2004) However it was found that most of the polluting water was bypassing these wetlands. Therefore a joint venture between Northumberland County Council and the University of Newcastle was undertaken to construct a permeable reactive barrier (PRB) and oxidation lagoons to treat the water from the spoil heap, before being allowed to flow into one of the existing constructed wetlands. This treatment system was completed in 2001.

Whittle

Whittle Colliery is 3 miles south of Shilbottle Colliery 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. 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. The wetlands were planted with *Typha latifolia* (wetlands 1 & 3), and *Phragmites australis* (wetland 2). The full system was completed in 2001.

Effect of filtration upon iron and manganese concentrations in water samples

Water samples were taken at each sample point in both treatment systems (figures 1 & 2). One half of the water was filtered through a standard filter paper (Whatman no.1) and the other half left unfiltered. Both samples were acidified with 10M nitric acid.

Appraisal of the removal efficiency of Shilbottle and Whittle treatment systems

Water samples were collected every 2-3 days for a total period of 23 days (May-July 2004) at each site. Samples were collected at approximately the same time each day in order to minimise diurnal variations. A water sample was collected at each sample point in the two treatment systems (figures 1 & 2) and acidified (10M nitric acid) for analysis of Fe and Mn. 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).

Diurnal variations in iron and manganese removal at Whittle treatment system

Preliminary investigations showed that variability at the Shilbottle site was too high to be able to identify short term changes in performance, therefore this study was only carried out at Whittle. For logistical reasons it was not possible to carry out sampling for 24 hours at all 8 sample points for Whittle. Therefore representative sites were selected and are illustrated on figure 2. Measurements and samples were taken as outlined above. All iron and manganese concentrations were determined using Atomic Absorption Spectrometry (Unicam 929 flame spectrometer). Adequate sample and analytical blanks were used to check for contamination.

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

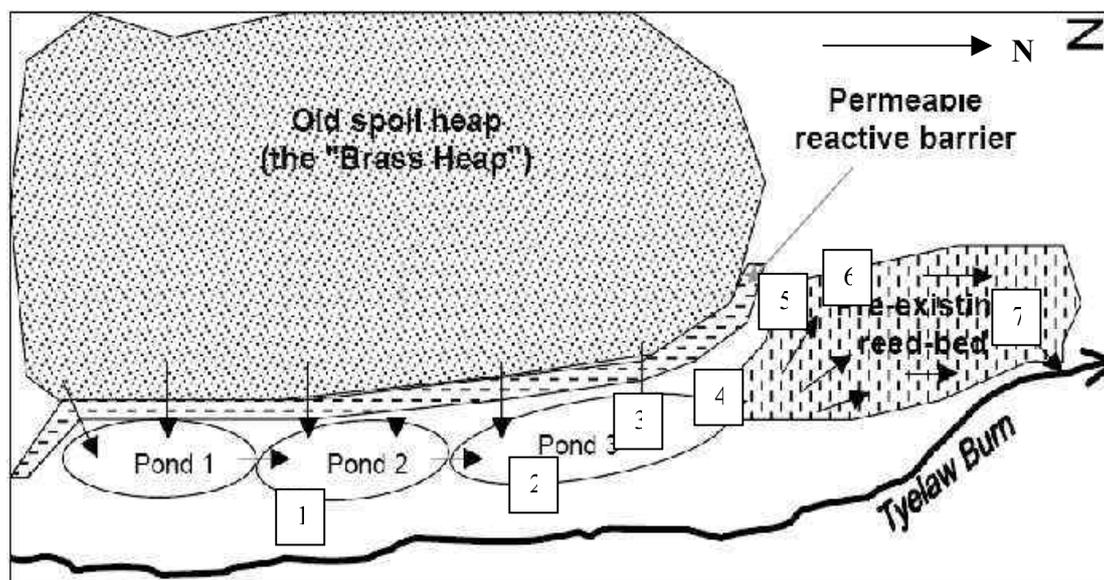


Figure 1. Plan of Shilbottle treatment system. Numbers indicate sampling points used in this study (adapted from Younger *et al.* 2002).

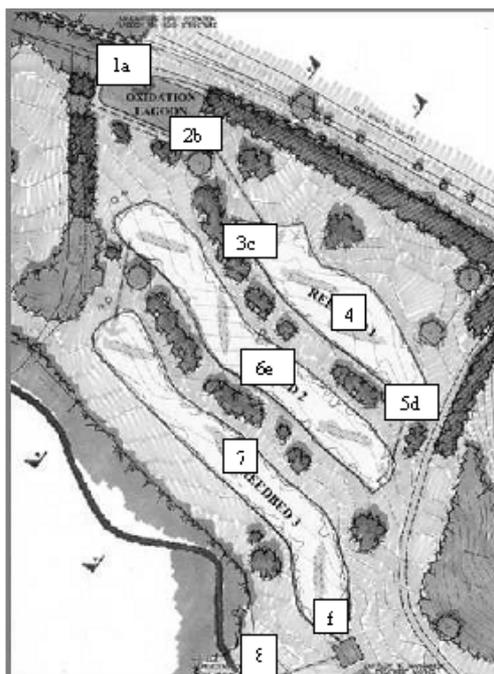


Figure 2. Plan of Whittle treatment system. Numbers indicated sampling points for the 3 week sampling period and letters indicate sampling points for the 24hour sampling period (adapted from www.coal.gov.uk)

RESULTS

Effect of filtration upon iron and manganese concentrations

Differences in iron concentrations were found between filtered and unfiltered samples from Shilbottle and Whittle (figure 3). Unfiltered samples contained higher concentrations of Fe up to sample point 5 for Whittle, and up to 8 for Shilbottle. This suggests that some of the iron was present as coarse particulates. At Whittle, the filtered iron was at concentrations of $<1 \text{ mg.L}^{-1}$ by sample point 3.

Manganese concentrations were much lower in Whittle samples and showed only small difference between filtered and unfiltered samples (figure 3). Filtration also had a small effect upon manganese concentration in Shilbottle samples. 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. It is more likely due to high variability in manganese concentrations within the samples, but further work is required to test this hypothesis.

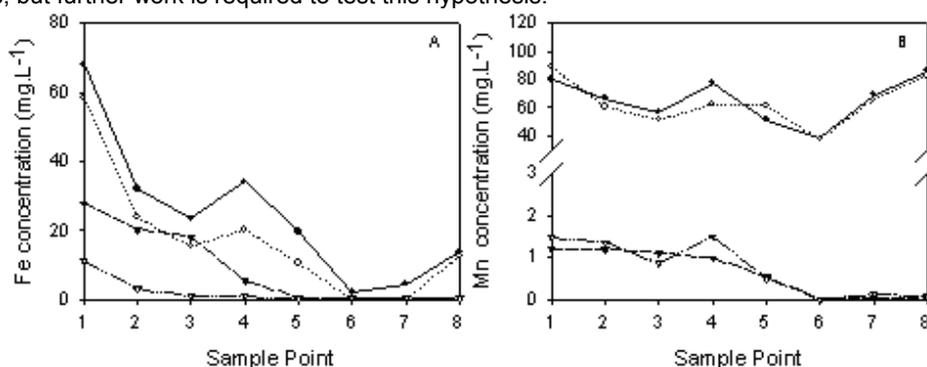


Figure 3. Effect of filtration on (A) iron concentrations and (B) manganese concentrations in water samples from Shilbottle and Whittle treatment systems. Shilbottle unfiltered —●—, Shilbottle filtered○....., Whittle unfiltered ---▼---, Whittle filtered ---▽---

Appraisal of the removal efficiency of Shilbottle and Whittle treatment systems

The flow rate of water through the Shilbottle wetland whilst the monitoring was undertaken was 10 – 36 litres/min. The typical pH recorded at the start of the system was 3.49 (± 0.24) and at the exit point was recorded at 3.21 (± 0.04).

There was a significant difference in Fe concentration between the sampling points at Shilbottle (ANOVA $p < 0.001$). Concentrations were higher at points 1-4 than 5-7 showing significant removal of iron by point 5 (figure 4A). Point 5 also had significantly lower concentrations than point 7 indicating that there was an increase in Fe

concentrations toward the distal regions of the wetland. There was no significant difference in Mn concentrations at Shilbottle (ANOVA $p > 0.05$).

The flow rate of influent water at Whittle was maintained at 1200 litres/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.

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 (figure 4B). Points 7 and 8 also had lower concentrations than points 1-5. Fe concentrations at the exit point (sample point 8) are consistently $\leq 1 \text{ mg.L}^{-1}$.

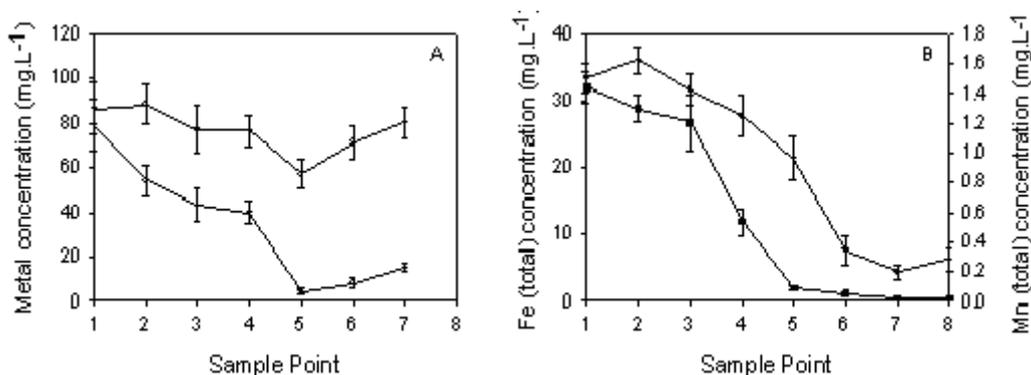


Figure 4. Iron —■— and manganese —○— concentrations of surface waters from (A) Shilbottle and (B) Whittle treatment systems. Error bars are mean \pm SE (n=12)

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. Manganese concentration in the effluent was consistently lower than $\leq 0.4 \text{ mg.L}^{-1}$.

Diurnal variations in iron and manganese removal

The 24hour monitoring was only performed for Whittle. The results from Shilbottle had been variable and indicated no specific removal pattern.

Removal of iron in the Whittle system was consistent throughout the 24 hour period with most of the iron being removed by the end of the first wetland (figure 5A), which is consistent with the longer term sampling (figure 4B). Concentrations of iron were consistently $< 1 \text{ mg.L}^{-1}$ by the end of the third wetland. The first three sampling points show very similar patterns in Fe concentration throughout the 24 hour 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 hour period at Whittle (figure 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.

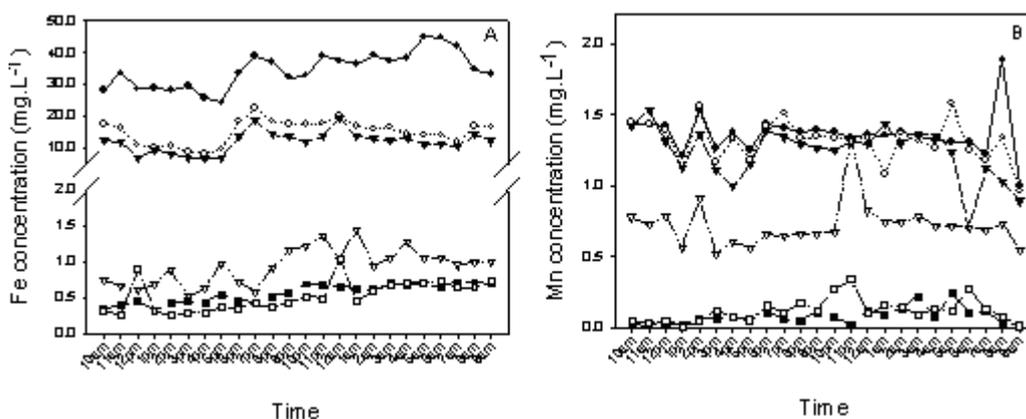


Figure 5. Fe (A) and Mn (B) concentrations in water samples from points a—●—, b—○—, c—▼—, d—▽—, e—■—, f—□— at Whittle treatment system.

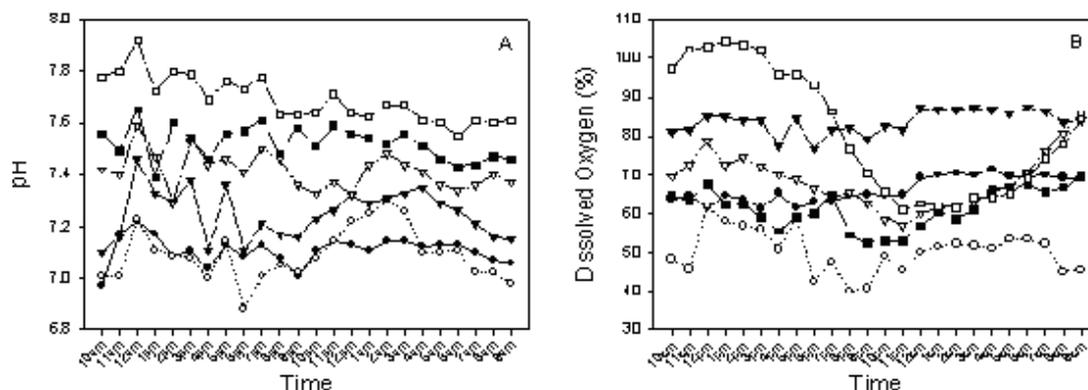


Figure 6. Field measurements of pH (A) and dissolved oxygen (B) from points a—●—, b—○—, c—▼—, d—▽—, e—■—, f—□— at Whittle treatment system.

pH measurements showed that there was a consistent increase in pH across the treatment system throughout the 24 hour period (figure 6A). Between points a and b (within the oxidation lagoons) there was some decrease in pH at times during the 24 hour period. However during the hours of 11pm 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% (Figure 6B). However, point f showed a very different pattern through the 24 hours period. Oxygen levels continued to increase between points e and f in the hours 9am to 7pm. However during the rest of the 24 hour period oxygen levels fell between points e and f.

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 $<1\text{mg.L}^{-1}$ and in most cases below 0.5mg.L^{-1} . The removal of iron at Whittle appeared to take place in the first 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 32mg.L^{-1} to an average level of 2mg.L^{-1} at the end of the first wetland. The final two wetlands act to 'polish' the remaining iron. 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 & 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. 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. In the latter parts of the wetland however, it is unclear what the dominant process was. The 24 hour sampling programme shows that patterns of iron concentration between the 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 hour period. There were no distinct patterns in iron concentrations during the 24 hour period within the three wetlands although there is some indication that iron concentrations were slightly higher between the hours of 10pm and 4 am (hours of darkness). Previous research has shown that strong diel changes in iron concentrations with treatment systems were related to oxygen and pH (Goulet & Pick 2001). This was attributed to the effects of plant photosynthesis. The possible rise in iron concentrations during hours of darkness suggests that this may also be a contributing factor in the present study. 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 hour period. The final wetland did show a dramatic decrease in oxygen levels during hours of darkness which suggests that photosynthesis may be the controlling factor on oxygen levels in this wetland. 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. This suggests that plant activity 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 $<2\text{mg.L}^{-1}$ (Batty & 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.

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 40 times the size of that required for removal of iron under similar conditions would be required (Hedin & Nairn 1993). This is largely due to the conditions required to for the oxidation of manganese. The abiotic oxidation of

manganese requires a pH above 8, and even then is very slow at pH < 9.0 (Stumm & 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⁻¹ to an average effluent concentration of 0.3 mg.L⁻¹. 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 & 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⁻¹. 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). 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 & 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 nanoparticles which would not be removed by filtration. Further research into this area needs to be undertaken. Aerobic wetlands are not normally used to treat net-acidic mine waters however the presence of the wetland at Shilbottle allowed the opportunity to compare treatment with Whittle. Iron was also removed very efficiently by the system at Shilbottle with most of the iron removal occurring within the oxidation ponds and in the early part of the wetland. The results suggest that iron concentration increased across the rest of the wetland but this was more likely due to the location of sampling points 5 and 6 which were close to the edge of the wetland (health and safety issues prevented samples being taken from more central regions). These areas have much lower flow and therefore may have given erroneous results. However, the wetland still showed net removal of iron across the system. Effluent concentrations were not as low as Whittle, but this was largely due to the higher concentrations of iron entering the system, and the much smaller size of the wetland. The results from Whittle demonstrated the need for a large wetland area to achieve removal of the final few mgs/L of iron, which was not present at Shilbottle. Filtration of water samples for Shilbottle showed that iron was present as coarse particulates across the whole system. Only at the effluent were filtered and unfiltered iron concentrations similar. This supports the results from Whittle which showed that oxidation of iron was the main removal process in the early parts of the treatment system where iron concentrations were higher. At Shilbottle iron concentrations do not fall to a level where other biotic processes may become more important. It is interesting to note that despite the oxidation of iron within the wetland there was no large drop in pH (this is also true at Whittle). The oxidation of iron produces hydrogen ions which can cause a reduction in pH, however it is evident that both within Shilbottle and Whittle systems there is buffering capacity within the environment that prevented this drop in pH. Manganese was not removed by the Shilbottle system. It is evident from the previous discussion that iron needs to be removed before manganese removal can occur, and iron concentrations did not fall to a level in the Shilbottle system where this can occur. It is important to note that manganese concentrations were lower at points 5 and 6 which support the above statement that due to the sample locations these points were giving erroneous results.

CONCLUSIONS

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 mgs/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.

ACKNOWLEDGEMENTS

The authors would like to thank Mr P. Orme (University of Newcastle) for his assistance with field and laboratory work and Professor P. Younger (University of Newcastle) for input into the project design. The Coal Authority provided access to Whittle. This work formed part of a research project undertaken for completion of an MSc in Environmental Engineering and was funded by the Engineering and Physical Science Research Council.

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