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NEWCASTLE

DESIGN, CONSTRUCTION AND PERFORMANCE OF PASSIVE SYSTEMS FOR THE TREATMENT OF MINE AND SPOIL HEAP DRAINAGE.

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A thesis submitted to the University of Newcastle upon Tyne in fulfilment of the requirements for the Degree of Doctor of Philosophy

October 2000

Abstract

Passive treatment systems for mine water pollution remediation require no chemical or energy inputs, and should only incur limited maintenance costs if properly constructed. This thesis investigates two such passive treatment systems that have been installed at sites in County Durham, UK. The overall objectives of the investigation were to improve understanding of the operation of passive systems in order to produce more accurate design guidelines, and to develop a new passive treatment option to complement existing technologies. To put the research into context the causes, impacts and extent of mine water pollution in the UK and overseas are outlined. In addition a detailed and up-to-date review of passive treatment research and development is provided, which highlights areas in which further research is required.

At Quaking Houses, County Durham, a full-scale compost wetland has been constructed to treat an acidic and metal-rich discharge from the spoil heap of an abandoned coal mine. Over the 27 month study period the discharge had pH ≥ 4, and mean iron, manganese and aluminium concentrations of 5.4 mg/L, 3.6 mg/L and 6.2 mg/L respectively. The unique design and construction of the 440 m^2 wetland is described. An examination of the performance of the wetland illustrates that it has yielded significant improvements in water quality since its construction. Mean reductions in acidity, iron and aluminium concentrations are all around 50%. Bacterial sulphate reduction may be an important contaminant removal mechanism, but its proportional significance is unclear. Comparison of the system at Quaking Houses with other wetlands reveals that the mean reduction in acidity in terms of mass removal per unit area (5.01 $g/m^2/d$) is comparatively low. However, it is shown that comparing wetland performance on this basis may be misleading where influent contaminant concentrations are relatively low, because contaminant removal is demonstrably influent concentration-dependent. A first-order removal assessment method of performance may be more appropriate, and on this basis the Quaking Houses wetland performs well when compared to systems in the USA. An algorithm for predicting wetland effluent iron concentrations is derived using a linear multiple regression technique.

Time series analysis strongly suggests that some effluent water quality variables (and therefore wetland performance measures) are significantly affected by seasonal climate changes. In particular aluminium and acidity removal rates rise with increasing air temperature. This implies that to meet the same effluent water quality targets passive treatment systems in cold climate locations may need to be larger than equivalent systems in warmer climates.

At Kimblesworth, also in County Durham, a pilot-scale passive treatment system has been operated for 4 months. The Kimblesworth discharge is a net-alkaline pumped mine water containing up to 2 mg/L iron and up to 1 mg/L manganese. The novel system at this site was designed to rapidly remove iron by oxidation and accretion of iron to high surface area media. The monitoring programme has revealed the system to be very efficient. Iron concentrations are consistently reduced to < 0.5 mg/L, and removal rates are an order of magnitude greater than in wetland systems. Furthermore, lithium tracer tests reveal that the residence time of water in the reactors is just 5 - 10 minutes. The results of this research suggest that the technology could be applied at full-scale.

The compost wetland at Quaking Houses and the new reactor at Kimblesworth may well complement each other. The Quaking Houses system generates alkalinity and removes metal contaminants, but effluent water still contains marginally elevated concentrations of iron (mean 2.4 mg/L). The Kimblesworth system is shown to be very effective at rapidly removing low concentrations of iron, and thus could conceivably be used as a polishing unit following a compost wetland such as that at Quaking Houses. Alternatively high surface area media reactors such as those at Kimblesworth could be used to treat discharges in topographically difficult locations, where the installation of a wetland is not feasible.

ACKNOWLEDGEMENTS

Many people have given generous advice and assistance during the course of this work. Most of all I would like to thank Paul Younger for being both a great friend and also a constant source of inspiration, enthusiasm, encouragement and technical brilliance throughout (Cheers marra!).

Also at Newcastle University, Pat Johnston, Fiona Reid and John Hamilton have tirelessly assisted in the lab. Also thanks to Almudena, Carlos, Paula, Ivan and María (all Oviedo School of Mines, Spain) for all their help in the lab and field. A big thanks to the ever evolving 'Coffee Room Crew' of the last 6 years for sharing advice, coffee and beer(s).

Almudena Ordóñez (Oviedo School of Mines) and Walter Cooper (Scottish Land Hire Ltd.) were invaluable aides during the construction of the wetland at Quakies. Thanks too to members of the Quaking Houses Environmental Trust for all their assistance with the construction of the wetland. In particular I would like to thank Chas Brooks, Alan McCrea and the late Terry Jeffrey. Finally I would like to acknowledge the financial assistance of the Northumbrian Water Kick Start Fund, and the many other organisations that helped fund the wetland at Quaking Houses

The work at Kimblesworth was funded by the Engineering and Physical Sciences Research Council (Grant number: GR/L55421). The financial support of IMC Consulting Engineers Ltd and the Coal Authority is also gratefully acknowledged. Adrian England and David Laine (IMC Engineering Consultants Ltd.) have both been generous with their vast experience, and were fundamental in setting up the pilot-scale reactors at Kimblesworth. Stephen Banwart and Sean Burke (Sheffield University) have collaborated with us on the Kimblesworth work, and I am grateful for their assistance and advice. I am also grateful to Keith Parker (Coal Authority) for his assistance with this work.

Finally, I am grateful to Dr Elaine Martin (University of Newcastle) for her patient advice on the use of statistical techniques.

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CHAPTER 1

INTRODUCTION

1.1 Overview

Mine water pollution is currently one of the most widespread forms of aquatic degradation in the United Kingdom (UK) (NRA, 1994). The metalliferous and sometimes acidic nature of waters emanating from abandoned mines and spoil heaps often results in the impacts of such discharges being severe (e.g. Jarvis and Younger, 1997; NRA, 1996). Two broad options are currently available for treating such discharges:

1) *Active treatment* entails the use of chemicals and energy to remove pollutants from mine waters. Alkali dosing, aeration and settlement is the most common active treatment method (Hedin *et al.*, 1994a).
2) *Passive treatment* is the remediation of mine water pollution using natural processes, and without the use of chemicals or energy (Hedin *et al.*, 1994a). Such systems may require infrequent but regular attention (William Pulles, Pulles Howard & de Lange, South Africa, personal communication, 2000), but overall maintenance costs should be far less than for an active treatment system. Most commonly passive treatment systems take the form of constructed wetlands. The area of land required for passive treatment systems is typically greater than that needed for an equivalent active treatment system.

The long-term nature of mine water discharges (Younger, 1997a) has made passive treatment technology an increasingly attractive proposition to industry and regulators alike, largely because of its low maintenance costs (Younger, 2000a). The uptake of passive treatment has increased rapidly in recent years, particularly in the UK, as the reliability of such systems has improved alongside an increased understanding of the operation of such systems (Younger, 2000a).

However, questions remain regarding the optimum design of constructed wetland treatment systems. Our understanding of the interaction of physical, chemical and (micro)biological processes within wetlands is particularly limited. As a consequence current design formulae are necessarily empirical. The derivation of process-based design guidelines currently appears to be some years away. The empirical design formulae most commonly used at present are those of Hedin *et al.* (1994a), but recent research (e.g. Tarutis *et al.*, 1999) suggests that there is scope for deriving more accurate empirical formulae for the design of passive treatment systems. This thesis addresses this design issue for the particular case of anaerobic (or compost) wetlands.

The installation of constructed wetlands is not always feasible, mainly because of the large land area required. As a consequence a second broad objective of this thesis was to investigate the potential utility of a novel compact treatment method for alkaline mine waters, which would otherwise be remediated using constructed wetland technology.

1.2 Study objectives

This thesis investigates the use of two types of passive treatment for remediation of mine water pollution. At Quaking Houses, County Durham, a full-scale compost wetland treatment system has been constructed. The work at Quaking Houses focused on the following key research objectives:

1) Evaluate the design and engineering aspects of the constructed wetland at Quaking Houses, with a view to assisting the design and construction of future projects.
2) Through regular monitoring of the wetland water quality, produce a detailed and relatively long-term set of data characterising the performance of the system.
3) Investigate which pollutant removal mechanisms are most important in this wetland.
4) Assess the performance of the wetland using a number of measures in order to ascertain which is the most appropriate measure in terms of comparing wetland systems.
5) Attempt to generate an algorithm for predicting effluent water quality at the Quaking Houses constructed wetland.

At Kimblesworth, also in County Durham, a pilot-scale reactor has been designed and built to investigate the potential utility of a novel passive treatment technique for iron-rich, alkaline mine waters. The approach entails encouraging the rapid oxidation and accretion of ochre to high surface area media. The research objectives for this second element of the work were as follows:

1) Through regular monitoring of the influent and effluent water quality from two reactors over the course of 4 months ascertain whether this novel passive treatment technology might be applicable at full-scale.
2) Measure residence times of water within the reactors and calculate metal loading rates in order to establish the most efficient operating conditions for such systems.
3) Compare performance of this novel treatment system with other passive technologies.

This thesis is an engineering evaluation of passive systems for mine water treatment, and is *not* intended to be a rigorous biogeochemical study in itself. The earliest work on the potential of wetlands to ameliorate mine drainage pollution focused on natural, or 'volunteer', wetlands (see Wieder and Lang (1984), for example), and these investigations were therefore biogeochemical in their nature. However, following this early recognition of the potential of volunteer wetlands for mine water treatment, there has been a significant shift towards the construction of wetlands, and other passive systems, for mine water remediation. Consequently there is currently a need to both continue to study the biogeochemistry of passive treatment technologies, but also to investigate the most appropriate engineering methods to create effective passive systems. The engineering aspects of constructed wetland application are particularly important given the site specificity of many mine water drainage problems. When discussing the engineering elements of passive treatment research, specific topics that require addressing are:

1) Selection of an effective physical and chemical monitoring regime for the discharge.
2) Design / selection of the most appropriate passive treatment technology for the discharge to be treated (which will, in part, depend on (3), below).
3) Effective and appropriate treatment site selection.

4) Selection of construction materials and methods, including wetland substrates (which will in all likelihood require some biogeochemical studies in the field / laboratory).
5) Design and implementation of effective treatment system monitoring programmes.

All of these aspects of wetland engineering are discussed in the following work to varying degrees. The difficulties encountered when addressing these issues are highlighted throughout the thesis, and are drawn together to form a working plan for the design and construction of passive treatment systems. Although the biogeochemistry of the two treatment systems studied is not investigated in its own right to any great extent, the close links between passive treatment system engineering and biogeochemistry are emphasised

1.3 Thesis structure

In Section 1.4, below, the study site locations are briefly introduced. Further details of the histories of the two sites, and features of importance at Quaking Houses and Kimblesworth, are contained in Chapters 4 and 6 respectively.

The remaining paragraphs of this Chapter outline the physical, chemical and biological conditions associated with the generation of mine waters, and the variety of chemical characteristics displayed by such discharges upon emergence into surface watercourses. Although the exposition is brief relative to the extensive research in this area, the discussion is sufficient to illustrate the typically long-term nature of mine water pollution, and to demonstrate the nature of pollutants associated with such discharges.

An overview of the extent and impacts of mine water pollution in the UK and overseas is included to illustrate the importance of addressing mine water pollution issues, and thus the need for designing effective systems for their remediation. This is followed by a discussion of the legislative framework relating to mine water pollution within the UK. It will be argued that the unusual legal position in the UK (and overseas to a lesser degree) has indirectly been one of the main driving forces behind the increasing adoption of passive systems as the preferred option for treatment of mine water discharges.

The remaining 6 chapters of this thesis are ordered as follows:

Chapter 2:	Field and laboratory analytical methods used at both sites are detailed.
Chapter 3:	A comprehensive literature review, which focuses on the current research status of passive treatment technology.
Chapter 4:	Construction of the Quaking Houses Community Wetland.
Chapter 5:	Treatment performance results and discussion for Quaking Houses.
Chapter 6:	Results and discussion of the Kimblesworth pilot-scale reactor investigation (although both the Kimblesworth and Quaking Houses investigations relate to passive treatment, the foci of the two studies are quite distinct. The results, discussion and conclusions of the Kimblesworth work are therefore all contained within this one chapter).
Chapter 7:	Conclusions and recommendations. Key points from both investigations are highlighted. The close links between the two elements of the research in terms of passive treatment technology as a whole are outlined.

In addition several appendices contain the original raw physical and chemical data on which this work is based (Appendices 2-7). Appendix 1 contains a bibliography of all of the publications by this author, highlighting those articles which have arisen from this work, and Appendix 8 details the statistical techniques used in the thesis.

1.4 Study sites

Quaking Houses Community Wetland is approximately 1 km to the west (by local footpaths) of the village of Quaking Houses and 200 m above sea level (NGR NZ 178509). Figure 1.1 illustrates the exact location of the site and its surrounding features. Easiest access to the site is from the A693 road to the north. Immediately to the west of the wetland is the 35 hectare spoil heap which is the source of contamination of the Stanley Burn. The Stanley Burn is a third order tributary of the River Wear,

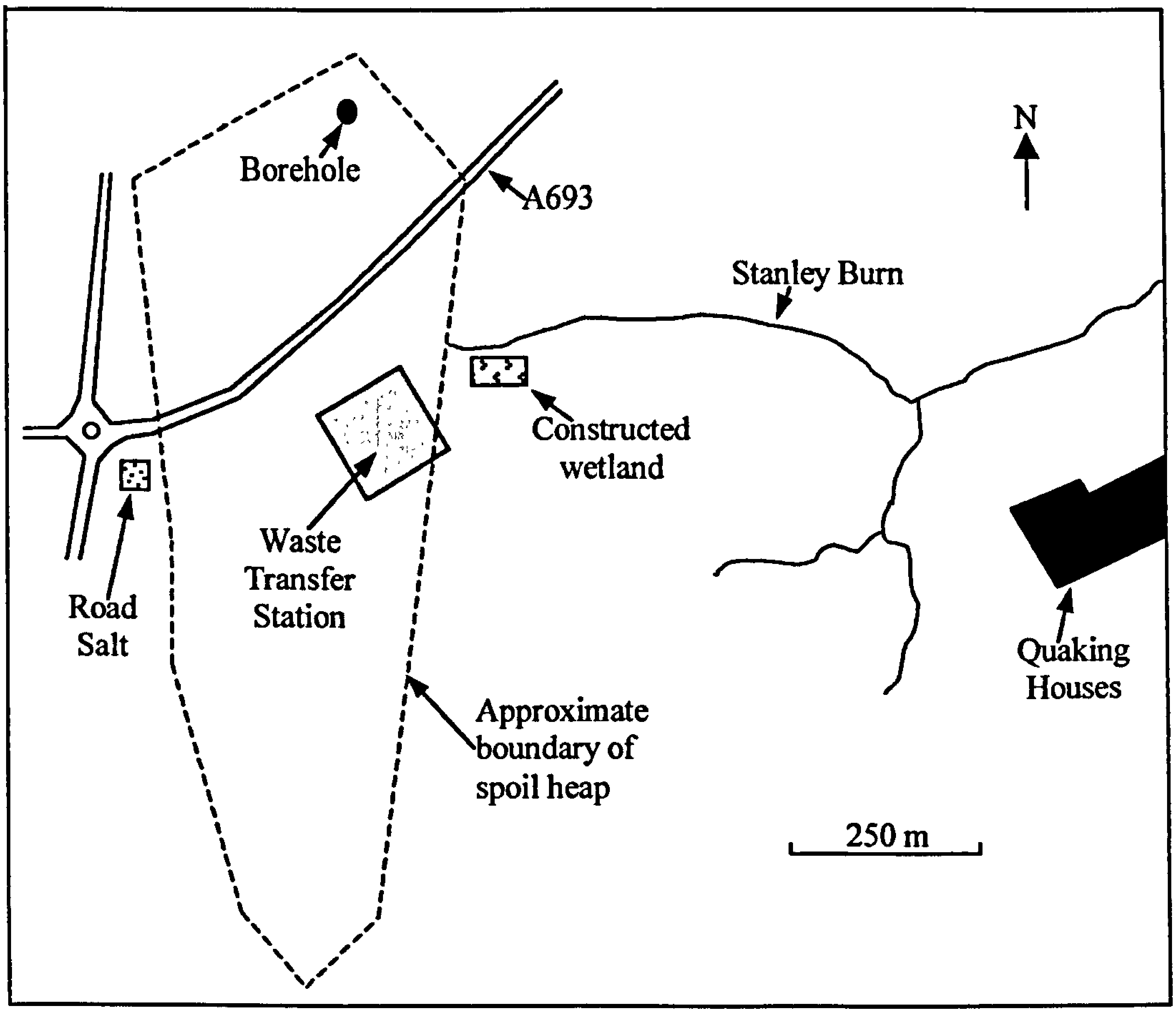

Figure 1.1 **Site of the Quaking Houses Community Wetland, and surrounding features** (see Figure 1.2 for location within the UK).

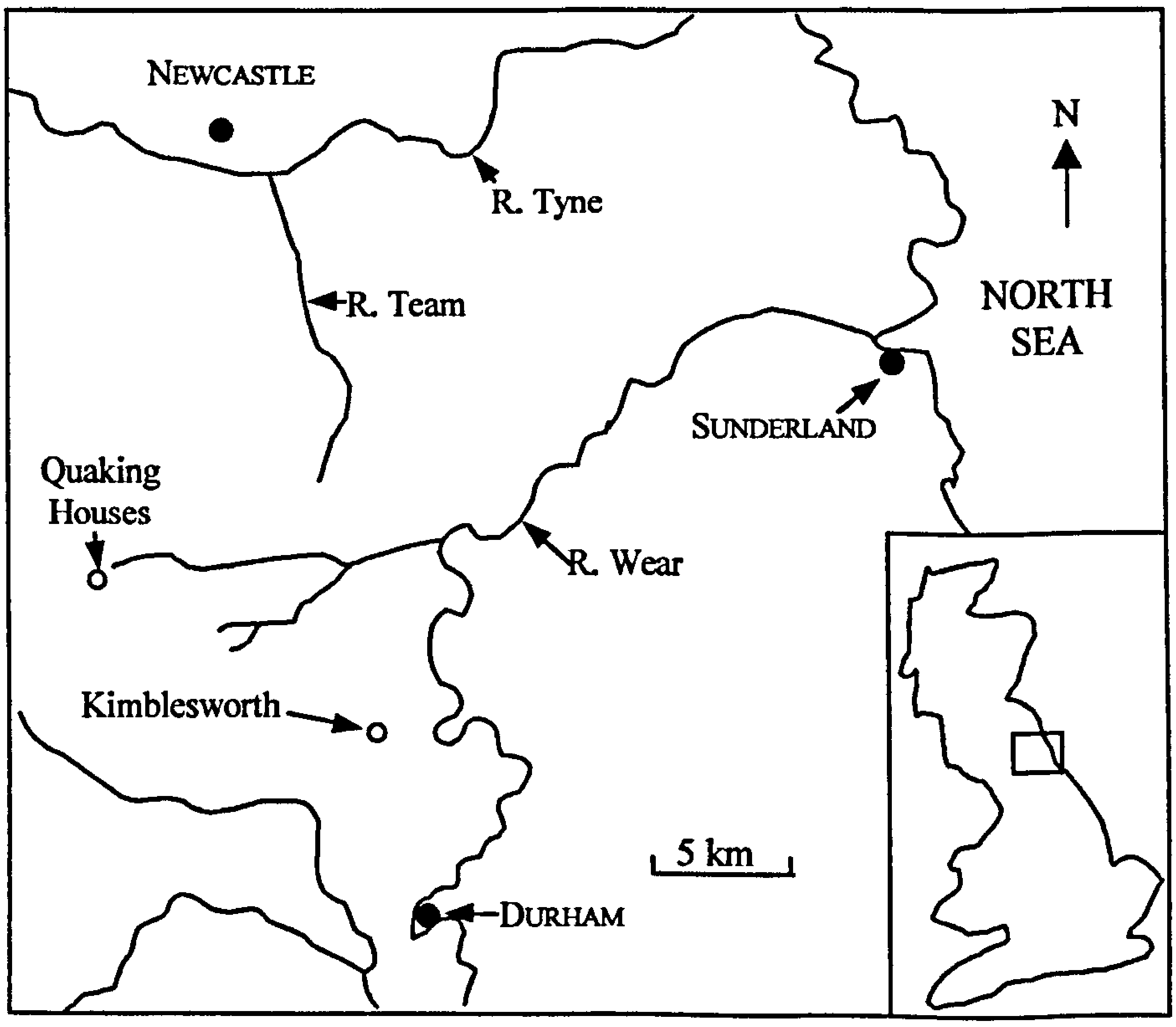

Figure 1.2 **Locations of the Kimblesworth and Quaking Houses mine waters.**

which it joins approximately 10 km downstream of the mine water discharge (shown on Figure 1.2). Built on the spoil heap is a waste transfer station (actually on the site of the old colliery headgear) (see Figure 1.1). Within the grounds of the station is the automatic weather station that has collected the meteorological data used in this work. An exposed stockpile of road de-icing salt is situated to the west of the waste transfer station. To the north of the A693 road the spoil heap is poorly vegetated, and a single borehole has enabled measurement of depths to the water table and collection of spoil water samples (vandals irreparably damaged two further boreholes during the course of this investigation).

Quaking Houses was selected as a research site for this work for a number of reasons. Specifically, though not necessarily in order of importance, these reasons were as follows:

1) The discharge had already been identified as a net-acidic spoil heap discharge by Younger and Bradley (1994), and therefore some historical data were available for the site.
2) A pilot-scale constructed wetland had already demonstrated the potential effectiveness of this type of passive treatment (see Younger *et al.*, 1997).
3) The land owner (the Coal Authority - formerly British Coal properties) made an area of land available for construction of the wetland at an early stage in the design process.
4) The site is easily accessible from Newcastle University.
5) The local community was actively involved in environmental restoration of the stream corridor prior to the instigation of the project, and subsequently played a key role in the construction of the wetland.

Even before the design and construction of the Quaking Houses community wetland began, however, it was evident that a number of engineering problems would be encountered during the project:

1) The area of land available for construction was the absolute minimum required, and therefore the wetland would have to be constructed to maximise the area of treatment.

2) Initial indications were that the site was very wet, and therefore operating machinery in anything but dry weather conditions may prove to be difficult.
3) The site was not secured, and therefore there was the potential for vandalism.

These, and other problems with the site that became evident during the site survey, are discussed in more detail in chapter 4.

Kimblesworth mine water is a pumped discharge on the site of a former colliery, approximately 5 km north of the city of Durham (NGR NZ 261469) (Figure 1.2). It is one of nine mine water pumping stations in the region (see Figure 5.1). The characteristics of these waters are described in Chapter 6. The pumping station is in a secured site in a small industrial yard, just off the A167 Chester-le-Street to Durham road. Water pumped to the surface discharges into an enclosed collection chamber, and is then routed through a culvert for approximately 0.5 km. The stream, an unnamed first order tributary of the River Wear, enters an open channel immediately to the east of the A167, and joins the River Wear some 2 km further downstream.

As with the site at Quaking Houses, Kimblesworth is easily accessible from Newcastle University. Permission to use the site was granted by the Coal Authority. The site is secure, and therefore there was no risk of vandalism. The discharge itself was ideally suited for the purposes of the research work i.e. a strongly net-alkaline discharge, with an elevated iron concentration. In addition, because the water was under pressure, it was a simple matter to raise the inlet level to the reactors to a suitable height above ground level. Anticipated engineering problems at the site related to the fact that the reactors were only constructed at pilot-scale. Greatest concerns related to the potential blocking of the small diameter pipes used to carry water to the reactors.

Further site details, and photographic illustrations of both sites, can be found in Chapters 4 (Quaking Houses) and 6 (Kimblesworth).

1.5 Mine water generation

The root cause of mine water pollution is the oxidative dissolution of sulphur-bearing minerals. Most commonly mine water pollution is associated with pyrite (FeS_2; "fool's gold"), as it is the most abundant of this group of minerals in coal-bearing strata (Banks *et al.*, 1997). The chemical evolution of mine waters by pyrite oxidation has been the focus of research for nearly a century (Appelo and Postma, 1993). Consequently the generalised stoichiometric reactions are well known, and now appear in numerous textbooks in various forms. For instance Stumm and Morgan (1996) present the formulae as follows:

$$FeS_2(s) + 7/2\,O_2 + H_2O \rightarrow Fe^{2+} + 2\,SO_4^{2-} + 2\,H^+ \qquad (1.1)$$

$$Fe^{2+} + 1/4\,O_2 + H^+ \rightarrow Fe^{3+} + 1/2\,H_2O \qquad (1.2)$$

$$Fe^{3+} + 3\,H_2O \rightarrow Fe(OH)_3(s) + 3H^+ \qquad (1.3)$$

$$FeS_2(s) + 14\,Fe^{3+} + 8\,H_2O \rightarrow 15\,Fe^{2+} + 2\,SO_4^{2-} + 16\,H^+ \qquad (1.4)$$

Oxidation of sulphide to sulphate releases ferrous iron and acidity (equation 1.1). This ferrous iron may itself be oxidised to ferric iron (equation 1.2). Hydrolysis of ferric iron forms ferric hydroxide and further acidity (equation 1.3). Additional ferrous iron may be produced via the oxidation of pyrite by ferric iron (equation 1.4), thus perpetuating the cycle as Fe^{2+} is fed back into equation 1.2. The overall process may be condensed into a composite equation, such as that given in the early work of Barnes and Romberger (1968):

$$4\,FeS_2 + 15\,O_2 + 14\,H_2O \rightarrow 4\,Fe(OH)_2 + 16\,H^+ + 8\,SO_4^{2-} \qquad (1.5)$$

Illustrating the stoichiometry in this way clearly reveals the strong acid-generating nature of pyrite oxidation and dissolution, with each mole of pyrite producing 4 moles of proton acidity.

It is important to emphasise that the description given above is a simplification of the complete process. For instance, it has been suggested that as many as 15 reactions are involved in the oxidative dissolution process (Nordstrom and Southam, 1997), and the kinetics of the entire process are highly complex (Appelo and Postma, 1993). A detailed discussion would be inappropriate, since the objective here is simply to illustrate the source of mine water pollutants and their nature. Lowson (1982) and Nordstrom (1982), among others, provide comprehensive reviews of pyrite oxidation.

One aspect of the kinetics that is relevant is the rate-determining step. At the low pH conditions typical in mines and spoil heaps (approximately pH 2 – 4) the rate limiting step is widely accepted as the oxidation of ferrous iron (Equation 1.2 above) (Singer and Stumm, 1970). The rate is such that in a purely inorganic environment, at low pH, the overall vigour of pyrite oxidation should theoretically be low (Appelo and Postma, 1993). However, Singer and Stumm (1970) demonstrated that the oxidation of ferrous iron is microbially catalysed, with the result that the rate of reaction may be increased by as much as a factor of 10^6. One of the key agents of microbial catalysis is the acidophilic bacterium *Thiobacillus ferrooxidans*, although other iron oxidising- and sulphur oxidising- bacteria have subsequently been implicated as having important roles. These include *Leptospirillum ferrooxidans* and *Sulfolobus brierleyii* (Silver, 1989).

Boon and Heijnen (1998) have recently demonstrated, through an elegant series of laboratory experiments, one way in which these bacteria catalyse the reaction. The rate of chemical oxidation of pyrite by ferric iron (Equation 1.4) is controlled by the ratio of ferric to ferrous iron ($[Fe^{3+}]/[Fe^{2+}]$) (which is reflected in the redox potential). Increasing rates of chemical oxidation are associated with an increase in the ferric to ferrous iron ratio. As the reaction proceeds this ratio, and hence the reaction rate, decrease. However, Boon and Heijnen (1998) determined that *Leptospirrilum ferroxidans* rapidly consumes the ferrous iron (Equation 1.2) produced in chemical oxidation (Equation 1.4), and hence the chemical oxidation rate can remain high. The authors were able to illustrate this point by first establishing that the chemical and bacterial oxidation reactions are in fact two separate sub-processes, and it was therefore possible to discriminate between the two rates.

The relevance of bacterial catalysis from a treatment perspective is that control of these microbial populations within a mine or spoil heap may significantly limit the potential for pyrite oxidation, and hence the severity of mine water discharges at the surface.

Thus, the use of biocides might be a very effective 'at source' remediation measure provided they could be successfully and sustainably applied (Singer and Stumm, 1970).

It is important to realise that other sulphide minerals are also susceptible to the oxidative dissolution processes described above. In fact Nordstrom and Alpers (1999) provide 20 examples of different sulphide mineral oxidation studies. Examples include chalcopyrite ($CuFeS_2$), arsenopyrite (FeAsS), and greenockite (CdS). Using sphalerite (ZnS) as an example, the monosulphides oxidise in the following manner (Banwart, 1998):

$$ZnS(s) + 2\,O_2(aq) \rightarrow Zn^{2+} + SO_4^{2-} \qquad (1.6)$$

Sulphides of the general form MS do not produce proton acidity upon oxidation (although they may do so upon hydrolysis), and as a result discharges at the surface generated from monosulphide weathering alone rarely have pH values as low as those associated with pyrite weathering (Banks *et al.*, 1997; Nuttall and Younger, 1999).

In hydrogeological settings where buffering capacity is low, and pyrite oxidation is vigorous, very low pH conditions may develop. Under these circumstances it is possible for aluminosilicates (such as kaolinite) to be attacked by these aggressive waters, resulting in the release of aluminium ions, as equation 1.7 illustrates (Younger, 1998a).

$$Al_2Si_2O_5(OH)_4 + 6\,H^+ \rightarrow 2\,Al^{3+} + 2\,H_4SiO_4 + H_2O \qquad (1.7)$$

Equally, where a significant buffering capacity is available natural attenuation may occur. Weathering of aluminosilicates consumes protons (equation 1.7 above), and is therefore an example of natural attenuation (Banwart, 1998). The most common sources of alkalinity are the carbonate minerals (calcite and dolomite) (Banks *et al.*, 1997). Calcite dissolves as follows (Banwart, 1998):

$$CaCO_3(s) + H^+ \leftrightarrow Ca^{2+} + HCO_3^- \qquad (1.8)$$

The consequent increase in pH results in most metals becoming less mobile either due to precipitation or sorption processes (Banwart, 1998). As a result metal ions may be precipitated before they reach the surface environment, and mine water discharges may have lower metallic ion concentrations. However, the predominant mineral phases in many coal measures are ankerite [$(Ca, Mg)Fe(CO_3)_2$] and siderite ($FeCO_3$) (Banks *et al.*, 1997). Oxidative dissolution of siderite in acid waters, illustrated below, initially consumes protons but subsequently releases them, with the result that there is no net change in acidity (Younger, 1995a).

$$FeCO_3 + 2\,H^+ \rightarrow Fe^{2+} + CO_2 + H_2O \qquad (1.9)$$

$$Fe^{2+} + 1/4\,O_2 + H^+ \rightarrow Fe^{3+} + 1/2\,H_2O \qquad (1.10)$$

$$Fe^{3+} + 3\,H_2O \rightarrow Fe(OH)_3 + 3\,H^+ \qquad (1.11)$$

Younger and Bradley (1994) and Younger (1995a) suggested that alkalinity may be generated in saturated workings by microbial sulphate reduction, under anoxic conditions. Hedin *et al.* (1994a) show the relevant reaction, where CH_2O represents organic matter:

$$2\,CH_2O + SO_4^{2-} \rightarrow H_2S + 2\,HCO_3^- \qquad (1.12)$$

Sulphate reduction is a key process in some passive treatment systems, and is discussed at length in Section 3.2.5.

It will have become clear in the preceding discussion that the essential requirements for the generation of mine waters are:

i. A sulphide-bearing mineral (usually pyrite)
ii. Oxygen
iii. Microbial catalysis
iv. Water

All four requirements are often satisfied in spoil heaps and deep mines alike. Infiltrating precipitation usually supplies spoil heaps with water, sometimes indirectly via a perched aquifer (Younger, 1998b). Pumping operations at active mines carry water to the surface. Contact with oxidised residues within the mine may be sufficiently widespread to render these pumped waters contaminated in some instances, but they are rarely as polluted as those waters emanating from abandoned mines (see Table 1.1). In abandoned mines a cessation of pumping allows local and regional water tables to rise up through the mined voids, a phenomenon referred to as groundwater rebound (Younger, 1995b). Eventually rising waters reach their pre-mining level, and invariably discharge into surface watercourses. Thus, there is substantial dissolution of oxidised residues. Timing of first emergence of rising waters at the surface, and prediction of the emergent water quality, is a complex field of research. Since these are currently very pressing issues in the UK, much of the relevant research has been undertaken here, and the reader is referred to the works of Adams and Younger (1997), Sherwood and Younger (1997), Smith and Colls (1996), Younger (1995b), Younger *et al.* (1995), Younger and Adams (1999) and Younger (2000b). Calculating time of first emergence, and predicting emergent water quality, are both important areas during the planning and implementation of remediation works.

1.6 Mine water quality, extent and impacts

1.6.1 Mine water quality

Despite the fact that mine waters all have their formative roots in the oxidative dissolution of sulphur-bearing minerals experience illustrates that their chemical quality at the surface is highly variable (eg. Banks *et al.*, 1997). Table 1.1 presents results of chemical analyses of a range of mine waters from around the UK. When addressing 'mine water' issues we are not just referring to discharges arising from abandoned coal mines and their associated spoil heaps, but also to discharges from operations mining for other minerals, and active mines of all types. Typically, when referring to 'mine water drainage', discharges from both coal and metal mines are implied. The most significant geochemical reaction, the oxidative dissolution of pyrite, is usually common to discharges arising from both coal and metal mines. In the case of metal mines the oxidative dissolution of other metal sulphides (such as sphalerite, ZnS) may also be important (see section 1.5), and consequently water discharges at the surface may

Name	Baads Bing East, Scotland	Aspatria, Cumbria	Kimblesworth, Co. Durham	Ynysarwed, south Wales	Bullhouse, Yorkshire	Wheal Jane, Cornwall	Frazer's Grove, Co. Durham
Type	Coal spoil heap	Coal spoil heap	Pumped coal mine water	Abandoned coal mine	Abandoned coal mine	Abandoned metal mine	Active[a] fluorspar mine
National Grid Ref	NT 005 612	NY 157 435	NZ 261 469	SS 793 998	SE 215 028	SW 778 411	NY 895 441
pH	2.8	2.9	7.03	4.2	6.1	3.8	6.8
Alkalinity (mg/L as $CaCO_3$)	0.0	0.0	722	0.0	67	0.0	56
Acidity (mg/L as $CaCO_3$)[b]	1517	495	5.3	339	107	581	-
Conductivity (μS/cm)	3350	3100	1753	-	1083	3400	890
Total Fe (mg/L)	550	198	2.27	180	45	142	3.5
Al (mg/L)	80	9.2	0.00	<0.5	0.5	50	-
Mn (mg/L)	6.3	14.5	0.66	6.1	13	23	-
Zn (mg/L)	0.4	0.9	0.02	0.06	<0.05	75	13
SO_4 (mg/L)	3077	2034	312	1554	838	1742	535
Cl (mg/L)	16	171	174	32	50	-	17
Source	Younger, 2000c	Jarvis and Younger, 2000a	This author's analysis	Banks *et al.*, 1997	Firth *et al.*, 1995	Environment Agency, 1998	Younger, 1998c

[a] Active at time of this sampling, but since abandoned

[b] Calculated by author using equation: $\text{Acidity}_{\text{calc.}} = 50[2Fe^{2+}/56+3Fe^{3+}/56+3Al/27+2Mn/55+1000(10^{-pH})]$, with total Fe assumed to be Fe^{2+} (after Hedin *et al.*, 1994a)

Table 1.1 **Water chemistry of a range of mine waters across the UK.** The table illustrates the varied water quality of mine waters.

contain elevated concentrations of these metals (see Wheal Jane and Frazer's Grove in Table 1.1). In this work 'mine drainage' is invariably used in association with discharges from abandoned coal mines and spoil heaps. Where reference is made to a discharge from a metal mine it is specifically noted.

Table 1.1 includes two spoil heaps, two abandoned coal mines, a pumped mine water from an abandoned coal mine, an abandoned metal (tin) mine, and an active fluorspar mine (the latter closed at the end of 1998, but was working when this sample was collected; Younger, 1998c). Wherever pyrite is abundant mine water discharges invariably contain elevated concentrations of iron. Increases in pH in surface streams (often due to dilution) and rapid oxidation of the iron results in affected streambeds having a characteristic orange coating of iron hydroxide and associated compounds. These deposits are collectively referred to as ochre. Figure 1.3 shows the typical appearance of an impacted receiving watercourse.

Many of the variations in water chemistry illustrated in Table 1.1 are due to the influences mentioned above, such as the type of sulphur-mineral, and the presence or otherwise of carbonaceous strata. Clearly the overall pyrite content is a significant control on mine water quality, although this typically proves difficult to quantify. The proximity of a worked seam to a marine-influenced bed has been used as a proxy measure of pyrite concentration (Younger, 2000b), since pyrite is commonly associated with strata of marine genesis (Williams and Keith, 1963). Caruccio (1975) suggests that both the morphology and grain size of pyrite are influential in determining the acid generating potential of these exposed strata. In addition to the character and extent of the pyrite itself, Younger (2000b, 2000c) argues that the proximity of the shallowest mined seam to the ultimate mine water discharge point will exert an important overall control on mine water quality. Indeed, Younger (2000b) goes on to explain that a first approximation of mine water quality may be made by knowing the proximity of the shallowest worked seam to (a) the ultimate discharge point and (b) the nearest marine bed.

In addition however, for waters emerging from deep mines following groundwater rebound, Younger (1997a, 1998a, 2000b) has demonstrated that the nature of a given mine water changes as it ‘matures’. Specifically a mine water appears to have an initial

Figure 1.3 **Deposition of ochre at Stony Heap, County Durham.** The red discolouration, known as ochre, is due to oxidation and precipitation of elevated concentrations of iron in receiving watercourses, and is characteristic of streams affected by mine water pollution (photograph by the author).

period during which very high contaminant concentrations are evident, which Younger (1997a) terms 'vestigial acidity' (metals contribute to acidity in this context as "mineral acidity"). There then follows a steady decline in acidity concentration over the initial 1 – 20 years after mine water emergence, as this 'first flush' proceeds (Younger, 1997a, 2000b). Eventually pollutant levels reach an asymptotic level, at which they may be sustained for centuries in some instances (typically at an iron concentration of 10 – 30 mg/L; Younger, 1997a). The contaminant load contributing to this "juvenile acidity" appears to be governed by successive oxidative dissolution events caused by near-surface water table fluctuations (Younger, 1997a, 1998a, 2000b). As an example, the iron concentration of the Wheal Jane discharge given in Table 1.1 is 142 mg/L. This is in fact the median value for the period June 1995 – January 1998 (Environment Agency, 1998). However, when mine water initially burst from the Nangiles adit in January 1992 iron concentrations were in excess of 1500 mg/L (Younger, 1997a) – over an order of magnitude higher.

Appreciating these temporal changes in mine water quality is clearly important during the planning phases of treatment schemes, since a treatment system designed on the basis of initial water quality alone may prove to be grossly oversized for effective long term remediation within a matter of years. In addition, Younger (1997a; 2000b) demonstrates that in certain hydrogeological settings mine waters that are net acidic (ie. acidity > alkalinity) at first emergence may subsequently become net alkaline. This is critical, since the decision as to what type of wetland system to construct (if this is indeed the appropriate form of treatment) is currently largely founded on whether a discharge is net acidic or net alkaline (see Hedin *et al.*, 1994a).

Such long term temporal changes in mine water quality are only likely to be witnessed in the case of discharges emerging from deep mines following groundwater rebound. There are no reported chemical parallels in the cases of spoil heap discharges.

1.6.2 Extent of mine water pollution

In the UK coalfield areas mine water pollution is second only to sewage as a major source of river pollution (NRA, 1994; Younger, 2000c). Jarvis and Younger (2000b) suggest that approximately 700 km of the UK's streams and rivers are currently affected. In the USA, Hedin (1997) estimates that 3000 km of streams are impacted by mine water discharges in Appalachia alone. Kempe (1983) and Norton (1996), among many others, provide examples of mine water pollution across other parts of Europe, and also Africa and Asia.

1.6.3 Mine water pollution impacts

(a) Ecological impacts

Johnson (1995) points out that it is now recognised that there exists a far more diverse acidophilic microflora in low pH (pH 2-4) mine waters than was initially thought. In addition to the widely cited *Thiobacillus ferrooxidans*, other iron-oxidising acidophiles also exist (*Leptospirillum ferrooxidans* for example). As well as other bacteria (prokaryotes), Johnson (1995) also details examples of some eukaryotes (and in particular protozoa) which survive in these acidic environments. It is possible that such organisms may be used in the bioremediation of acid discharges, and the interested reader is referred to Johnson (1995) for further details.

Despite the recognition of an increasingly diverse acidophilic, the effects of mine water pollution on the ecology of receiving watercourses are predominantly deleterious. As acidity concentrations increase, the diversity of algal populations in receiving watercourses invariably decreases. Deposition of iron precipitates in receiving watercourses is invariably instrumental in floral depletion (Kelly, 1988). Of algae that can adapt to low pH conditions, *Euglena mutabilis* is one of the most widely cited, although the diatom *Pinnularia acoricola* has subsequently been found to be common in acidic streams in England (Kelly, 1988).

Numerous investigations have focused on the effects of elevated iron concentrations and acidity concentrations on benthic macroinvertebrate communities (e.g. Armitage, 1980; Byrne and Gray, 1995a; Jarvis and Younger, 1997; NRA, 1996; Scullion and Edwards, 1980).

The generalised impacts of mine water pollution on benthic invertebrates was well established by the 1970s. A reduction in both the abundance and diversity of invertebrates in receiving watercourses is typical (Herricks and Cairns, 1972).

Specifically, Brown (1977) identified reductions in the numbers of Mollusca, Hirudinea, Oligochaeta, Crustacea and Platyhelminthes in response to a mine water discharge containing zinc, iron and copper. Where faunal depletion is not complete fly larvae (Diptera) invariably dominate the surviving invertebrate community (Brown, 1977; Dills and Rogers, 1974). Low pH is well accepted as a major cause of this faunal degradation (Scullion and Edwards, 1980), and the deposition of ferric precipitates is also widely cited (e.g. Dills and Rogers, 1974; Greenfield and Ireland, 1978). More recently Jarvis and Younger (1997) confirm elevated acidity and iron concentrations as the most influential causes of invertebrate impoverishment for two receiving streams in County Durham, UK. Similarly, Byrne and Gray (1995b) identified sediment toxicity, water toxicity and substrate compaction as significant causes of community depletion.

Fish rely upon the stream substrate for food and shelter. Thus, heavy coatings of metal precipitates can be seriously detrimental to their welfare. In particular, the gravels of upper stream reaches are important areas for egg laying by salmonids. A healthy macrophyte flora is essential to salmonids as a food source, as well as providing protection. Low pH, and elevated concentrations of metals such as aluminium, may be directly toxic to fish (Pentreath, 1994).

(b) Other impacts

A number of other impacts are associated with groundwater rebound and pollution of watercourses by mine waters. Most important amongst these are the following effects:

1) Water supplies may be severely affected. A cessation of pumping in the Durham Coalfield, although apparently unlikely at the time of writing, may result in pollution of the River Wear and the Basal Permian Sands and Magnesian Limestone aquifer, which are important sources of public supply water (Younger and Sherwood, 1993). Surface water supplies are also under threat where mine waters are currently rebounding. One of the most high profile examples of this is the potential pollution of the River Coquet in Northumberland, a Site of Special Scientific Interest (SSSI). Whittle colliery closed in 1997, and is therefore outside the current legal framework for government control (see below). Early predictions suggested that water rebounding within the workings might decant into the River Coquet as early as January 2000. Untreated, the metal laden water would have

severely threatened the operation of the Warkworth water treatment works. In this case a government announcement in September 1998 ensures that a system will be completed in time to treat the emerging water (Dr Paul Younger, Newcastle University, UK, personal communication, 2000).

2) Younger (1993) outlines some of the problems associated with groundwater rebound following a cessation of pumping activities. Specifically these include:
   - Interception of 'bord-and-pillar' workings can lead to collapse of pillars causing subsidence.
   - Interception of buried infrastrucure such as sewers, foundations and landfills could lead to flooding, chemical attack (due to high sulphate content) and leaching of pollutants respectively.
   - Emission of carbon dioxide and methane as it is forced ahead of rising waters can occur, sometimes resulting in asphyxiation of people entering confined spaces near old mine entrances (Burrell and Friel, 1996).

1.6.4 Mine water pollution legislation in the UK

A significant amendment to the law relating to pollution from abandoned mines came into effect on 1/1/2000, and this important change is explained below. However, this new legislation does not affect the status of many current discharges with respect to the law, and therefore the legal position prior to 1/1/2000 is outlined first.

The powers of the environmental regulatory authorities of the UK, in relation to discharges from abandoned and currently operational mines, are stipulated by the 1991 Water Resources Act (WRA) for the Environment Agency (England & Wales), and the 1974 Control of Pollution Act (Scotland) for the Scottish Environmental Protection Agency (SEPA) (Fry, 1997). The relevant legislation is effectively the same in both Acts. Under Section 85(1) of the WRA 1991 a pollution offence is committed if a person

> *"... causes or knowingly permits any poisonous, noxious or polluting matter or any solid waste matter to enter any controlled waters"* (see Fry, 1997).

However, Section 89(3) of the WRA 1991 determined, until 31/12/1999, that

> "... *a person shall not be guilty of an offence under section 85...by reason only of his permitting water from an abandoned mine or an abandoned part of a mine to enter controlled waters*" (see Fry, 1997).

Thus, prior to 1/1/2000 the owner of a mine could be prosecuted for causing *or* permitting pollution, whereas a former mine owner or owner of an abandoned mine could only be prosecuted for causing pollution. Proving causation in the highly complex hydrological setting of mines resulted in there being only one successful prosecution of a former mine owner under the WRA 1991. In that case the National Coal Board was prosecuted for causing pollution from the abandoned Dalquharran colliery, Ayrshire, Scotland in 1981.

Section 89(3) of the WRA 1991 provided a loophole in the legislation. However, this defence for former mine owners was removed at the end of 1999, when new legislation came into force. The Environment Act 1995 amended the WRA 1991 such that

> "*...subsection (3)* [of section 89] *above shall not apply to the owner or former operator of any mine or part of a mine if the mine or part in question became abandoned after 31st December 1999*" (see Fry, 1997)

From 1/1/2000 therefore, "permitting" pollution from an abandoned mine became an offence. The time delay between the publication of the Environment Act 1995 and its actual implementation had some serious implications however. South Crofty tin mine, Cornwall, Gwynfynydd gold mine, Wales, and Frazer's Grove fluorspar mine in County Durham, all closed before 31/12/2000, thus avoiding post-abandonment liabilities. Although these mines were all being squeezed financially by cheap imports to the UK from overseas, there is little doubt that the timing of closure was also guided by the 31/12/2000 legislative "deadline".

Until the end of 1999 the central principle of the UK's environmental protection policy, that "the polluter pays", was compromised with respect to polluted discharges from abandoned mines. As a consequence financial resources for remediation initiatives have been severely limited, and many mine waters continue to contaminate watercourses unabated. It is perhaps as a direct result of this that the *raison d'être* of many proponents of constructed wetlands in the UK has been their purportedly low capital and maintenance costs.

Although discharges from abandoned mines are not explicitly mentioned in any of the relevant directives, Williams (1998) has suggested that European Community (EC) laws may provide a basis upon which to bring a prosecution. Critically however, Williams (1998) does not consider the difficulties of proving causality, which may be especially significant in situations where ownership has changed, or where potentially polluting waters have flooded into adjacent workings which are owned by a different operator. It is exactly these types of issues that make prosecution difficult.

Nevertheless, if the UK Government is pressurised to meet the regulations of European Community laws these directives may prove to be important in the future with regard to mine water discharges. The relevant directives have been highlighted by McGinness (1999), as follows:

- *Council Directive of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community* (76/464/EEC)
- *Council Directive of 18 July 1978 on the quality of fresh waters needing protection or improvement in order to support fish life* (78/659/EEC)
- *Council Directive of 30 October 1979 on the quality required of shellfish waters* (79/923/EEC)
- *Council Directive of 17 December 1979 on the protection of groundwater against pollution caused by certain dangerous substances* (80/68/EEC)

Following recent catastrophic collapses of tailings dams at "Baia Mare" goldimne, Romania, and at Aznalcollar, Spain, the European Commission is now considering introducing new legislation specifically aimed at preventing similar disasters in the future (Commission of the European Communities, 2000). Such legislation would apply particularly to the mining of metal minerals, and it appears that it is likely to focus on issues such as risk assessment and appropriate management of mining waste (Commission of the European Communities, 2000).

It was stated above that because environmental regulators in the UK are unable to enforce their "polluter pays" policy at mines abandoned before 1/1/2000 constructed wetlands are appealing in particular because of their comparatively low long-term maintenance costs. However, one potential problem with the application of constructed wetland technology in view of environmental legislation is the difficulty of predicting wetland effluent pollutant concentrations (discussed in detail in the following chapters). Most of the larger watercourses in the UK have a maximum admissible concentration for metal ions, and therefore wetland effluents must be of a suitable quality to ensure these are not exceeded. Active treatment systems are more reliable in terms of predicting effluent metal ion concentrations, and may therefore be viewed more favourably in some instances. These limits are not applied to all watercourses in the UK (in the UK these streams, usually minor watercourses, are typically referred to as unclassified). Discharges of mine waters to such streams are often not targeted by environmental regulators for treatment unless there are reasons to do so beyond the immediate environmental impact of the discharge. One example is where a discharge has a high socio-economic impact, such as at Quaking Houses.

CHAPTER 2

ANALYTICAL METHODS

2.1 Introduction

Analytical methods used both in the field and in the laboratory are outlined in this chapter. Laboratory methods used are predominantly those endorsed by APHA (1998). The reader is directed to this work for more detailed descriptions of the analytical methods employed.

2.2 Field methods

Labile variables have been measured in the field for this work, using a variety of hand-held meters and field titration equipment. Only two physical parameter measurements have been made during the course of this work - flow-rate (in the field) and suspended solids concentration (in the laboratory). The following measurements have been made in the field, at varying frequencies depending on the site and the availability of sampling personnel:

Flow-rate: Recorded in units of L/minute or L/hour, flow-rate has been measured by the 'bucket and stopwatch' method. Wherever possible the bucket has been allowed to fill for at least 10 - 20 seconds to gain an accurate flow measurement. Three measurements are taken, and the average is then calculated to give a final value.

Temperature: measured in units of degrees centigrade (°C) temperature has been measured with a portable meter. Upgrades to field equipment were made during the course of this work and therefore two types of meter have been used. Initially a Palintest portable pH / temperature probe was used (Model PT 110). More recently a Camlab 6T Ultrameter has been used for temperature measurement.

pH: As above a Palintest portable pH / temperature probe was initially used, followed by a Camlab 6T Ultrameter. Typically meters have been calibrated prior to each site visit, or weekly as a minimum. Standard buffers of pH 4, pH 7 and pH 9 have been used for this purpose. Electrodes are kept moist in KCl solution whilst not in use. The Palintest probe is on the end of a lead, which is held in the watercourse to be tested. By contrast the Camlab meter has its probes contained within a "sample cup" housed within the body of the meter. After rinsing the cup with the water to be sampled several times an aliquot of water is scooped from the watercourse into the sample cup. Readings are allowed to stabilise for a few seconds before a recording is made. The manufacturers' guidelines for both the Palintest and Camlab units specify that the meters are accurate to ±0.01 pH units. pH measurements are therefore reported to two decimal places in this work.

Eh: Eh (in millivolts, mV) has been measured with the Camlab 6T Ultrameter. However field measurement of Eh are notoriously unreliable. Numerous factors, such as irreversible reactions and the presence of multiple redox couples, may affect the Eh value (APHA, 1998). Stumm and Morgan (1996) conclude that only in the absence of oxygen (a condition not fulfilled with the waters studied here), and with extreme care, can accurate Eh measurements be made. On the basis of experiments using two identical metal electrodes attached to the same reference electrode Kölling (2000) suggests that the accuracy of Eh measurement is not likely to be better than ± 50 mV. For these reasons only the most cautious significance is attached to results of Eh measurements in this work.

Conductivity: APHA (1998) now prefer the term "conductivity" to the alternative "specific conductance", and the former term is used throughout this work. Measurements are reported here in units of microsiemens / centimetre (μS/cm). Conductivity has been measured with a Palintest Conductivity meter and more recently with a Camlab 6T Ultrameter. A standard solution with a conductivity of 1483 μS/cm has been used to regularly calibrate field meters. As with pH, measurements are allowed to stabilise before recording a value.

Alkalinity concentration: Measurements (reported in units of mg/L as $CaCO_3$) have been made in the field using a Hach Alkalinity test kit (Model AL-DT). A sample of 100 mL is collected in a measuring cylinder and decanted to a conical flask pre-rinsed with the water to be analysed. Bromcresol Green-Methyl Red indicator is added to the sample. A digital titrator is then used for the titration, using 1.600 N (± 0.005 N) sulphuric acid. The end-point is reached when the solution turns from green to permanent pink. Typically at least two titrations have been made for each sample during this work. If the first two titration measurements are not within 10% of each other a third titration is made, and the mean of the closest two results are used. With experience, and careful use of the equipment, results are consistently within 5% of each other.

Dissolved oxygen concentration: Dissolved oxygen (DO) concentrations (in mg/L) have been routinely measured at the Kimblesworth site. Using the appropriate reagents the same Hach test kit as described above is used for DO measurement. The method is the azide modification of the iodometric technique (APHA, 1998). The necessary reagents are provided in "powder pillows" for convenience. A sample is collected in a 250 mL BOD (Biochemical Oxygen Demand) bottle. The bottle is allowed to fill to overflowing, and agitation is avoided during collection, to minimise the potential for changes in gaseous content. The contents of one manganous sulphate powder pillow and one alkaline iodide-azide reagent powder pillow are added to the sample, which is then stoppered and inverted several times. The sample is allowed to stand for several minutes before inverting again, to ensure complete reaction. The contents of one sulphamic acid powder pillow is then added to the sample, which dissolves the precipitate formed. 100 mL of sample is decanted into a conical flask. 0.200 N (± 0.001 N) sodium thiosulphate is used to titrate this solution to a pale straw end-point. 5 drops of starch indicator is then added, and titration then continues until the blue solution formed upon addition of the starch reaches a colourless end-point. DO concentration (in mg/L) is then calculated by multiplying the number of digits recorded on the titration unit by a digit multiplier, the value of which depends upon the sample volume and titrant concentration, as detailed in Table 2.1 below. The equipment manufacturer (Hach Company) suggest that this method has a precision of ± 1%.

Sample volume (mL)	Sodium thiosulphate concentration (N)	Digit multiplier
200	0.200	0.01
100	0.200	0.02
50	0.200	0.04

Table 2.1 **Calculation of dissolved oxygen concentration using titration method.** The number of units of titrant used is multiplied by the relevant digit multiplier to calculate an actual dissolved oxygen concentration in mg/L.

2.3 Laboratory methods

2.3.1 Metals sample collection and analysis

Polyethylene bottles (usually 150 mL capacity) have been used for collection of samples for metal ion analysis. Approximately 1 mL (depending on sample size) of concentrated nitric acid was added to the clean bottles prior to sample collection, in order to ensure that metals remained in solution during storage. In order to prevent the acid being washed out of the bottle when sampling from high flow-rate streams and discharges, the bottles for metals analysis were often filled from a second clean container. Only one sample was collected for metal analysis and one for anion analysis on each site visit. Replicate samples were not taken, mainly due to logistical constraints. The mine water research programme at Newcastle University includes an intensive water sampling regime. Doubling or trebling the number of samples for analysis would have significantly increased the time and cost of laboratory work with a minimal return in terms of scientific insight. Additionally, most of the work discussed here is concerned with time series data. When shown graphically outliers, which may be due to analytical error, become obvious in these large data sets.

Samples were stored at 4°C. Although APHA (1998) report that samples may be stored for up to 6 months when metals concentrations are in the order of several milligrams per litre, samples for this work were invariably analysed within one month of collection.

Metal ion concentrations have been measured by atomic absorption spectrophotometry (AAS). For this work a Unicam 929 Atomic Absorption Spectrometer has been used. The only metals not analysed by AAS were calcium, magnesium, sodium and potassium, which have been analysed by ion chromatography (see below).

Three standard solutions are used to calibrate the AAS machine, typically made up to concentrations of 1 mg/L, 5 mg/L and 10 mg/L. Spectrosol standard solutions have been used for this work. Clean volumetric flasks and deionised water have been used for preparation of all standards and any sample dilutions required.

Detection limits for AAS vary for different metals. The detection limit also depends on the type of machine used, and the method in which the particular machine is set up. The detection limits for the Unicam 929 AAS are not specified in the manufacturer's handbook. APHA (1998) provide typical detection limits for analysis by AAS. Detection limits for the metals analysed are provided in Table 2.2.

Metal element	Detection limit (mg/L)
Iron	0.02
Manganese	0.01
Zinc	0.005
Aluminium	0.1

Table 2.2 **Typical detection limits for metals analysis using atomic absorption spectrophotometry** (APHA, 1998).

Concentrations of calcium, magnesium, sodium and potassium have been measured using single column ion chromatography with automatic chemical suppression of the eluent conductivity. A Dionex DX-100 ion chromatograph was been used for this purpose. The same equipment was used for analysis of anions (see below). For cation analysis an IonPac CS12A (4 x 250 mm) column with a 22 millimolar eluent solution of sulphuric acid was used. All samples were injected through a 0.2 μm filter to prevent blockages occurring. The principle of the method is that an aliquot of sample is injected into the eluent stream, which then passes through the chromatographic system. The column packing material contains active sites with particular affinities for the various cations under investigation. Once separated by the column in this way the conductivity of the eluent with the individual cations is measured. The final concentration is calculated by comparison against a standard solution. Different cations are distinguished by their retention time within the column.

The standard solution used contains 10 mg/L each of Ca, Mg, Na and K. To produce an accurate result it is necessary to dilute the sample such that the concentrations of Ca, Mg, Na and K approximate those of the standard solution. However, sodium concentrations in the Quaking Houses mine water are highly elevated, and consequently this is not always possible. The accuracy of the chromatograph output is sometimes in doubt because sodium concentrations occasionally exceed the capacity of the chromatograph, and therefore reported results may be underestimates of the true concentration. The same problem is evident for the analysis of chloride, and a more detailed discussion of the potential inaccuracies of the ion chromatograph in this regard are given in Section 2.3.3, below.

Some sediment water samples have been collected from the Quaking Houses wetland. These samples invariably contain high solids loads. Samples of sediment water were collected through a 200 mm long hypodermic needle attached to a 60 mL syringe. Efforts were not made to ensure anaerobic conditions during sampling, since the objective was only to ascertain the total metal concentrations of the samples collected. In order to determine the concentration of metals sorbed to particulate matter, as well as the concentration of metals in the water column itself, these samples were subjected to an acid digestion procedure. One aliquot was filtered (0.45 μm) in the field prior to acidification, for subsequent determination of dissolved metal concentrations. A second well-mixed but unfiltered aliquot was digested with nitric acid to determine a total metal ion concentration. The nitric acid digestion procedure detailed in APHA (1998) was used for all digestions, and will not be repeated here.

2.3.2 Calculation of acidity concentration

Acidity: Acidity is not measured by titration with a base (NaOH) in this work. Instead it is calculated from the pH and the concentrations of iron, manganese and aluminium, according to the following equation (after Hedin *et al.*, 1994a):

$$\text{Acidity}_{calc} = 50[2Fe^{2+}/56 + 3Fe^{3+}/56 + 2Mn/55 + 2\ Al/27 + 1000(10^{-pH})]$$

where metal ion concentrations are in mg/L and acidity concentration is reported in mg/L as $CaCO_3$. Hedin *et al.* (1994a) have shown that the results of this calculation very closely match those of traditional titrations.

2.3.3 Collection and analysis of samples for anions

In addition to the sample collected for metals analysis, a second aliquot was routinely collected for analysis of anionic concentrations. Again, 150 mL polyethylene containers were typically used for sample collection. However, no preservatives were added to these bottles. The clean bottles were rinsed thoroughly with the water to be collected before the final sample was taken. Samples were stored at 4°C and analysed within one month of collection.

The same Dionex DX-100 ion chromatograph used for analysis of Ca, Mg, Na and K was also been used for anion analysis. However, in this case the column used was a Dionex IonPac AS4A-SC 4mm column, and the eluent used was a carbonate-bicarbonate solution.

As with cation analysis a standard solution is required. Table 2.3 illustrates the chemical composition of the standard solution used for anion analysis. To produce an accurate result it is necessary to dilute the sample such that the concentrations of anions in the sample approximate those of the standard solution. Dilutions are prepared with clean glassware and deionised water is used throughout. It is apparent that the sample matrix is very different to the standard solution matrix however. Unfortunately this is an unavoidable problem. A preferable method would be to use a standard solution specifically prepared for the analysis of minewaters. However, the Dionex DX-100 used for this work only operates with one generic standard solution, selected for its general applicability to the types of waters analysed in the environmental engineering laboratories at Newcastle University.

Ion	Concentration (mg/L)
Fluoride	2
Nitrite	5
Nitrate	10
Phosphate	15
Chloride	10
Sulphate	20

Table 2.3 **Chemical composition of the standard solution used for analysis of anions using ion chromatography.** Samples for analysis require dilution so that anionic concentrations approximate those of the standard.

Because the concentration of sulphate is considered the most significant in the context of mine water discharges, dilutions were made such that the sulphate concentration of the sample would approximate that of the standard (i.e. 20 mg/L). Table 2.4, below, is an example of the output from the Dionex DX-100 machine. Because sulphate and chloride concentrations in the Quaking Houses mine water are so high, it was typically necessary to dilute samples by a factor of 1:100. It is clear from Table 2.4 that chloride concentration is still greater than that of the standard solution (see Table 2.3), but any greater dilution would lower the output sulphate concentration to unacceptably low levels. Output concentrations of all other anions are very low, because their actual concentrations are at least an order of magnitude lower than that of chloride. If the sample was not diluted to this level, however, the concentration of chloride would be so high that it would severely contaminate the column, which is clearly unacceptable. The accuracy of the analyses of fluoride, nitrate and phosphate must therefore be questioned, particularly in view of the very high dilutions. Hereafter analysis results for these anions are therefore disregarded (the accuracy of fluoride determination by this method is in doubt even under ideal operating conditions (APHA, 1998)). When chloride concentrations were particularly high the ion chromatograph reported results that were actually underestimates of the true concentrations. Whilst this is clearly undesirable calculations of the cation-anion balance for the Quaking Houses discharge data reveal that this discrepancy appears to be minor in most instances.

The only means of avoiding these problems, with the equipment currently available in the environmental engineering laboratories at Newcastle University, would be to dilute the sample sufficiently to bring actual chloride concentration down to the level of the standard. Because the concentrations of all other anions measured by the ion chromatograph under these circumstances would be unreliably low, all of them would have to be measured by gravimetric means (see APHA, 1998). Given the frequency of sampling at Quaking Houses and Kimblesworth the cost of such an undertaking, in terms of both reagents and time, would have been unfeasible. The use of ion chromatography alone for these analyses was therefore considered acceptable, particularly since the sulphate concentration is of critical importance.

Ion	Concentration (mg/L)
Fluoride	0.551
Nitrite	-
Nitrate	0.237
Phosphate	0.312
Chloride	35.025
Sulphate	7.637

Table 2.4 **The output concentrations of anions from the ion chromatograph for the Quaking Houses mine water (sampled 4/2/00).** The sample was been diluted to 1:100, resulting in F, NO_3 and PO_4 output concentrations being very low, but Cl concentration remaining very high, compared to the standard solution concentrations (cf. Table 2.3).

2.3.4 Other laboratory analyses

The only other analysis carried out on a regular basis was determination of suspended solids concentration. Suspended solids concentration (in mg/L) has been determined by drying the residue from a known sample size on a pre-weighed glass-fibre filter paper at 103 - 105 °C. The residue on the filter paper is dried for 1 hour, cooled, and then re-weighed to calculate the suspended solids concentration. This is the standard method for determination of suspended solids concentration, and is described in detail by APHA (1998).

2.4 Tracer experiments

Tracer tests have been undertaken at both Quaking Houses and Kimblesworth in order to attempt to establish the residence time of waters within the two systems. Tracer tests have not been undertaken by this author at Quaking Houses, but the methods and results of experiments performed by Robins (1998) are briefly detailed in Section 5.4.

At Kimblesworth tracer tests have been undertaken using lithium chloride (LiCl) as the trace element. A solution with an Li concentration of 2000 mg/L was used for these tracer tests. The Kimblesworth reactors are fed with water from above, via a perforated section of PVC pipe (see Section 5.3 for a detailed description). It was therefore possible to inject 10 mL of the concentrated solution directly into the feed pipe to each reactor via an hypodermic needle. Effluent samples were collected after 20 seconds, and then every 10 seconds for up to 10 minutes. Lithium concentrations were subsequently analysed by Atomic Absorption Spectrophotometry (see above).

2.5 Meteorological data collection

An automatic weather station was installed in the grounds of the Waste Transfer Station (see Figure 1.1) by Environmental Measurements Ltd. (EML), Sunderland, UK, in July 1998. The unit is a modular weather station, comprising a number of different components manufactured by several different companies; namely EML, Vector Instruments, Campbells, ELE International and Sky Instruments. The station automatically logs values of the following variables, on an hourly basis (the units of measurement are given in parentheses):

- Relative humidity (%)
- Temperature (°C)
- Rainfall depth (mm)
- Net radiation (W/m^2)

- Solar radiation (W/m^2)
- Wind speed (m/s)
- Wind direction (degrees)

The weather station is downloaded by EML every 2-3 months, and the data are forwarded to Newcastle University. For this work only the rainfall depth and temperature variables have been used, and weekly means have been calculated (since that is the frequency of water quality data collection).

CHAPTER 3

LITERATURE REVIEW

3.1 Introduction

The following review of current research literature is restricted to a discussion of passive treatment technologies for mine water pollution, with only a brief summary of active treatment systems. Natural attenuation processes are harnessed within the confines of some types of passive treatment system (Hedin *et al.*, 1994a). At appropriate points through the text reference is therefore made to relevant literature in this field. A detailed discussion of topics such as mine water generation, classification and rebound is beyond the scope of this study. Recent literature in these fields has already been cited in the Introduction of this thesis.

The key to mine water treatment is the removal of metal contaminants, especially iron, manganese and aluminium, together with the sulphate anion. In those instances where discharges are acidic this will necessitate the generation of alkalinity to raise pH. Currently treatment methods for mine waters can be divided into two main categories:

A. *Passive treatment* systems, designed and operated correctly, require no ongoing chemical or energy inputs and are largely maintenance free (Hedin *et al.*, 1994a; Younger 1998b). Key objectives of this thesis relate to the design and performance of anaerobic (compost) wetlands and a novel new approach to passive treatment. However, the nature and application of all common types of passive treatment system currently in use are discussed below. This is because in reality passive treatment removal mechanisms are rarely mutually exclusive; an anaerobic wetland will contain aerobic zones, and zones of carbonate dissolution (such as in limestone drains).

B. *Active treatment* is essentially conventional wastewater treatment technology, most commonly utilising oxidation, alkali dosing, and settlement lagoons to remove metal pollutants (Freeman and Harris, 1995; Younger, 2000d). The comparative costs of passive and active treatment are highlighted. Younger (2000d) reviews other active treatment processes.

In the following discussion there is an intentional emphasis on the removal of iron, manganese, aluminium, and zinc from mine waters (as well as acidity and sulphate). This is not to say that other metals (such as copper, lead, nickel) are not significant pollutants at some sites. However, these four metals are those of concern at the sites studied as part of this work, and are also typically prevalent in mine drainage world-wide.

3.2 Passive treatment of mine waters

3.2.1 Introduction

Constructed wetlands have been used for wastewater treatment for nearly 50 years (Vymazal *et al.*, 1998). They have been applied to the treatment of a range of wastewaters, from highway runoff through to abattoir waste. Vymazal *et al.* (1998) provide an (edited) history of the first uses of constructed wetlands for these various purposes.

The earliest indications that wetlands may be appropriate ecosystems for the amelioration of mine water pollution arose from investigations of catchment hydrochemistry in West Virginia, USA (Wieder and Lang, 1984). One of the three catchments studied by Wieder and Lang (1984) contained both a natural peat bog (Tub Run Bog) and an abandoned opencast mine. Observations of water chemistry above and below this wetland area revealed that significant reductions in concentrations of H^+, Fe^{2+} and SO_4^{2-} were occurring as the mine drainage flowed through the wetland system. The authors correctly surmised that this discovery could have potential application to the remediation of mine water discharges in other areas.

Since then the number of investigations into the potential use of wetlands for mine water treatment has proliferated. Although there are still a number of sites where natural wetlands ameliorate mine water discharges (see for example Sobolewski, 1997; Younger, 1997b) the main thrust of recent research has been towards the use of constructed or engineered wetlands for pollution abatement. Vymazal *et al.* (1998) define constructed wetlands as *"...former terrestrial environments that have been modified to create poorly drained soils and wetland flora and fauna for the primary purpose of contaminant or pollution removal from wastewater".*

The primary objectives of constructed wetlands for mine water treatment are the elevation of pH (where necessary) and the removal of metals. Studies of natural attenuation of mine waters has repeatedly suggested the critical importance of pH. The fate of iron, manganese, aluminium and zinc in surface watercourses are all pH dependent (Hedin *et al.*, 1994a; Nordstrom and Ball, 1986; Stumm and Morgan, 1996). The solubility, and therefore mobility, of all of these metals increases with decreasing pH (Stumm and Morgan, 1996). Conversely, as pH rises the potential for precipitation and immobilisation of these metals by sorption increases (Banwart, 1998). While hydroxides of iron and aluminium are actually amphoteric (Langmuir, 1997), the very high pH required for increases in solubility under alkaline conditions are not encountered in passive treatment systems. In view of the pH-dependence of metal fate in receiving waters investigators at the U.S. Geological Survey (among others) have undertaken experiments involving pH modifications of these streams as a route to establishing metal ion transformations and sinks (e.g. Broshears *et al.*, 1996; McKnight and Bencala, 1989; Runkel *et al.*, 1996). Production of a definitive set of formulae to which chemical transformations within streams will adhere is impossible, since the complexity and variability of natural fluvial systems is simply too great (Broshears *et al.*, 1996; Runkel *et al.*, 1996). The same *caveat* applies equally, if not more so, to treatment wetlands. Nonetheless, it is possible to distil from these and other studies the key processes which control metal concentrations, speciation and transport in streams, as follows (Chapman *et al.*, 1983; Kuwabara *et al.*, 1984; McKnight and Bencala, 1989):

1) Dilution by tributaries and groundwater
2) Advection and dispersion
3) Oxidation and reduction (abiotic and biotic)
4) Precipitation / coprecipitation and dissolution

5) Adsorption and ion exchange
6) Photoreduction
7) Biological assimilation

With the exception of the physical processes ((1) and (2)), the following discussion illustrates that these are also some of the critical removal mechanisms in constructed wetlands.

There are currently a number of types of passive treatment technology in use, and under investigation. Predominantly these involve the application of constructed wetlands and limestone drains. The flow-chart of McCleary and Kepler (1994), which is based on the classification system of Hedin *et al.* (1994a), provides a summary of the main types of system currently in use (Figure 3.1), and summarises the key determinations necessary during system selection. Details of the research status of each type of system are provided below.

3.2.2 Aerobic wetlands

The overall aim of an aerobic wetland is to encourage the oxidation and precipitation of metals (predominantly iron) within the confines of the wetland cell. In order to be effective the mine water must possess certain chemical characteristics i.e. the water should be net-alkaline, circum-neutral, and rich in dissolved oxygen (Hedin *et al.*, 1994a). In circumstances where the influent water is net-alkaline, circum-neutral, but with low dissolved oxygen content, a simple aeration step prior to an aerobic wetland may be incorporated (see Hedin *et al.*, 1994a). The reasons these chemical conditions are important for effective metal removal are made apparent in the paragraphs below.

The most common contaminant of mine waters is iron (Hedin *et al.*, 1994a). It is widely accepted that under favourable conditions the oxidation of ferrous iron and its subsequent precipitation as ferric oxyhydroxide within a constructed wetland is the most significant removal mechanism (Eger, 1994; Hedin *et al.*, 1994a; Tarutis and Unz, 1994; Wieder, 1988). Although it is possible to precipitate ferrous hydroxide directly without oxidation the pH required for this reaction is unrealistically high in a constructed wetland setting (Hustwit *et al.*, 1992). Therefore the first of the favourable

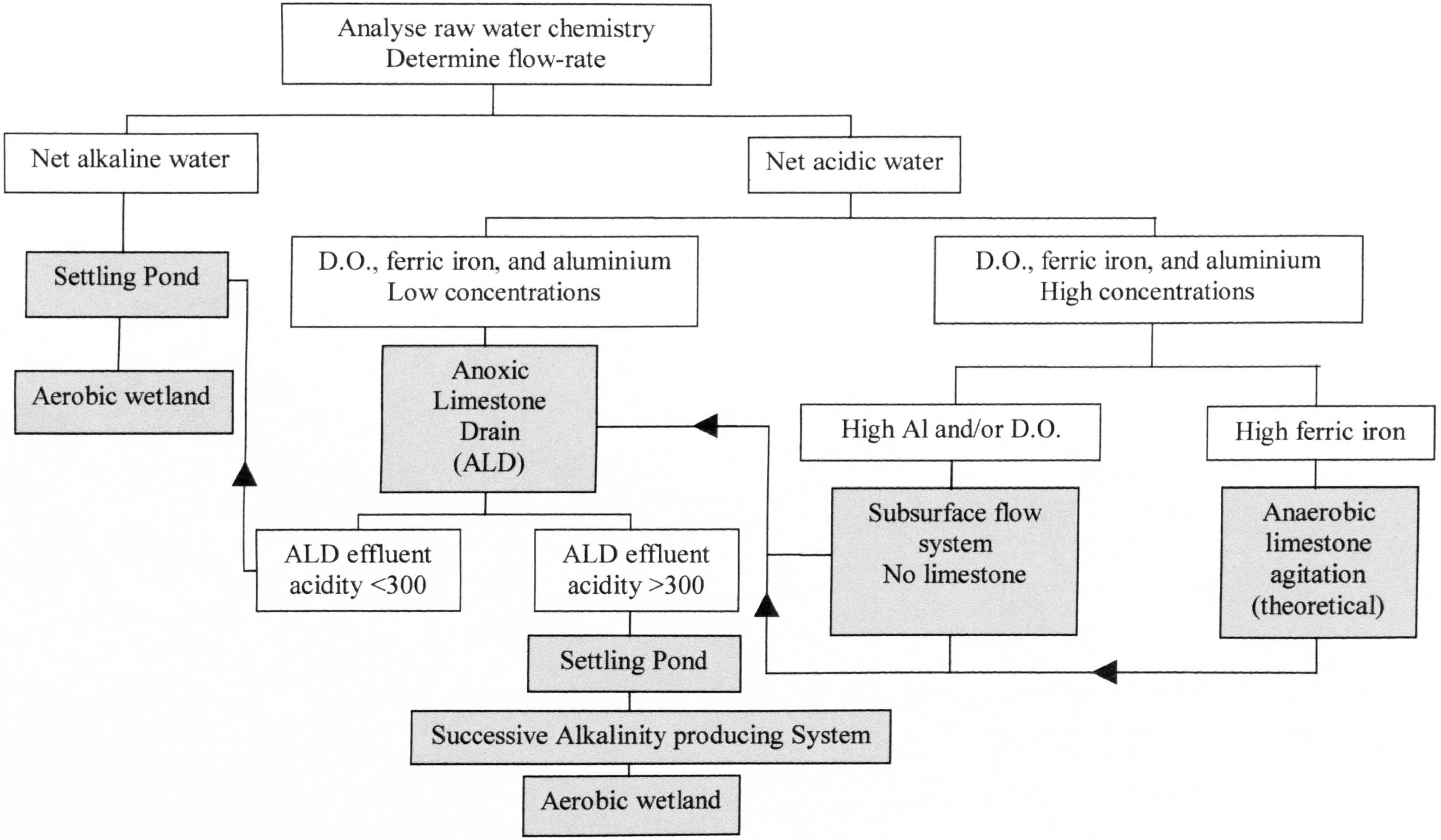

Figure 3.1 **Flow chart showing dichotomous determinations necessary for design of passive wetland treatment systems** (from McCleary and Kepler, 1994). Shaded boxes indicate actual treatment units. Acidity concentrations are in mg/L as $CaCO_3$.

conditions necessary for the effective precipitation of iron oxyhydroxide is that dissolved oxygen is present to facilitate the oxidation of ferrous to ferric iron. Secondly the water must be net-alkaline (i.e. alkalinity > acidity), and of circum-neutral pH (Hedin *et al.*, 1994a). This is because the oxidation and hydrolysis of ferrous iron generates proton acidity, as shown by the overall reaction below (Langmuir, 1997):

$$Fe^{2+} + \tfrac{1}{4} O_2 + 5/2\, H_2O \rightarrow Fe(OH)_3 + 2\, H^+ \qquad (3.1)$$

Bicarbonate alkalinity serves to buffer the proton acidity generated via the oxidation and hydrolysis of iron, thus maintaining a circum-neutral pH (Hedin and Nairn, 1993):

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2 \qquad (3.2)$$

If oxidation and precipitation proceeds under net-acidic conditions the generation of proton acidity may lead to a decrease in pH. For example Brodie *et al.* (1993) report on a constructed aerobic wetland in Tennessee, USA, where influent pH is 5.5 and effluent pH is 2.9.

Circum-neutral pH is also necessary for effective oxidation of iron because the rate of abiotic oxidation is far greater at high pH. At pH ≥ 5 the reaction is governed by the rate law, commonly written as (Stumm and Morgan, 1996):

$$\frac{-d\,[Fe^{2+}]}{dt} = \frac{k_H\,[O_2(aq)]}{[H^+]^2}\,[Fe^{2+}] \qquad (3.3)$$

Where, $k_H = 3 \times 10^{-12}\ \text{min}^{-1}\ \text{litre}^{-1}$ at 20°C

The reaction is first-order with respect to Fe^{2+} and O_2 and second order with respect to H^+ (Millero, 1990). As a result the rate may increase 100-fold for an increase of one pH unit (Stumm and Morgan, 1996). The oxidation reaction may occur in a matter of seconds at pH > 8 (Hedin *et al.*, 1994a). The significance of pH in controlling the reaction rate is illustrated in Figure 3.2(a), which shows the rate of oxidation of Fe^{2+} at various pHs. The oxidation reaction is autocatalytic in the sense that the oxidation

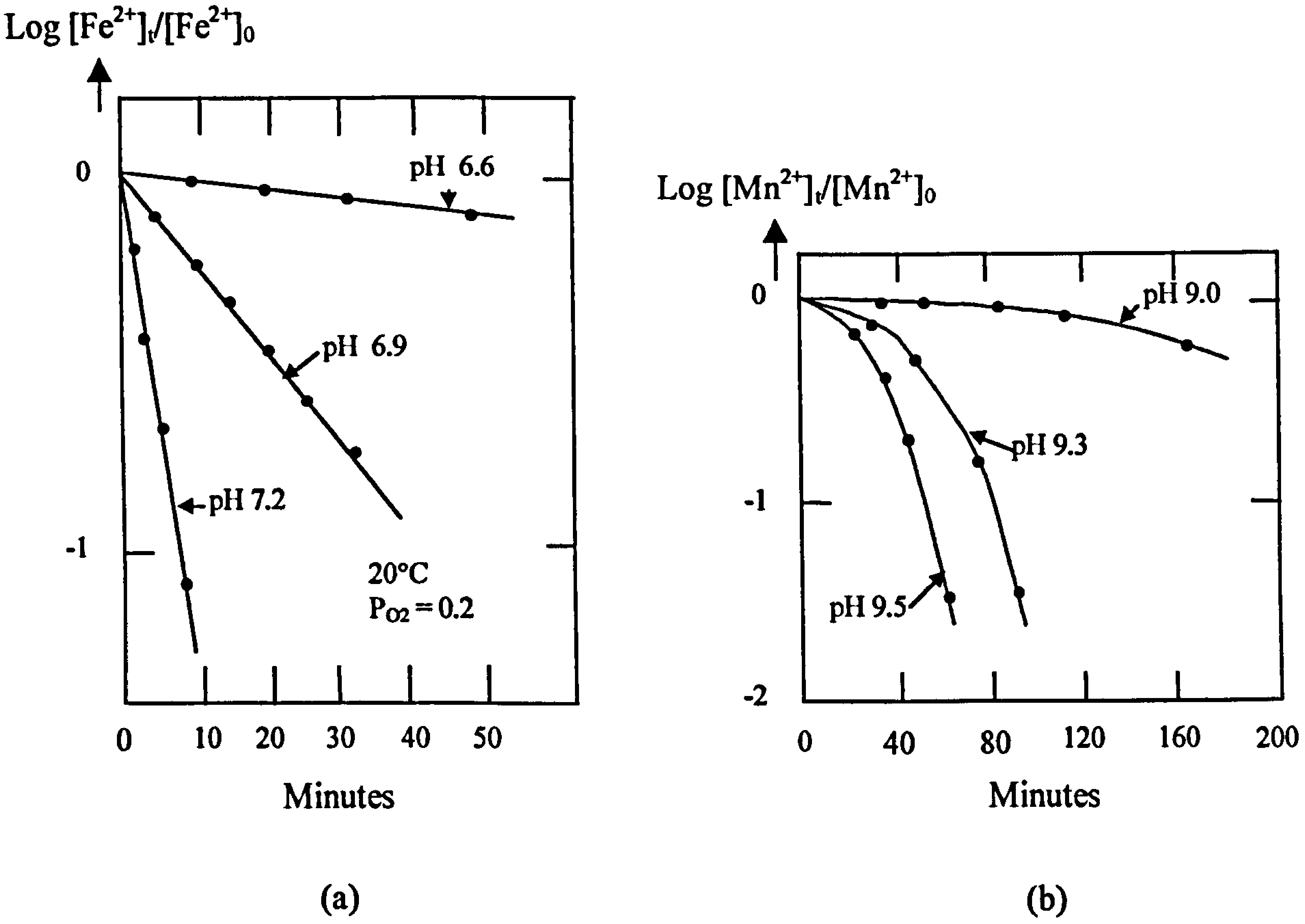

Figure 3.2 **Rate of removal of (a) Fe^{2+} and (b) Mn^{2+} by oxygenation in bicarbonate solutions at various pH** (from Stumm and Morgan, 1996). Rates increase with increasing pH, and for manganese pH ≥ 9 is necessary for rapid removal (on y-axis labels t = time i.e. concentration after time, t and 0 = initial concentration).

product, ferric hydroxide, increases the rate of oxidation at concentrations in the range 5 – 600 mg/L (Stumm and Lee, 1961; Tamura *et al.*, 1976; Tüfekci and Sarikaya, 1996). Abiotic reaction rates in nature tend to be higher than those measured in laboratory experiments (Langmuir, 1997) because of the catalytic effect of other trace metals, especially copper and cobalt (Stumm and Morgan, 1996), but also manganese and aluminium (Stumm and Lee, 1961; Singer and Stumm, 1970). Elevated temperatures increase the rate of reaction, as do some anions which will form complexes with Fe^{3+} e.g. HPO_4^{2-} (Stumm and Lee, 1961). On the other hand oxidation may be hindered by high concentrations of SO_4^{2-} and Cl^- (Nealson, 1983; Stumm and Morgan, 1996).

Below pH 6 abiotic Fe^{2+} oxidation rates are very slow, and under these conditions microbially mediated oxidation predominates. In fact biotic oxidation is most rapid at a pH in the range of 2-3 (Nealson, 1983). Of the acidophilic bacteria present in mine waters *Thiobacillus ferrooxidans* has been the focus of most study (Nealson, 1983), and is consequently widely cited. However, other bacteria such as *Leptospirillum ferrooxidans* may be as, if not more, important in some locations (Pronk and Johnson, 1992). Literature relating to the quantification of microbial oxidation of ferrous iron in natural environments is very sparse, and it is therefore difficult to assess its relative significance in terms of natural or constructed wetland attenuation. Hedin and Nairn (1993) report that whilst biotic oxidation may occur at pH < 5 the rate of this reaction is 5 - 10 times slower than abiotic oxidation at pH > 5.5. At pH > 6 the rate of abiotic oxidation of ferrous iron is very rapid (Hedin *et al.*, 1994a). Hence, aerobic wetlands operate more effectively when abiotic oxidation predominates, at circum-neutral pH.

There is a considerable degree of uncertainty surrounding the presence and role of "iron-bacteria" at circum-neutral pH. Establishing whether bacteria have an important role in oxidation *per se*, or whether they simply accumulate iron at these pH ranges, has been a source of much debate (Nealson, 1983). However, iron-oxidising bacteria operating in the neutral pH range have recently been identified (e.g. Emerson and Moyer, 1997; Johnson *et al.*., 1992). The relative importance of this group of bacteria in iron-oxidation, in the context of mine water pollution, is still unclear.

For an aerobic wetland to function efficiently it is necessary for the iron oxidation and hydrolysis products to precipitate on the substrate surface. If this does not occur ferric iron may be flushed through the system in suspension. Laboratory investigations have indicated that at circum-neutral pH aggregation of these hydrolysis products may lead to the formation of solid ferric oxyhydroxide precipitates within 2-3 hours (Grundl and Delwiche, 1993). The growth rate of crystals increases with temperature, and is considered to be approximately proportional to the Fe^{2+} concentration, and to a lesser extent the Fe^{3+} concentration (Langmuir, 1997; Langmuir and Whittemore, 1971). Although six types of ferric oxyhydroxide precipitate have been identified (Langmuir and Whittemore, 1971) the amorphous form (known as ferrihydrite or hydrous ferric oxide (HFO)) is typically the initial precipitate. Subsequent partial crystallisation of HFO causes the precipitate to become less soluble (that is, an increase in solubility product, pK_{sp}). Where iron concentrations are in excess of 1-2 mg/L crystallisation of HFO may occur in a matter of hours or days (Langmuir, 1997). Whilst amorphous HFO is invariably the first precipitate formed, Langmuir and Whittemore (1971) found that poorly formed goethite (and sometimes lepidocrocite, γ-FeOOH) may also be a significant constituent of the ochre coating many stream beds. Certainly the long-term ageing of HFO leads to the formation of the less soluble goethite. Extensive ageing under dry conditions may also lead to the formation of hematite (Langmuir and Whittemore, 1971). Elevated concentrations of Fe^{3+} (Grundl and Delwiche, 1993) and sulphate (Baltpurvins *et al.*, 1996) are reported to inhibit formation of goethite / hematite from ferrihydrite. It seems likely that these reactions are operational within aerobic wetlands, although Grundl and Delwiche (1993) point out that reconciling the results of laboratory investigations with actual precipitation rates and reactions in the field is still a problem.

Oxidation and precipitation may not be the only iron removal mechanism operational under aerobic conditions, although there seems little doubt that it is the most important. In his early work on *Sphagnum* wetlands Wieder (1988) identified five potential processes involved in iron retention:

i. uptake by *Sphagnum*
ii. cation exchange
iii. specific adsorption
iv. precipitation as insoluble oxides and
v. precipitation as insoluble sulphides

Of these he considers processes (iii) and (iv) by far the most important. In subsequent laboratory mesocosm experiments Wieder *et al.* (1990) went some way to quantifying the relative significance of each process. Using a serial extraction procedure the dry weight of iron per unit weight of *Sphagnum* substrate was calculated for the various iron retaining mechanisms. The authors found that saturation of the substrate was reached at 1 - 5 mg/g Fe for cation exchange, and 10 - 15 mg/g for specific adsorption. The formation of insoluble oxides did not appear to reach saturation until approximately 200 mg/g however. It should be noted that the water used for these experiments had an influent pH of 3.5, which is so low that it would be expected to have had considerable influence over retention of metals (see above).

Tarutis and Unz (1990) also recognise the precipitation of oxides / hydroxides as the dominant process, and suggest that the relative contribution of the other processes is dependent upon the sediment redox profile and the particular metal of interest. One example is that precipitation of metal sulphides (requiring anaerobic conditions) may occur even in aerobic wetlands, since anaerobic conditions may prevail even at shallow depths below the substrate surface (Eger, 1994). In compost wetlands (see below) these conditions are actively encouraged.

Manganese is typically present in mine waters at lower concentrations than iron. Aesthetic and environmental impacts of manganese appear to be minimal below approximately 10 mg/L. However, it is often second only to iron in its prevalence in mine waters. In some instances environmental regulatory authorities have identified manganese removal as a potential requirement of proposed treatment. Examples in the UK include the treatment of the Whittle colliery discharge in Northumberland (Paul Younger, University of Newcastle, UK, personal communication, 2000), and the Six Bells mine water discharge in south Wales (David Laine, IMC Consulting Engineers, UK, personal communication, 2000). Usually these requirements are driven by European Union directives relating to manganese concentrations in receiving watercourses. As illustrated below the removal of manganese is much more difficult than the attenuation of iron, and for these reasons the remediation of manganese contamination in passive treatment systems is discussed below.

The removal of manganese in aerobic wetlands is thought to be mechanistically similar to that of iron, but is estimated to be 20 - 40 times slower (Hedin and Nairn, 1993). Where it occurs the oxidation (from Mn^{2+} to Mn^{4+}) and hydrolysis of manganese proceeds as follows (Hedin and Nairn, 1993):

$$Mn^{2+} + 1/2\, O_2 + 2\, H^+ \rightarrow Mn^{4+} + H_2O \qquad (3.4)$$

$$Mn^{4+} + 2\, H_2O \rightarrow MnO_2 + 4\, H^+ \qquad (3.5)$$

As for iron, the oxidation of manganese is strongly pH dependent (Figure 3.2(b)), but the pH required for rapid removal is much higher.

Brodie (1993), among others, has postulated that manganese may be coprecipitated with iron in aerobic wetlands, citing the positive correlation between influent alkalinity and Mn removal rate as being suggestive of such a process. However, examination of 11 wetlands in western Pennnsylvania by Hedin and Nairn (1993) revealed no significant removal of Mn, irrespective of influent alkalinity. The only notable removal of manganese occurred at sites where dissolved ferrous iron concentrations dropped below 1 mg/L. Hedin and Nairn (1993) argue that this is likely to be indicative of the reduction and resolubilisation of manganese by ferrous iron:

$$MnO_2 + 2\, Fe^{2+} + 2\, H_2O \rightarrow 2\, FeOOH + Mn^{2+} + 2\, H^+ \qquad (3.6)$$

Hedin *et al.* (1994a) report that five constructed wetlands they studied (all with effluent Fe concentration < 1 mg/L) showed significant removal of manganese. The authors concluded that the typical black deposits were manganese oxide. The effluent pH of the relevant waters was in the range 6.1 - 7.4, and yet Diem and Stumm (1984) have suggested that the rate of abiotic oxidation of manganese at circumneutral pH may be measured on the scale of years. If the findings of both research groups are assumed to be correct then the removal of manganese observed by Hedin *et al.* (1994a) must either be by some unknown mechanism or by microbially catalysed or autocatalytic oxidation of manganese. Rates of removal may be increased by bacterially-mediated oxidation, autocatalysis, coprecipitation and adsorption to solid surfaces (Hem, 1992). Bacteria such as *Leptothrix* and *metallogenium* have been reported to be able to increase rates of

Mn oxidation by as much as five orders of magnitude (Tebo *et al.*, 1997). Bacterially mediated Mn oxidation is now considered to be a widespread phenomenon in natural waters (Tebo *et al.*, 1997). Nealson *et al.* (1989) provide details of the various direct and indirect mechanisms of bacterial manganese oxidation. Davies and Morgan (1989), Junta and Hochella (1994) and Murray *et al.* (1985) have all investigated the autocatalytic adsorption of manganese to solid phases in laboratory experiments. It appears that the geometric nature of the adsorbing solid surface may be an important control on continued adsorption-oxidation (Junta and Hochella, 1994). What controls the final mineral phase formed is unclear - the three research groups cited above produced differing results. Junta and Hochella (1994) suggest that bacterial catalysis may be influential, but this is yet to be proven.

Aluminium is removed in aerobic wetlands by formation of the hydroxide ($Al(OH)_3$) (Hedin *et al.*, 1994a). Below pH 4.0 the free ion Al^{3+} dominates (Hem, 1992), and in this state aluminium appears to behave conservatively. However, increasing pH (generation of alkalinity) causes a switch to non-conservative behaviour (at pH 4.6 – 4.9), and hydrolysis proceeds (Nordstrom and Ball, 1986). Laboratory experiments by Lydersen *et al.* (1991) suggest that the formation of aluminium polymers of the form $Al(OH)_3(s)$ (amorphous or gibbsite) is almost instantaneous above pH 5.0. Thus, gibbsite / amorphous $Al(OH)_3$ solubility seems to control aluminium concentrations above pH 4.6 – 4.9. Under-prediction of Al concentrations in watercourses with pH < 4.6 implies that there may be other sinks for Al under these conditions (see Cronan *et al.*, 1986 and references therein). Cronan *et al.* (1986) suggest that organic matter may play an important role in aluminium attenuation, via ion exchange reactions. In addition Nordstrom and Ball (1986) and Langmuir (1997) highlight the possible role of other minerals, such as alunite ($KAl_3(SO_4)_2(OH)_6$) and jurbanite ($Al(SO_4)OH \cdot 5H_2O$) as possible sinks for Al. However, Appelo and Postma (1993) explain that jurbanite has never actually been identified in sediments or soils, and its existence in natural environment therefore remains controversial. Formation of secondary minerals may also be an important sink for iron, and a host of other heavy metals (Langmuir, 1997). Such reactions may be of considerable significance in constructed wetlands. Because elevated concentrations of aluminium are associated with low pH conditions an anaerobic (compost) wetland is the more appropriate type (see below), but some aerobic conditions will be required to remove the aluminium since it will not form a sulphide in anaerobic conditions (Hedin *et al.*, 1994a). It seems likely however, given the abundance of gibbsite in soils and minerals, that aluminium will form a hydroxide under anoxic conditions.

The geometry and number of aerobic wetlands (and indeed all constructed wetlands) is typically dictated by site conditions. For example on relatively flat sites one large wetland of the appropriate size (see below) may be built, usually with impermeable baffles or dikes prudently positioned to encourage a circuitous flow path and mitigate against short-circuiting. On steeper sites a series of smaller terraced wetlands may be more realistic (Brodie, 1993). In an effort to integrate constructed wetlands with the local ecology and landscape there has been an increasing trend to avoid 'concrete boxes' in the construction of wetlands (Brodie, 1993; Laine, 1998; Younger *et al.*, 1998). In the UK at least retaining embankments are typically constructed from *in situ* earth (Laine, 1998), clay, or in one UK example (see Chapter 4) pulverised fuel ash (fly ash). To prevent erosion and slippage slope angles are typically no less than 2:1 length to width (Brodie, 1993). A PVC or clay liner may be required to prevent water egress and toe drainage where the *in situ* soil is insufficiently impermeable. Hedin *et al.* (1994a) recommend a freeboard in the order of 1.0 m to allow for accumulation of solids on the wetland substrate, and provide a predicted lifetime of 20-25 years.

A variety of materials have been successfully used in aerobic wetlands for the colonisation of wetland flora. *In situ* soil (Hedin *et al.*, 1994a; Laine, 1998), gravel, and alkaline spoil materials have all been utilised (Hamilton *et al.*, 1997; Hedin *et al.*, 1994a). *Typha latifolia* (commonly known as Cattails in the USA, but as greater reed-mace, or bulrush in the UK) have been the most common wetland plants used in constructed wetlands in the USA (eg. Brodie, 1993; Hedin *et al.*, 1994a), and this trend has continued in the UK and the rest of Europe (eg. Hamilton *et al.*. 1997; Laine, 1998). However, many other groups of plants have been used successfully, including *Juncus effusus* (soft rush), *Phragmites australis* (common reed) and the *Scirpus* (Bull Rush) genus. Many constructed wetlands are now planted with six or seven different species (eg. Brodie, 1993; Laine, 1998), and colonisation by others may occur naturally. For example Brodie (1993) reports that after 10 years the Impoundment 1 wetland in Tennessee, originally planted with just 6 species, now has in the order of 70 vegetative species. Figure 3.3 illustrates a heavily vegetated aerobic wetland at the Woolley

Figure 3.3 **Woolley Colliery aerobic wetland, West Yorkshire, in September 1997.** The wetland is heavily vegetated with *Typha latifolia*, but was also planted with 6 other plant species (Laine, 1998) (photograph by Dr Paul L. Younger, University of Newcastle upon Tyne, UK)

Colliery site in West Yorkshire, UK. In the UK planting of wetlands typically takes place in autumn (September / October). 200 mm high pot-grown plants have been used in many of the successful aerobic wetlands currently operational (David M. Laine, IMC Consulting Engineers, UK, personal communication, 2000). As long as wetlands are not flooded during their early growth in the following spring, specimens may be established within a year of planting.

Bioaccumulation of metal contaminants by wetland vegetation appears to have a negligible overall impact on total removal of metal ions. Both Sencindiver and Bhumbla (1988) and Mitsch and Wise (1998) calculate that iron accumulation in plant tissue accounts for less than 1% of the total removal of iron in constructed wetlands. More significant may be the effect that plant root systems have on the redox environment of the sediment. Sencindiver and Bhumbla (1988) found significantly greater reducing conditions in wetlands planted with *Typha* than those without, and concluded that this may encourage precipitation of metals as sulphides (via sulphate reduction). This is consistent with the findings of Mitsch and Wise (1998), who showed that sulphate concentrations were lower, and metal concentrations higher, in sediment samples taken from around vegetated areas of a wetland. The authors suggest that additional carbon from the plants may encourage sulphate reduction. Certainly as plants die-back the addition of carbon to the substrate may be significant. Additionally removal of metals by dead vegetation has been suggested as a potentially important process (Steephen McGinness, Houses of Parliament Library, UK, personal communication, 2000).

3.2.3 Limestone Drains

The key to successful amelioration of net-acidic (i.e. acidity > alkalinity) mine water discharges is accepted as the generation of alkalinity and raising of pH (Hedin *et al.*, 1994a). Anoxic Limestone Drains (ALDs) have been developed as one option for alkalinity generation, usually used as a pre-treatment step prior to an aerobic or anaerobic system (Hedin *et al.*, 1994a). Hedin *et al.* (1994a) stress that the purpose of an ALD should not be to remove metal contaminants, but merely to raise pH and alkalinity. High $CaCO_3$ content (in the region of 90%) of the limestone used is considered essential for effective operation of an ALD, and thus dolomite is to be avoided (Brodie *et al.*, 1993; Hedin *et al.*, 1994a). Successful long-term operation is achieved by ensuring that concentrations of Al, Fe^{3+} and dissolved oxygen are all < 1 mg/L in the influent water (Hedin *et al.*, 1994a). At higher concentrations armouring of limestone by iron oxyhydroxide may occur, reducing the rate of calcium carbonate dissolution. In addition precipitation of iron oxyhydroxide and aluminium hydroxide may cause plugging and ultimately failure of the system in the long-term (Hedin *et al.*, 1994a). This is particularly the case where high metal loads are associated with comparatively low flow rates, which allows for rapid precipitation without the possibility for solids to be flushed through the system (Robbins *et al.*, 1999).

Brodie *et al.* (1993) summarise the key reactions as follows:

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2CO_3 \qquad (3.7)$$

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- \qquad (3.8)$$

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad (3.9)$$

Thus, limestone reacts with acidity in equation 3.7, with further alkalinity production in equation 3.8 as limestone reacts with carbonic acid. As pH rises above 6.4 equation 3.9 predominates, and bicarbonate is the dominant CO_2 species (Brodie *et al.*, 1993). Anoxic conditions are ensured by enclosing the limestone used in heavy duty plastic, and burying the entire drain under at least 0.3m of clay or spoil (Brodie *et al.*, 1993; Hedin *et al.*, 1994a).

Figure 3.4 illustrates a typical ALD system, the Morrison ALD, USA. This particular system is constructed in a 46m long trench (0.9 m wide), filled to a depth of 0.9 m with limestone gravel. The total pore volume of the system is estimated at 19 000 L (Hedin *et al.*, 1994b). The system is reported to have generated an average alkalinity of 248 mg/L as $CaCO_3$ over a 30 month period (Hedin *et al.*, 1994b). Whilst a linear configuration is considered ideal systems up to 10 - 20 m wide have been constructed where this is not feasible, and Hedin *et al.* (1994a) suggest that alkalinity generation is similar. Maximum alkalinity generation currently reported to be possible (approximately 300 mg/L as $CaCO_3$ (Hedin *et al.*, 1994a)) has been calculated to be achievable with a retention time of 14 hours (Hedin *et al.*, 1994b). Sizing of ALDs can

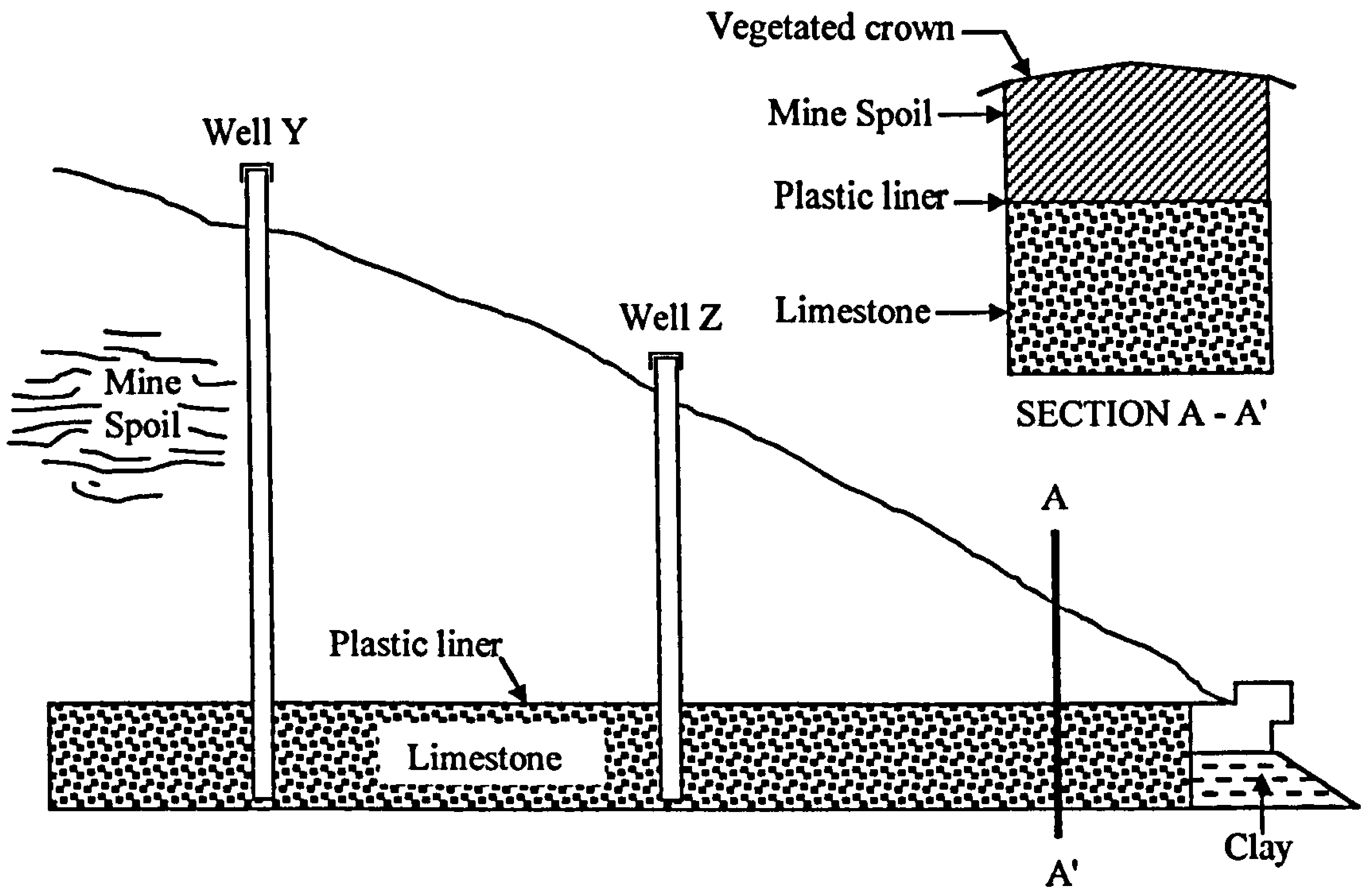

Figure 3.4 **Cross-sections of the Morrison anoxic limestone drain.** The figures are not drawn to scale (after Hedin *et al.*, 1994b). Water flows horizontally through the system, which must be kept anoxic for alkalinity to be generated without armouring of the limestone with iron and aluminium precipitates.

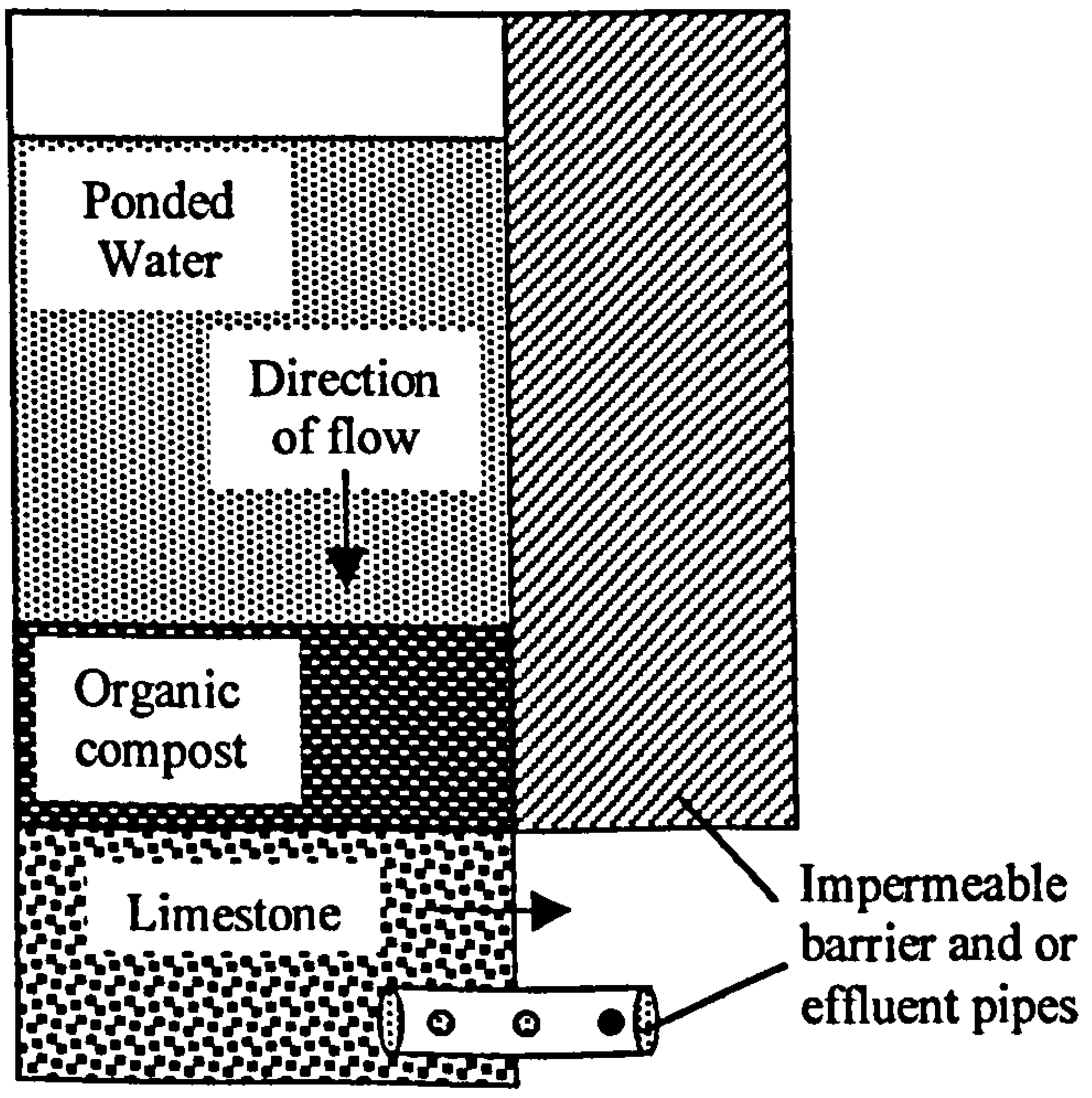

Figure 3.5 **Typical cross-sectional view of a successive alkalinity producing system (SAPS) treatment unit.** Metal-rich water is reduced in the organic compost in order that alkalinity can subsequently be generated without the limestone plugging with metal precipitates (from Kepler and McCleary, 1994).

then be based on the necessary retention time. Hedin *et al.* (1994a,b) assume a limestone porosity of 50% for these calculations, although Cravotta and Trahan (1999) report much lower values (0.14 or 14%) which would result in a significant difference in size calculations. The latter authors suggest that this discrepancy may be due to their calculations being made in the field, where compaction and sorting of limestone may decrease calculated porosity values. Brodie *et al.* (1993) recommend oversizing limestone drains in any case in order to both extend their longevity and minimise the potential for hydraulic failure. Brodie *et al.* (1993) suggest that properly designed ALDs may successfully generate alkalinity for 20 - 80 years. Hedin *et al.* (1994a,b) also give lifetime estimates within these boundaries, but point out that no system has yet reached such an age so these are no more than theoretical calculations.

Clearly the efficiency of an ALD is directly dependent upon the rate of calcite dissolution. The overall rate of calcite dissolution is governed by the pH, CO_2 pressure (P_{CO2}), and the activities of Ca^{2+} and HCO_3^- (Cravotta and Trahan, 1999). Rapid dissolution of calcite is associated with low pH and Ca^{2+} and HCO_3^- activities, and high P_{CO2}. Hedin *et al.* (1994b) observed that little calcite dissolution occurred in the second portion of ALDs. They suggest that this may be due to the sharp decrease in the kinetics of calcite dissolution as equilibrium is approached. They also suggest that the presence of high concentrations of Fe^{2+} and Mn may lower the rate of reaction. Mine waters often have high P_{CO2} due to CO_2-producing processes within mined ground, and influent water P_{CO2} is cited as a key factor in the subsequent efficiency of an ALD (Hedin *et al.*, 1994b). Indeed influent water chemistry as a whole is critical to the successful operation of an ALD. Wildeman *et al.* (1997) have questioned the reliability of some of the field measurements for key variables (especially Al). For sites they studied in Colorado, USA, they also suggest that if the pH < 4 then Al will almost certainly be present in concentrations in excess of the required 1 mg/L, and that DO concentration is invariably higher than 1 mg/L at all sites.

Recently Nuttall and Younger (2000) have proposed a novel use of ALD systems for removal of zinc. Laboratory and field systems were installed to investigate the potential of using an ALD to precipitate zinc as smithsonite ($ZnCO_3$) at a pH of 7.5 - 8.0. With a 14 hour retention time the laboratory system removed on average 50% of the influent zinc concentration (approximately 5.5 mg/L), and the field system 22% of the influent concentration (approximately 7.3 mg/L). Since then Jarvis and Younger (2000c) have applied this new technology to a discharge from an active mine in Scotland. Although the results of this work were mixed, they nonetheless suggested that given sufficient alkalinity generation zinc could indeed be removed in an ALD.

Perhaps as a consequence of the observation that many mine waters do not conform to the general stipulation of Fe^{3+}, Al and dissolved oxygen all less than 1 mg/L some researchers have recently begun to investigate the potential utility of open limestone channels (Ziemkiewicz *et al.*, 1997) or Oxic Limestone Drains (OLDs) (Cravotta and Trahan, 1999) for alkalinity generation *and* metal attenuation.

Ziemkiewicz *et al.* (1997) performed a range of laboratory and field experiments to compare the efficiency of armoured and unarmoured limestone in terms of acidity neutralisation. However, they only report acidity values, and never consider metallic ion concentrations. Whilst it may be argued that acidity reflects metals in solution insofar as they contribute to total acidity, it is nonetheless important to know influent and effluent metal concentrations for an holistic treatment approach. Ziemkiewicz *et al.* (1997) conclude that contrary to earlier reports armoured limestone was only 2 - 45% less effective than unarmoured limestone at neutralising acidity. However, they do not report in their conclusions the difference in time needed to either neutralise acidity or generate maximum alkalinity. In terms of time required, according to their results, unarmoured limestone is 33 - 83% more effective. Since contact time is critical to sizing of systems this is arguably the more significant result.

Cravotta and Trahan (1999) argue more persuasively for the use of oxic limestone drains (OLDs). These are not open limestone channels as examined by Ziemkiewicz *et al.* (1997), but are buried trenches such as ALDs. However they receive oxygenated water, certainly in excess of 1 mg/L dissolved oxygen. Cravotta and Trahan (1999) examined three identical OLDs in Pennsylvania, USA, with the objective of establishing hydrogeochemical processes within OLDs, and assessing their potential as a treatment unit, for a period of 1 year. pH and concentrations of calcium and alkalinity increased through the systems throughout the period of investigation, and acidity was consistently decreased. Throughout the sampling period the effluent water also contained less than 5% of the influent acidity, Fe and Al concentrations. Observations revealed that initially metal floc was present only in the first 1 m - 2 m of the OLD. This distance increased over time, and was matched with a gradual increase in removal of dissolved Mn, Co, Ni and Zn. After the 12 month period evidence of floc in the effluent water was noted. At the high velocities maintained (greater than 0.4 m/minute) it was hypothesised that floc would not precipitate and cause armouring and plugging, but would be transported through the OLD. However, visual evidence from many sites suggests that armouring may be caused by rapid oxidation and accretion of iron and aluminium. This evidence is in the form of thick accretions of iron and aluminium on rocks below mine water outfalls, where flow is turbulent. Rapid oxidation and accretion of iron is the very process used to successfully remove iron at the Kimblesworth reactors described in detail in Chapter 6 of this work. Cravotta and Trahan (1999) fail to account for the potential of this process to cause armouring OLDs.

Removal of trace metals, in particular Mn, was concluded to be due to sorption and coprecipitation reactions with hydrous oxides of Fe, Mn and to a lesser extent Al. The ratio of Mn/Fe and Mn/Al increased with distance through the OLD, commensurate with an increase in pH. Cravotta and Trahan (1999) cite the autocatalytic sorption and coprecipitation of Mn to $Fe(OH)_3$ as the predominant Mn removal process, represented as:

$$2\,Fe(OH)_{3(s)} + Mn^{2+} + 2\,H^+ \rightarrow MnO_{2(s)} + 4\,H_2O + 2\,Fe^{2+} \qquad (3.10)$$

Interestingly this is the reverse reaction of that proposed by Hedin and Nairn (1993) (Equation 3.6) for the *resolubilisation* of MnO_2 by Fe^{2+}, despite the fact that the pH ranges measured are almost identical (6.2 - 7.0 by Cravotta and Trahan (1999) cf. 6.1 - 7.4 by Hedin and Nairn (1993)). Given this information it is worth referring back to the work of Junta and Hochella (1994) discussed in Section 3.2.2. Perhaps it is the differing geometric nature of the Fe precipitates on organic substrates and calcite that causes the observed discrepancy in Mn adsorption onto the two different media.

This last hypothesis would clearly need clarification by further detailed investigation, but there is little doubt that the work of Cravotta and Trahan (1999) supports the notion that an OLD may be effective for acidity and metal attenuation. The authors are quick to recognise that long-term evaluation would be required to establish whether flushing of the precipitated hydrous oxides may occur, but suggest that with the incorporation of an underdrain system these flocs may be removed. Given an OLD's apparent ability to remove 'difficult' trace metals such as Mn and Zn these technologies clearly warrant further research.

Robbins *et al.* (1999) identified a range of bacteria and fungi in their studies which they felt may be influential in metal removal, as well as a potential source of difficulty due to fouling and plugging of limestone drains. However, the mechanisms of bacterial and fungal metal removal are not provided, and Robbins *et al.* (1999) conclude that further investigation would be required to establish the exact roles of these organisms in ALDs. Thornton (1995) and Brant and Ziemciewicz (1997) demonstrate the efficacy of biologically mediated Mn removal in limestone drains as an effective treatment process.

3.2.4 Successive Alkalinity Producing Systems (SAPS)

The condition that influent water to an ALD should have less than 1 mg/L Fe^{3+}, Al and dissolved oxygen has limited the application of this technology to many mine waters. In addition the potential for alkalinity generation by an ALD is limited to approximately 300 mg/L (Hedin *et al.*, 1994a), since this is the maximum observed increase in alkalinity for any one ALD. It is not possible to have two ALDs with an intervening aerobic step due to the need for anoxic conditions to be maintained (Kepler and McCleary, 1994). Where further alkalinity generation is required following an ALD a compost (anaerobic) wetland may be installed, since this may generate alkalinity via the dual processes of dissolution of carbonaceous material in the compost and dissimilatory sulphate reduction (see below). However, Kepler and McCleary (1994) argue that such a system may be prohibitively large, and have therefore proposed an alternative hybrid passive treatment option that they term a Successive Alkalinity-Producing System (or SAPS). More recently these systems have perhaps more accurately been referred to as Reducing and Alkalinity Producing Systems (RAPS) (Watzlaf *et al.*, 2000). In this configuration (illustrated in Figure 3.5) a layer of standing water provides the necessary head to drive water downwards through a layer of compost and then a layer of limestone, with discharge of effluent water at the base of the system.

The high oxygen demand of the organic substrate lowers dissolved oxygen concentrations to less than 1 mg/L (0.2 mg/L in the operational examples of Kepler and McCleary (1994)), and ensures reduction of any Fe^{3+} present to Fe^{2+}, thus eliminating the potential for armouring. Bacterially-mediated sulphate reduction (see below for details) generates alkalinity in the first instance, and subsequent dissolution of calcite in the limestone zone generates further alkalinity, with a concomitant decrease in acidity concentrations (Kepler and McCleary, 1994). Three examples of operational systems in Pennsylvania, USA, which all consistently removed 70 - 350 mg/L acidity as $CaCO_3$, are used to demonstrate the potential of these units (Kepler and McCleary, 1994). Analyses of influent and effluent iron concentrations demonstrate that very little iron is removed within these SAPS, and therefore armouring cannot be occurring to any great degree. Furthermore Kepler and McCleary (1994) suggest that a SAPS may entail considerably less land-take than alternative systems.

In addition to the three USA examples of operational SAPS provided by Kepler and McCleary (1994) this technology is now being investigated and implemented in the UK and the rest of Europe (eg. Laine, 1998; Ordóñez *et al.*, 1999; Younger, 1998b; Younger *et al.*, 1998), although performance data are sparse because the systems are either under construction or only in the very early stages of operation.

3.2.5 Anaerobic wetlands

If a mine water is net-acidic, but does not meet the criteria of low dissolved oxygen, Fe^{3+} and Al required for successful alkalinity generation using an ALD, the use of a compost or anaerobic wetland is recommended by Hedin *et al.* (1994a) (although a SAPS may also be used under these circumstances (Kepler and McCleary, 1994)). An effective compost wetland may serve the dual roles of generating alkalinity and removing metals (Eger, 1994). The former is widely accepted as being due to two processes (Hedin *et al.*, 1994a):

(i) dissimilatory sulphate reduction and
(ii) dissolution of carbonaceous material within the compost

Metal removal is predominantly attributed to (Walton-Day, 1999):

(i) sulphate reduction and
(ii) adsorption (to mineral phases / organic matter)

Typically a compost wetland is used as one part of the treatment process, in combination with aerobic wetlands (Hedin *et al.*, 1994a). The depth of compost used in such systems generally varies from 0.30 - 0.60 m (Hedin *et al.*, 1989; Hedin *et al.*, 1994a; see Chapter 4). In the USA spent mushroom compost has been the substrate of choice, though other materials such as rice hulls, sawdust and chicken litter have been experimented with, and have performed similarly to spent mushroom compost at the laboratory scale (Gross *et al.*, 1993). In a comparison of municipal compost, composted garden waste, mixed hardwood sawdust and horse manure, Eger (1994) found municipal compost to be the most effective in terms of sulphate reduction. In the UK, laboratory mesocosm studies by Younger *et al.* (1997) found a local stable waste to be more effective in lowering concentrations of both sulphate and iron than either farm waste or *in situ* organic material from the proposed wetland site. Rates of sulphate reduction in peat are thought to be slow due to the comparatively slow breakdown of complex organic compounds in this material (Eger, 1994). Irrespective of the substrate used Hedin *et al.* (1989) stress that it is important to maintain a free water surface above the substrate. Lowering of the water may result in oxidation of reduced sulphide species, which would then be remobilised.

The potential benefits for water quality of microbially mediated sulphate reduction have recently been summarised by Walton-Day (1999) as follows:

(i) increases in alkalinity and pH
(ii) precipitation of metal ions as insoluble sulphides within the wetland substrate, reducing aqueous metal and sulphate concentrations
(iii) production of reduced sulphur species which may degas to the atmosphere
(iv) reduced sulphur from sulphate reduction may be incorporated into organic complexes, thus reducing sulphate concentrations, and in some instances reducing proton acidity.

The utilisation of sulphate as a terminal electron acceptor for microbial respiration under anaerobic conditions is termed dissimilatory sulphate reduction[1], and the reaction can be written as (Walton-Day, 1999):

$$2\,CH_2O + SO_4^{2-} + 2\,H^+ \rightarrow 2\,CO_2 + H_2S + 2\,H_2O \qquad (3.11)$$

or

$$2\,CH_2O + SO_4^{2-} \rightarrow H_2S + 2\,HCO_3^- \qquad (3.12)$$

where CH_2O is a general expression representing carbohydrate. Mills (1999) points out that the predominant sulphate reducing genus, *Desulfovibrio*, cannot use carbohydrate directly, and therefore other microbial groups must first break down these complex organic compounds to simpler substances, such as acetate and lactate. At $pH < 4.5$ the sulphate reduction process may lead to an increase in pH (via the consumption of protons) without production of alkalinity (Equation 3.11), whilst at higher pH production of bicarbonate occurs (Walton-Day, 1999). Whether these reactions ultimately result in a measurable increase in pH and alkalinity depends on the fate of the H_2S produced, which is directly linked to the fate of metal ions, and to iron in particular (Walton-Day, 1999). Hedin *et al.* (1994a) detail both the various sinks for H_2S in a wetland environment and the net effects of these reactions on acidity and alkalinity. The information is reproduced in Table 3.1.

From a water quality viewpoint the advantage of these reactions over aerobic oxidation and precipitation of metals is that there is never a net increase in protons (and therefore decrease in pH), irrespective of the exact reaction mechanism (Walton-Day, 1999). Also Table 3.1 illustrates that there is invariably a reduction in mineral acidity (due to precipitation of metals) and / or an increase in alkalinity (Hedin *et al.*, 1994a).

Divalent metals other than iron will also form sulphides in the manner shown in Table 3.1, and the generalised reaction can be written as (Hedin *et al.*, 1994a):

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[1] in assimilatory sulphate reduction the reduced sulphate is incorporated into biochemical compounds and is therefore unavailable for further biogeochemical transformation (Walton-Day, 1999)

$$M^{2+} + H_2S + 2\,HCO_3^- \rightarrow MS + 2\,H_2O + 2\,CO_2 \qquad (3.13)$$

where M^{2+} represents a divalent metal ion. The readiness with which these metals will precipitate as a monosulphide (including iron) depends on the solubility product of the particular metal, the pH and the concentration of reactants (Hedin *et al.*, 1994a). The order in which metals will precipitate as sulphides according to their respective solubility products is given in Table 3.2 (CuS precipitates first and MnS precipitates last). Hedin *et al.* (1994a) suggest that removal of metals as sulphides occurs sequentially. Thus, only when the metal with the lowest sulphide solubility product is removed from solution to a concentration of less than 1 mg/L will the next metal be precipitated as a sulphide.

Reaction	Effect	
	Acidity[a]	Alkalinity[b]
(1) $H_2S + 2HCO_3^- \rightarrow H_2S(g) + 2HCO_3^-$	0	+100
(2) $H_2S + 2HCO_3^- + Fe^{2+} \rightarrow FeS + 2H_2O + 2CO_2$	-100	0
(3) $H_2S + 2HCO_3^- + 2Fe^{3+} \rightarrow S^0 + 2Fe^{2+} + 2H_2O + 2CO_2$	-100	0
(4) $H_2S + 2HCO_3^- + 2Fe(OH)_3 \rightarrow S^0 + 2Fe^{2+} + 2H_2O + 4OH + 2HCO_3^-$	+200	+300
(5) $H_2S + 2HCO_3^- + \frac{1}{2}O_2 \rightarrow S^0 + H_2O + 2HCO_3^-$	0	+100
(6) $H_2S + 2HCO_3^- + FeS + \frac{1}{2}O_2 \rightarrow FeS_2 + H_2O + 2HCO_3^-$	0	+100
(7) $H_2S + 2HCO_3^- + 2O_2 \rightarrow SO_4^{2-} + 2H_2O + 2CO_2$	0	0

[a] Effect based on change in mineral acidity (units are mg/L as $CaCO_3$).

[b] Effect based on summed change in bicarbonate and hydroxyl alkalinity (units are mg/L as $CaCO_3$).

Table 3.1 **Sinks for H_2S in constructed wetlands and their net effect on mine water acidity and alkalinity** (from Hedin *et al.*, 1994a).

The sulphate reducing bacteria (SRB) operate at an optimal pH of 5 - 9 (Eger, 1994), and are reported to be inactive at pH < 4.2 (Walton-Day, 1999). However, Hedin *et al.* (1989) document pore water pH values of 6-7 in wetlands receiving mine water with pH 3, and the pH is apparently therefore rarely a limiting factor to sulphate reduction in compost wetlands. Other conditions reported to be required for successful colonisation of SRB populations are the presence of suitable low-molecular weight organic compounds (lactate, acetate), the absence of oxidising agents such as O_2, Fe^{3+} and Mn^{4+}, and the presence of high sulphate concentrations (Hedin *et al.*, 1994a). Johnson *et al.*

(1993) have noted that some acidophilic SRB do not in fact grow in the low-molecular weight organic compounds mentioned above, but will colonise an acidified glycerol / yeast extract media.

Metal sulphide	Solubility product
CuS	4.0×10^{-38}
PbS	1.0×10^{-29}
ZnS	4.5×10^{-24}
CdS	1.4×10^{-23}
NiS	3.0×10^{-21}
FeS	1.0×10^{-19}
MnS	5.6×10^{-16}

Table 3.2 **Solubility products of some metal sulphides** (from Hedin *et al.*, 1994a).

The presence of SRB in compost wetlands and their role in metal attenuation within the substrate is in little doubt. However, Webb *et al.* (1998) have raised valid concerns that whilst the generalised mechanisms for metal removal and alkalinity generation via sulphate reduction are well established, and the general requirements for SRB colonisation are known, there has been little attempt to quantify the influence of different SRB species on metal attenuation. In their study Webb *et al.* (1998) cultured SRB populations from two natural and one constructed wetland. Solutions enriched with metals (Fe, Mn, Zn), and solutions containing various carbon sources, were then inoculated with the bacterial isolates. Subsequent chemical analysis of the solutions over a period of up to 8 days revealed significant differences in the generation of sulphide and the removal of metals. The authors attributed these differences to the different carbon source and the uniqueness of the SRB species composition for each wetland. In particular Webb *et al.* (1998) noted the significant difference of communities between a natural and a constructed wetland. Specifically bacterial communities from natural wetlands were observed to generate significantly more H_2S (critical to metal sulphide formation) than those from the constructed wetland, which clearly has implications for the efficiency of constructed systems. However despite this difference Webb *et al.* (1998) found no correlation between sulphide production and Fe removal, suggesting to them that other processes may be more influential in Fe dynamics. Zn removal showed a much better correlation with sulphide generation. Webb *et al.* (1998) make no reference to the solubility products of metal sulphides, but this stronger correlation is perhaps a consequence of the lower solubility product of ZnS than FeS (see Table 3.2). Also noted was a significantly lower metal removal rate when mixed solutions of cations rather than a single cation solution was used for these experiments, again suggesting that removal mechanisms may be more than a simple function of SRB activity and H_2S production. Finally, Webb *et al.* (1998) stress that the use of certain carbon sources by SRB (proprionate and acetate) was very limited, implying that the choice of substrate for compost wetlands may be crucial for successful metal attenuation. Webb *et al.* (1998) conclude that:

> *"At present there are no investigations of the carbon flow (nor presence of potential SRB substrates) within wetland treatment systems. It is inconceivable that such an important factor can easily be ignored when the efficiency of such systems may depend on the function of the SRB within it. It seems to be generally assumed that the bacteria will naturally function at an immutable preset activity level regardless of species composition or carbon flux. Sulphate-reducing bacteria populations will differ over time and between sites."*

The other metal attenuation processes which Webb *et al.* (1998) refer to may be metal adsorption, complexation and ion exchange. In her extensive review of metal sorption Smith (1999) notes that organic matter and the hydrous oxides of iron and manganese are amongst the most important adsorbents of dissolved metals. The composition, crystallinity and surface area of the adsorbent all influence the degree of adsorption, and in terms of the aqueous phase pH is critical. An increase in pH tends to favour the adsorption of cationic species, whereas a decrease in pH favours the adsorption of anionic species (Smith, 1999). The relative importance of metal adsorption to hydrous metal oxides and organic matter in constructed wetlands may vary between metals, due to competition for sorption sites and/or the presence of metal-specific binding sites (Smith, 1999). Smith (1999) provides an extensive list of the order of selective sorption of metals to a variety of adsorbent media.

In terms of its role in overall metal attenuation in a constructed wetland the contribution of metal sorption is considered to be minor in the long-term compared to other processes (Walton-Day, 1999). Machemer and Wildeman (1992) performed a range of laboratory and field studies investigating the role of adsorption. They conclude that adsorption may be a significant process during the early operation (on the scale of months) of a constructed wetland, but that saturation of sorption sites limits the long-term utility of this mechanism of metal removal. Competition for sorption sites favoured specific metals in the following order: Fe=Cu>>Zn=Mn. After this initial period sulphate reduction was considered to be the more dominant removal mechanism. Walton-Day (1999) concludes that adsorption and ion exchange reactions may not be a reliable method of metal attenuation in wetland systems because adsorbed metals may be remobilised and ion exchange reactions are readily reversible with changes in environmental conditions.

In addition to sulphate reduction other microbially-mediated mechanisms may be influential in metal attenuation and alkalinity generation. One particular mechanism which has received little attention in the relevant literature is that of iron reduction. If iron reduction is a significant process in constructed wetlands it has important implications, since the reduced form of iron, Fe^{2+}, is more mobile than Fe^{3+}. Sulphate reduction itself leads to the reduction of ferric iron, but in this instance the ferrous iron thus produced combines with sulphide to form an insoluble precipitate (see above) (Mills, 1999). Under anaerobic conditions Mills (1999) demonstrates how oxidation of glucose (Equation 3.14), and especially lactate (Equation 3.15), can generate alkalinity (and reduce Fe^{3+} to Fe^{2+}):

$$\begin{aligned} 3\,Fe(OH)_{3(s)} + 6\,(CH_2O) \rightarrow\; & CH_3CH_2OCOO^- + CH_3COO^- \\ & + CO_{2(g)} + 3\,Fe^{2+} + 4\,OH^- + 0.5\,H_{2(g)} + 4\,H_2O \end{aligned} \tag{3.14}$$

$$\begin{aligned} Fe(OH)_{3(s)}\; CH_3CH_2OCOO^- \rightarrow\; & CH_3COO^- + CO_{2(g)} \\ & + Fe^{2+} + 2\,OH^- + 1.5\,H_{2(g)} \end{aligned} \tag{3.15}$$

As iron precipitates as hydrous oxide in aerobic zones of a compost wetland it may sequester sulphate, which is thus transported to the anaerobic water/sediment interface (Mills, 1999). Direct diffusion of sulphate to these zones is minimal (Mills, 1999), and this may therefore be a significant factor in the rate of sulphate reduction in anaerobic wetlands. Subsequent reduction of iron in the anaerobic zone will both generate alkalinity and release sulphate, thus enabling sulphate reduction to occur simultaneously, and presumably encouraging the formation of insoluble iron sulphide (Mills, 1999). Figure 3.6 illustrates these processes, and furthermore illustrates the complexity of iron and sulphur cycling in wetland systems. In their earlier work Hedin *et al.* (1988) postulated that the contemporary design trend for wetlands, namely a horizontal flow system with a high surface:volume ratio, may encourage disconnection of aerobic and anaerobic zones due to increasing precipitation of iron oxyhydroxides in the relatively large aerated areas. The authors therefore suggest that a system designed such that influent water arises from the bed of the wetland and rises up through the substrate would favour anaerobic reactions, and in particular sulphate reduction. This may well be the case. Observations of high pH pore water in compost wetlands (Hedin *et al.*, 1989) certainly support the notion that effective generation of alkalinity is occurring in anaerobic zones *within* the substrate. However the more recent review of Mills (1999) suggests that the sediment/water interface, where aerobic and anaerobic processes meet, may be the most active area in terms of metal attenuation. If this is the case it would be pertinent to maintain the high surface:volume ratios of compost wetlands to maximise interactions at the sediment/water interface, but perhaps combine this with an upflow system as recommended by Hedin *et al.* (1988).

Adsorption of sulphate to metal precipitates other than iron may also be a significant means of sulphate attenuation, but Mills (1999) points out that whilst the role of iron is poorly researched, literature relating to the role of aluminium and manganese in this regard is non-existent.

The interaction of aerobic and anaerobic processes and pysicochemical and microbial processes within compost wetlands, typified by the sediment/water interface, makes these the most complex of passive treatment systems. In conclusion, the generalised mechanisms by which metals and acidity are attenuated in compost wetlands are widely cited as adsorption (Machemer and Wildeman, 1992; Smith, 1999; Walton-Day, 1999), carbonate dissolution (already detailed in Section 3.2.3), and especially sulphate reduction (eg. Hedin *et al.*, 1994a; Machemer and Wildeman, 1992; Mills, 1999; Walton-Day, 1999). However, whilst many of the biogeochemical reactions involved have been demonstrated in laboratory experiments such as those undertaken by Machemer and Wildeman (1992), the relative importance of each mechanism, and the

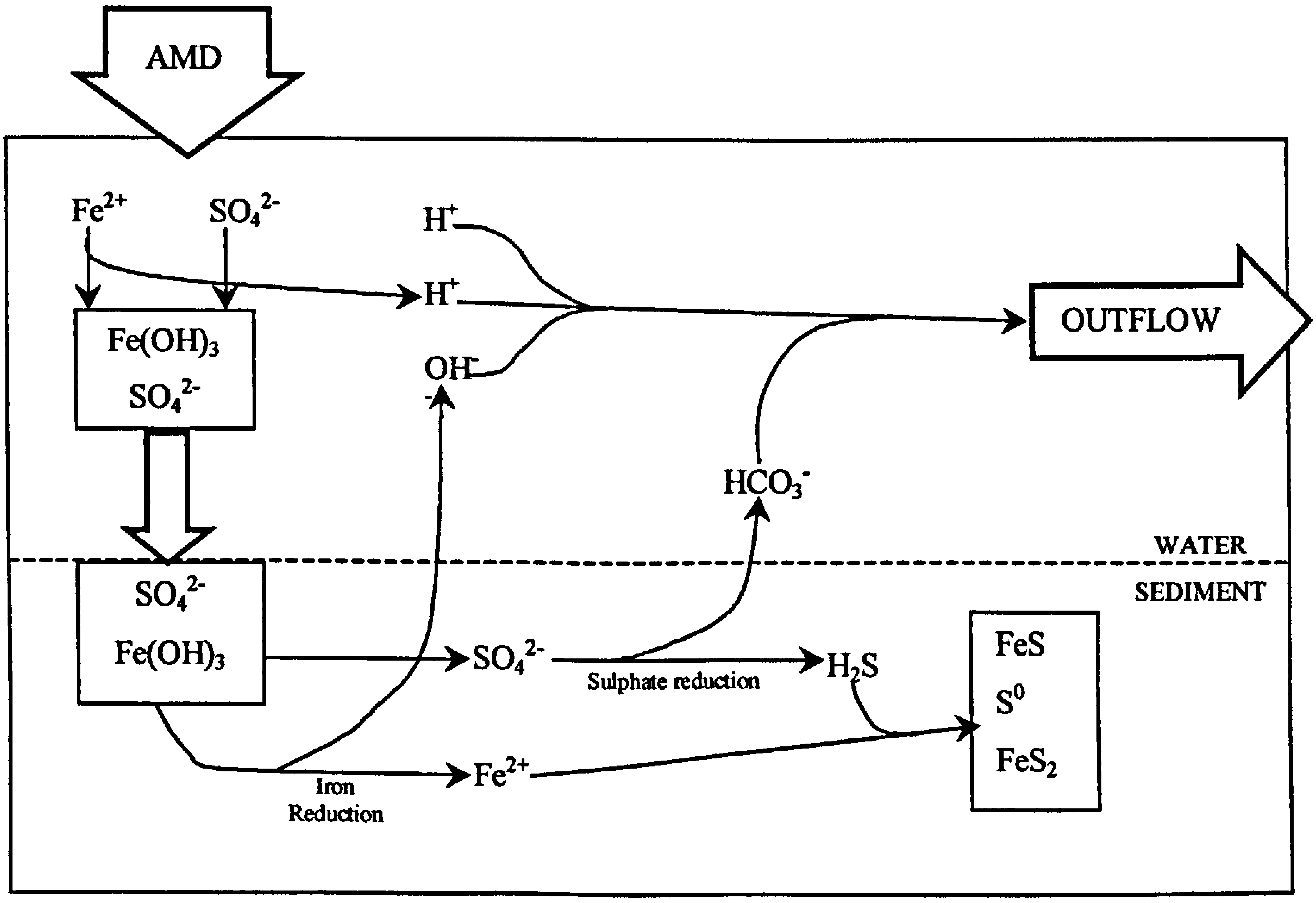


Figure 3.6 **The role of iron and sulphate in the neutralisation of acid mine drainage** (from Mills, 1999). The figure illustrates the potential role of iron reduction in metal cycling in wetlands, and also shows the complexity of iron and sulphur cycling in general.

significance of the interactions between aerobic and anaerobic processes at the sediment/water interface, are poorly understood. Even less is known about potentially crucial transformations such as microbially mediated reduction of other metals, and their subsequent influence on the rate and extent of sulphate reduction (Mills, 1999). Webb *et al.* (1998) have forcefully argued that a lack of research into carbon and sulphur cycling in wetlands is a serious impediment to our further understanding of these systems. All of these issues clearly have ramifications for design of wetland systems, which probably apply to both anaerobic and aerobic wetlands, since the latter too will invariably contain anaerobic zones. Design of efficient systems will only be possible when we possess a clearer picture of which of the numerous mechanisms involved are quantitatively important. Until that time design will inevitably have to be based on the empirical formulae derived from operational systems, such as the widely applied equation of Hedin *et al.* (1994a).

3.3 Design and performance assessment of passive systems

Effective monitoring of a constructed wetland is crucial. Firstly it will establish whether the wetland effluent is meeting any regulatory requirements. Secondly it should enable an assessment of the efficiency of the wetland to be made, the results of which can be fed back into future designs, hence improving the efficiency and reliability of future systems. However, there has been some debate as to the most effective way of monitoring constructed wetlands in such a manner that the results of monitoring from different constructed wetlands can be usefully compared. The simplest and cheapest approach to monitoring is simply to measure concentrations of contaminants at influent and effluent points. This is known as treatment efficiency, and has been adopted largely because effluent concentrations are normally the regulatory basis of compliance (Tarutis *et al.*, 1999). Using the notation of Tarutis *et al.* (1999) this is calculated as follows:

$$(C_{in} - C_{out})/C_{in} \times 100 \tag{3.16}$$

where, C_{in} = influent concentration

C_{out} = effluent concentration

However, treatment efficiency is a relative measure (Tarutis *et al.*, 1999), which takes no account of either flow-rate to the system or wetland size (Hedin *et al.*, 1994a). Hedin and Nairn (1993) and Hedin *et al.* (1994a) therefore propose an alternative measure based on contaminant load. From Hedin *et al.* (1994a), using iron as an example, the calculations are as follows:

$$\text{Fe (g/d)}_{in} = 1.44 \times \text{Q (L/min)} \times \text{Fe (mg/L)}_{in} \tag{3.17}$$

$$\text{Fe (g/m}^2\text{/d)}_{in} = \text{Fe (g/d)}_{in} / \text{SA} \tag{3.18}$$

$$\text{Fe (g/d)}_{rem} = \text{Fe (g/d)}_{in} - \text{Fe (g/d)}_{eff} \tag{3.19}$$

$$\text{Fe (g/m}^2\text{/d)}_{rem} = \text{Fe (g/d)}_{rem} / \text{SA} \tag{3.20}$$

where, Q = flow-rate

Fe_{in} = influent Fe concentration, load, or loading rate

Fe_{eff} = effluent Fe concentration, load, or loading rate

Fe_{rem} = Fe removed, absolute (g/d) or per unit area (g/m^2/d)

SA = wetland surface area (m^2)

Equation 3.17 calculates the Fe load, by multiplying flow-rate by concentration and a unit conversion factor (1.44). Loading rate to the wetland per unit area can be calculated in Equation 3.18. Subtracting effluent Fe load from influent Fe load gives the Fe load removal figure (Equation 3.19), which is then divided by surface area to provide an area-adjusted removal rate (Equation 3.20). Recognising that measurement of both influent and effluent flow-rates may not always be feasible Hedin and Nairn (1993) suggest the use of the conservative ion magnesium to calculate a dilution factor (DF) to account for diluting inflows:

$$\text{DF} = \text{Mg}_{eff} / \text{Mg}_{in} \tag{3.21}$$

Thus, a dilution-adjusted Fe removal figure can be calculated:

$$\text{Fe}_{rem} = \text{Fe}_{in} - (\text{Fe}_{eff} / \text{DF}) \tag{3.22}$$

Monitoring in terms of contaminant loadings in this way enables data to be subsequently used for design calculations (Hedin *et al.*, 1994a), as described below. In addition Hedin *et al.* (1994a) only investigated systems where the effluent iron concentration was greater than 2 mg/L. The reason for this was that Hedin *et al.* (1994a) felt that more could be learned about the rate of biogeochemical reactions in constructed wetlands that did not remove all of the contaminants. Use of area-adjusted removal rates has been adopted by many groups involved in constructed wetland monitoring, including Eger (1994) and Mitsch and Wise (1998).

Stark and Williams (1995) have expressed some concerns in the use of area-adjusted removal rates, favouring treatment efficiency in some circumstances. For example, in their investigation of 35 natural wetlands Stark and Williams (1995) found treatment efficiency to be a better indicator of Fe and Mn retention. However, the authors reached their conclusions by undertaking numerous correlations between the influent and effluent concentrations of the key contaminants and the two performance indices (treatment efficiency and area-adjusted removal). Tarutis *et al.* (1999) have more recently suggested that such correlations must be interpreted very cautiously, since all of the performance indices used are derived from essentially the same operating data. Apparent results may therefore be artefacts of the analysis. In any case treatment efficiency data alone are insufficient for design purposes. Indeed Kadlec and Knight (1996) describe such data, in the context of design, as *"...nearly useless when used outside the context of surface water concentrations and hydraulic loading rates"*.

Tarutis *et al.* (1999) have recently compared treatment efficiency and area-adjusted mass removal indices as measures of performance and utility as design tools. This exceptional piece of research arguably represents the future direction of design calculations for constructed wetlands, and is central to this work (see Discussion). It is consequently discussed in some detail below. To appreciate the full implications of this work however, it is worth first presenting the widely applied empirical formula for sizing of constructed wetlands, derived by Hedin *et al.* (1994a) from Equation 3.20 above.

Hedin *et al.* (1994a) studied 13 varied constructed wetland systems in western Pennsylvania, USA, using the area-adjusted mass removal monitoring scheme outlined above, and incorporating the dilution factor in all cases. The authors only investigated wetlands that always received contaminant concentrations of a magnitude great enough to ensure that the system would never be limited due to a lack of the contaminant. Hedin and Nairn (1993) explain that at completely effective systems contaminant removal rates are limited under very low loading conditions, and as a consequence most information will be gleaned from systems that are effectively undersized. Sites where effluent contaminant concentrations were less than 2 mg/L were excluded. Based on these constructed wetlands Hedin *et al.* (1994a) have calculated average removal rates (in $g/m^2/d$) for these systems, and used these as the basis for sizing guidelines, as shown in Table 3.3. These removal rates (RR) are used to calculate wetland area required by dividing the daily influent load (either Fe for net-alkaline waters or acidity for net-acidic waters) by the appropriate number:

$$\text{Wetland area } (m^2) = \text{loading } (g/d) \,/\, RR \qquad (3.23)$$

	Abandoned Mined Land Criria, $g/m^2/d$		Compliance Criteria, $g/m^2/d$	
	Alkaline	Acid	Alkaline	Acid
Fe	20	NAp	10	Nap
Mn	1.0	NAp	0.5	Nap
Acidity	NAp	7	Nap	3.5

Table 3.3 **Recommended sizing for passive treatment systems** (from Hedin *et al.*, 1994a). Wetland area required is calculated by dividing influent contaminant load by the relevant removal rate.

Hedin *et al.* (1994a) explain that the abandoned mined land criteria have been developed for those sites where a significant improvement in water quality is required, but where consistent adherence to regulatory standards may not be necessary. Where regulatory standards have to be rigorously met the more conservative compliance criteria are recommended. Hedin *et al.* (1994a) include this because the authors recognised that there may not be a linear relationship between removal rate and influent iron concentration. Specifically, as influent iron concentration decreases the removal rate decreases, and therefore the relative size of wetland required will increase.

It is this issue of the kinetics of contaminant removal at differing concentrations that is central to much of the discussion of Tarutis *et al.* (1999). Because the empirical formula above is independent of concentration, as Hedin *et al.* (1994a) recognise, the sizing method implicitly assumes the contaminant removal reaction conforms to zero-order kinetics. Assuming constant flow-rate throughout the wetland, this equates to:

$$k_0 = (C_{in} - C_{eff})\, Q/A \qquad (3.24)$$

where, k_0 = zero order reaction

This is equivalent to Equation 3.20, as proposed by Hedin *et al.* (1994a), and therefore k_0 can be determined empirically as shown by Hedin *et al.* (1994a). Tarutis *et al.* (1999) propose that contaminant removal in a wetland is better represented by a first-order reaction, since both the oxidation of iron to form hydrous ferric oxide and the reduction of iron to form a sulphide are known to be first order with respect to iron. For receiving watercourses the first-order rate of iron oxidation has already been demonstrated in Section 3.2.2 (see Equation 3.3). Again assuming a constant flow through the entire wetland:

$$k_1 = Q/A \ln (C_{in} / C_{eff}) \qquad (3.25)$$

where k_1 = first-order reaction coefficient

As with Equation 3.24 the units are Q as m^3/d, C as g/m, A as m^2, but k_1 as m/d rather than $g/m^2/d$ for k_0.

Tarutis *et al* (1999) argue that the use of a first-order rate equation is a closer representation of the actual rate of reactions within a constructed wetland, and provide supporting evidence from constructed wetlands in the USA. Flanagan *et al.* (1994) and Mitsch and Wise (1998) have modelled iron oxidation in wetlands using a first-order rate model, and Tarutis and Unz (1994) have also adopted first-order kinetics for modelling decomposition and sulphide precipitation under reducing conditions.

Because the flow-rate and concentration components are separated in a first-order reaction formulation a much better comparison between the performance of different systems can be made than using the alternative zero-order reaction model. Consequently better design guidelines might be obtained. Area-adjusted removal makes no such division between the flow-rate and concentration components. Thus, for example, a high flow, low concentration discharge may be equivalent to a low flow, high concentration discharge.

Rearranging Equations 3.24 and 3.25 to provide sizing guidelines produces

$$A = (C_{in} - C_{eff})\, Q/k_0 \tag{3.26}$$

and

$$A = Q/k_1 \,\ln (C_{in} / C_{target}) \tag{3.27}$$

respectively (where C_{target} is target effluent concentration). A comparison of the effect of using these two equations for wetland sizing is shown graphically in Figure 3.7. The graph shows that using the area-adjusted design calculation for high flow, low concentration discharges will result in undersizing if removal obeys first-order kinetics. Conversely wetlands receiving high concentration discharges (greater than the equivalence point, EP) will be oversized.

Whilst the first-order removal design approach appears to be a promising and more accurate alternative to the area-adjusted method, Tarutis *et al.* (1999) highlight the fact that whilst empirical values for k_0 have been widely determined through previous studies, no such values are available for k_1. The authors suggest that the lack of such data is an issue that needs addressing. In the absence of such information they recommend the use of a median value (k_1 = 0.18) obtained during their study of 35 natural wetlands. This may be the best data currently available for such calculations, but the fact that this figure is drawn from natural wetlands only is of some concern.

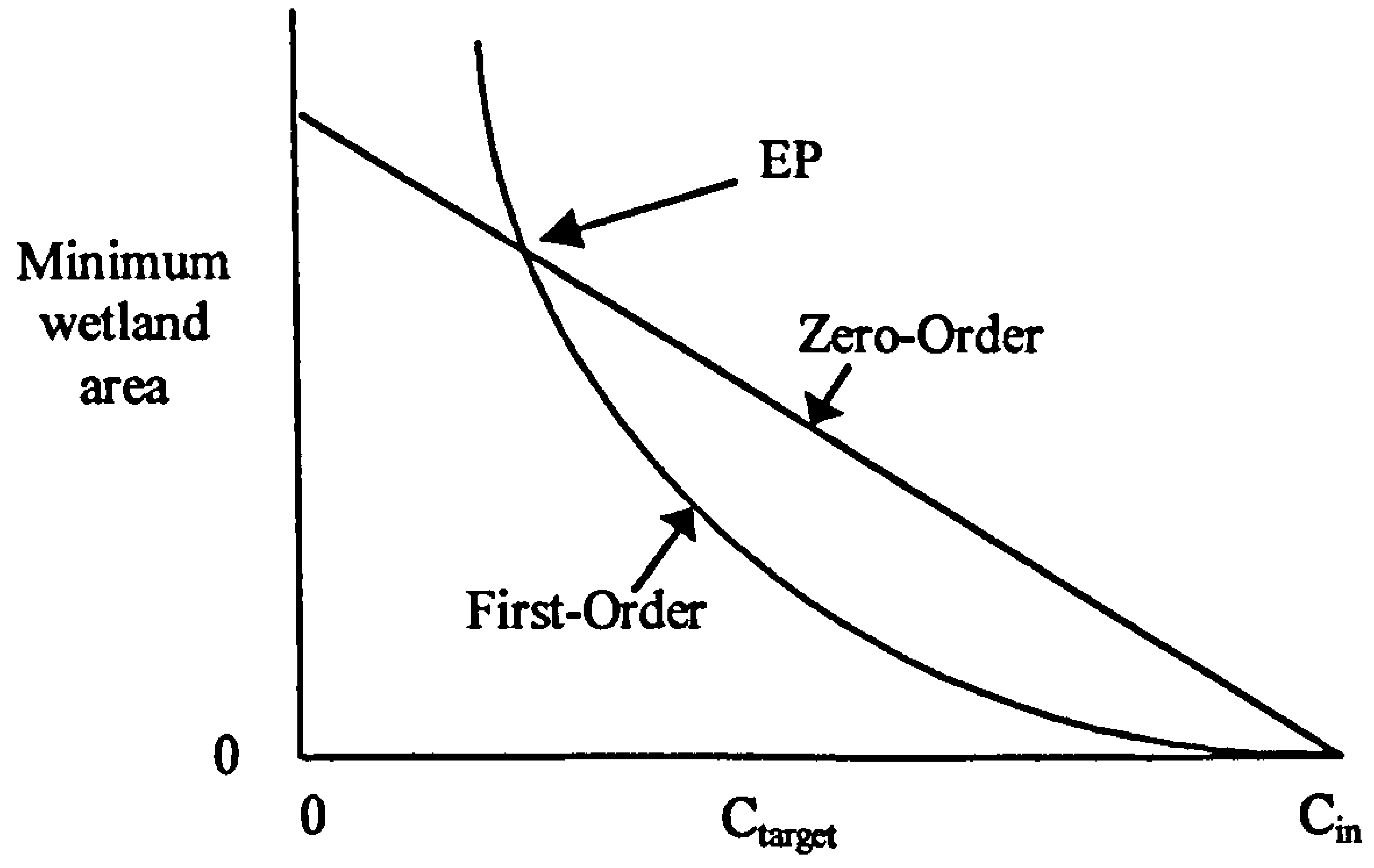


Figure 3.7 **Graphical comparison of minimum wetland area requirements assuming zero-order (area-adjusted) or first-order removal.** For relative influent concentrations less than the equivalence point (EP), using area-adjusted removal results in undersized wetlands. For concentrations greater than EP, oversized wetlands result. Zero-order equation: $A=(C_{in} - C_{target})Q/k_0$; first-order equation: $A=Q/k_1 \ln(C_{in}/C_{target})$ (from Tarutis *et al.*, 1999).

McGinness *et al.* (1996), for example, have suggested that the trend towards an engineering emphasis in constructed wetlands, rather than attempts to replicate the biological dynamism of natural systems, may ultimately result in less effective systems. In their particular study McGinness *et al.* (1996) noted significantly less organic content in sediments of constructed wetlands, and a correspondingly lower plant and bacterial diversity than in natural wetlands. A pressing research topic may therefore be the establishment of values of k_1 for a range of constructed wetlands.

On the basis of laboratory mesocosm studies by Manyin *et al.* (1997), Tarutis *et al.* (1999) also mathematically describe the effect on wetland area of altering flows and concentrations whilst maintaining a constant loading. For first-order removal Tarutis *et al.* (1999) introduce what they term a 'concentration factor', f, and graph the wetland area predictions at a range of flow and concentrations with constant loading rate (i.e. $QC_{in} = fQ^*C_{in}/f$). Incorporating the concentration factor into Equation 3.27 produces:

$$A = fQ/k_1 \ln[C_{in}/(fC_{target})] \qquad (3.28)$$

Using this formulation Figure 3.8 shows that for a constant loading the predicted wetland area will vary depending upon the concentration and flow-rate. Whether flow-rate leads to an increase in predicted wetland size depends on influent concentration. Specifically, at a constant loading an increase in flow will result in a decrease in predicted wetland area only if $C_{in}/C_{target} < 2.718$ i.e. the discharge is only moderately polluted. If $C_{in}/C_{target} > 2.718$ a higher flow-rate will require a larger wetland area (Tarutis *et al.*, 1999). It is for this reason that, for high flow low concentration discharges, the area-adjusted model for wetland sizing always predicts area requirements that are insufficient and *vice versa.*

For future calculations of k_1 to be accurate, background concentrations of contaminants must be accounted for. In mine water treatment wetlands such background concentrations may arise from solubilisation of metal oxides within sediments. Ignoring background concentrations will result in underestimation of k_1, and consequent oversizing of wetlands. Tarutis *et al.* (1999) therefore modify Equation 3.25 thus:

$$A = Q/k_1 \ln[(C_{in} - C^*)/(C_{target} - C^*)] \qquad (3.29)$$

where, C^* = background concentration

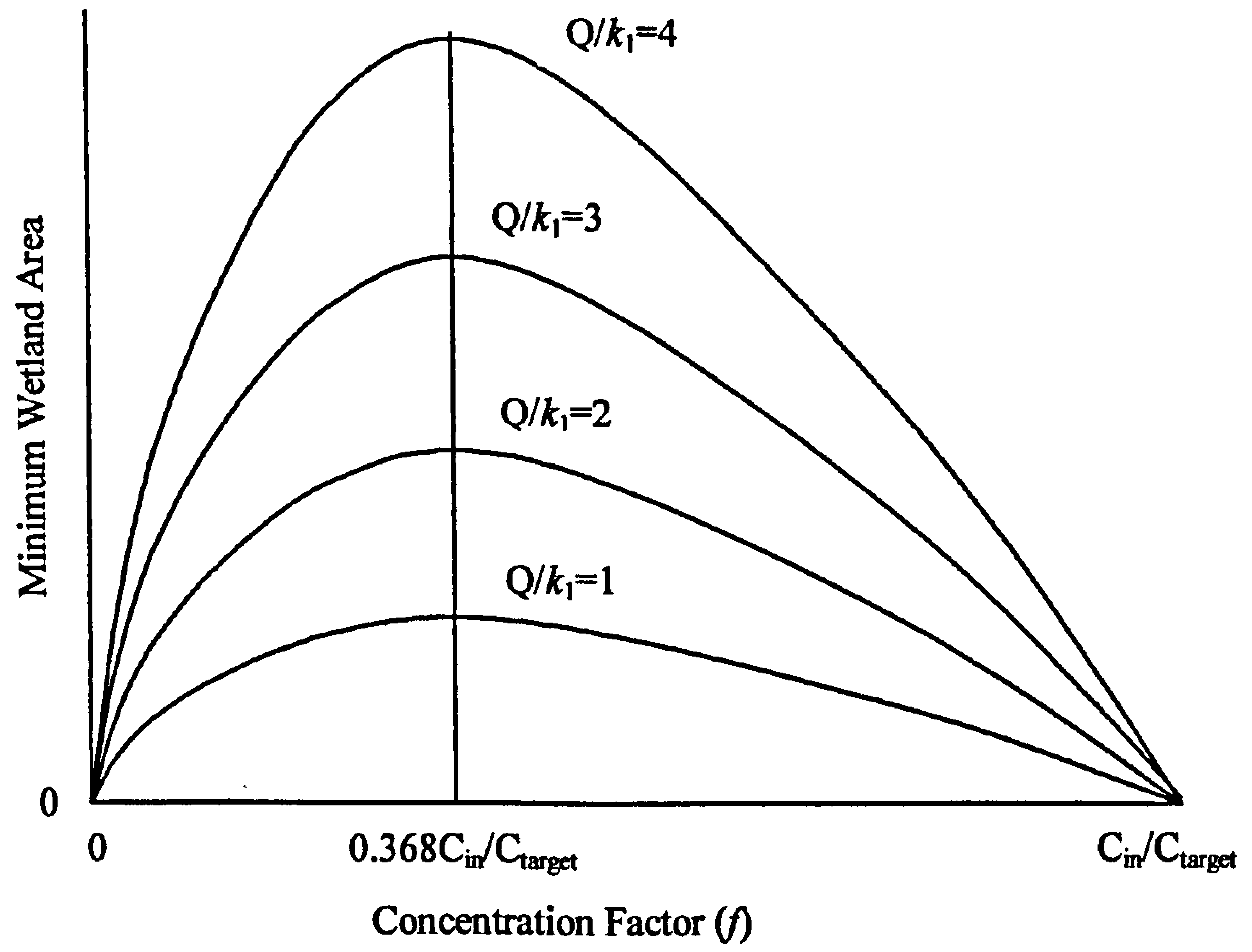


Figure 3.8 **Graphical representation of the effects of flow rate and concentration on minimum area requirements assuming first-order removal.** Each line represents the predicted wetland area for a constant metal loading rate (QC_{in}). The 'concentration factor' f accounts for changes in relative influent concentration due to varying flow rates while keeping the metal loading rate constant (ie. $fQ*C_{in}/f$). Generalised equation: $A=fQ/k_1 \ln[C_{in}/(fC_{target})]$. Predicted area maxima occur when f is 0.368 times the relative influent concentration (from Tarutis *et al.*, 1999).

To this author's knowledge the work of Tarutis *et al.* (1999) is the first generalised mine water wetland sizing equation proposed which is based on first-order kinetics as opposed to zero-order kinetics. First-order rate models for specific metal attenuation mechanisms have been developed, as referenced above, and wetland sizing equations based on first-order kinetics for wetlands removing contaminants such as Biochemical Oxygen Demand and phosphorous have also been developed (Kadlec and Knight, 1996). As such equations become more refined, not least with more accurate calculations of the rate constant k_1, it seems likely that first-order removal equations will come to the fore in terms of reliable constructed wetland sizing for mine water treatment. However, whilst a first-order model may go some way to improving descriptions of constructed wetland removal mechanisms, Tarutis *et al.* (1999) point out that other physical, chemical and biological factors may also play a significant role. Such factors may include physical layout (eg. length to width ratio), aspect, seasonality, plant abundance and diversity, microbial activity, and hydraulic routing to name but a few.

3.4 Passive *in situ* remediation of mine water pollution

3.4.1 Reactive Barriers

Permeable reactive barriers are emerging as a potential alternative passive mine water treatment system in appropriate locations. At the most basic level a reactive barrier is a wall of reactive material placed in the path of a polluted groundwater flow, as illustrated in Figure 3.9 (Gavaskar *et al.*, 1998). Most applications of such systems have been in the amelioration of groundwater polluted with chlorinated solvents, for which granular zero-valent iron has been effectively used as the barrier media (Gavaskar *et al.*, 1998). Gavaskar *et al.* (1998) provide extensive details regarding the design, construction and performance of reactive barriers for organic waste remediation, but do not consider the application of the technology to mine water treatment. Benner *et al.* (1997) have constructed and monitored a reactive barrier for treatment of a low pH, high iron concentration, tailings discharge in Ontario, USA. The barrier is 3.6 m deep, 15 m long and 4 m thick. The barrier media consists of municipal compost, leaf compost, wood

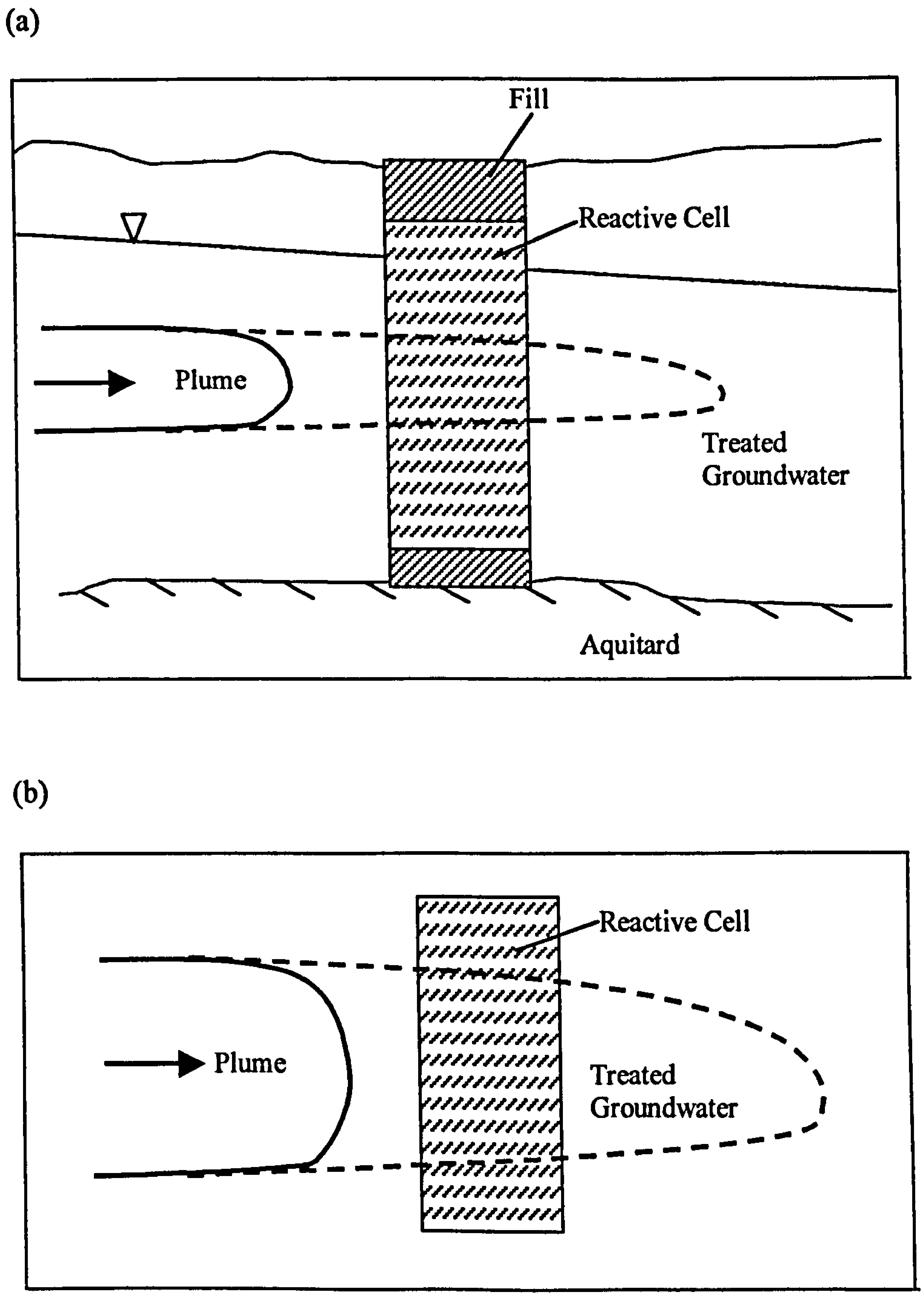


Figure 3.9 **Elevation (a) and plan (b) view of simple permeable reactive barrier** (from Gavaskar *et al.*, 1998).

chips and pea gravel. These media were selected with the objective of maximising sulphate reduction, and hence removal of iron as a monosulphide, with concomitant generation of bicarbonate alkalinity. Benner *et al.* (1997) showed significant reductions in sulphate, iron and acidity concentrations, and increases in pH and alkalinity. The authors estimate the lifetime of the system to be in the region of 15 years. The most significant potential problem identified by Benner *et al.* (1997) is maintaining a constant hydraulic conductivity across the barrier media. Development of preferential flow paths may cause notable reductions in treatment efficiency.

The cost of installation of this reactive barrier system was $30 000 (Benner *et al.*, 1997), which is approximately equal to the cost of an anaerobic compost wetland in County Durham, UK, which also treats spoil heap leachate (£18 000) (see Chapter 4). However, the wetland system described in Chapter 4 treats an average flow volume of 100 L/minute, whereas the reactive barrier of Benner *et al.* (1997) only treats approximately 0.5 L/minute. However, reactive barriers appear to occupy less land than alternative passive treatment options, and since land area requirements have often been viewed as one of the major impediments to construction of wetland systems, this is a major advantage of reactive barriers. Reactive barriers may increasingly become an attractive option for *in situ* remediation of spoil heap leachate, where groundwater flow patterns in the near subsurface are well understood. It seems less likely that they will find much application for discharges arising from deep mines however.

The author and his colleagues have recently observed that a spoil heap in County Durham, UK, contains areas of very highly contaminated water when compared with other locations within the heap. This led them to conclude that it may be possible to undertake a programme of selective grouting of the spoil, aimed at limiting the oxidation of pyrite in these pollution 'hot spots'. Such an approach may be viewed as 'at-source pollution prevention', rather than remediation (see below), but it remains to be seen whether this particular method of control would be feasible.

3.4.2 Prevention at source

Ideally prevention of mine water pollution at source would be a more attractive option than the curative technologies so far discussed. Prevention (or at least limitation) of sulphide mineral oxidation would be one such preventative strategy. Nyavor and Egiebor (1995) and Georgopoulou *et al.* (1996) have investigated the potential application of iron phosphate coating of pyrite as a method of limiting its oxidation, in much the same manner as phosphate coating is used to prevent corrosion of metals. Georgopoulou *et al.* (1996) suggest that successful coating of spoil heaps in this way may be a cheaper alternative to lime dosing treatment of the potentially contaminated effluent from them. However, the authors concede that the long term durability of the coating requires investigation. The experiments of both Nyavor and Egiebor (1995) and Georgopoulou *et al.* (1996) were performed at the laboratory scale. Neither group discusses how such technology may be applied to actual mining situations.

3.5 Active treatment of mine waters

Younger (2000d) defines active treatment as "...the improvement of water quality by the sustained input of reagents and/or energy". Most commonly this involves settlement, oxidation and alkali dosing (Younger, 2000d). Settlement alone may be sufficient treatment where:

i. the discharge is net-alkaline
ii. $pH > 6.5$ after the initial aeration step, and
iii. the only contaminant is iron.

Such systems should allow for adequate aeration, and should be large enough to allow for the relatively slow settlement of ferric hydroxide (Younger, 2000d). In other cases settlement must be preceded by oxidation and alkali dosing. Oxidation of Fe and Mn is required to allow them to precipitate in their most insoluble form (i.e. Fe^{3+} and Mn^{4+}) (Freeman and Harris, 1995). Calcium hydroxide is the most widely used alkali dosing agent (Younger, 2000d). Younger (2000d) discusses the relative benefits of other alkali reagents at length, and also demonstrates how the volume of alkali required is calculated for any given discharge. Both Freeman and Harris (1995) and especially Younger (2000d) provide detailed reviews of metal removal by oxidation, alkali dosing and settlement, and further details will not be given here.

Alkali dosing and settlement is a proven technology which has been widely applied to the treatment of mining effluents (Freeman and Harris, 1995). However, the relatively high operating and maintenance costs, coupled with the generation of substantial volumes of metalliferous sludge (Freeman and Harris, 1995) have resulted in the development of a range of other innovative technologies which may be classified as active treatment. Younger (2000d) has recently summarised current options as follows:

1) Sulphidisation - involving reduction of sulphate to sulphide, and subsequent precipitation of metals as sulphides (as in a compost wetland).
2) Sorption and ion exchange to minerals / organic surfaces.
3) Membrane processes.

Younger (2000d) details the current research status of these various fields, which will not be expanded upon here.

3.6 Costs of active and passive treatment

Cost is a key consideration during planning of remediation schemes, and may often be the main decision-making tool (Wieder *et al.*, 1989). The low cost of passive treatment options, and in particular the low operating costs associated with them, are often cited as one of their biggest advantages over more conventional active treatment (Kadlec, 1995). Minimal operating costs can be achieved by ensuring proper design and construction, especially with respect to embankments, spillways, and freeboard availability (Hedin *et al.*, 1994a).

Cost per unit area has often been used as a measure of wetland construction. For example Wieder *et al.* (1989) report that the costs of the Tennessee Valley Authority wetlands range from \$3.58/m^2 to \$32.03/m^2. In the UK Younger and Harbourne (1995) report an average cost of £51/m^2, comparable to the figure of £41/m^2 calculated in Section 4.3.3, but much greater than the £5/m^2 reported by Laine (1998) for the Woolley aerobic system, UK.

In terms of the absolute cost of a passive system compared to an active system the IMP1 aerobic wetland system in Tennessee cost \$43 000 to construct (in 1985), and \$13 000 / annum maintenance from 1985-1990, making a total cost of \$121 000 (Brodie, 1993). In comparison chemical treatment costs for this discharge were calculated at \$250 000 for the period 1985-1991 (Brodie, 1993). Recent estimates from a mine water treatment feasibility study for a site in the UK calculated costs for active treatment at approximately £170 000 plus £32 500 / annum maintenance, compared to £145 000 plus £3 400 / annum maintenance for a passive alternative (Bullen Consultants, 1999). Thus, whilst initial capital outlay may be similar, long-term maintenance and operation costs for passive treatment systems may be far less.

3.7 Summary of key issues

1) The primary objectives of passive treatment are the generation of alkalinity (and increase of pH) and / or the removal of metal ions as immobile precipitates. Many of the processes encouraged within a passive treatment system are mechanistically similar to those of metal attenuation in watercourses receiving mine water pollution.
2) Aerobic wetlands are recommended for mine waters that are net-alkaline (i.e. alkalinity > acidity). Usually vegetated, these systems remove metals primarily through oxidation and precipitation reactions. Removal of manganese in aerobic systems has proved unpredictable because the exact removal mechanisms, and especially the role of bacteria, are unclear.
3) The key objective of an Anoxic Limestone Drain (ALD) is the generation of alkalinity via carbonate dissolution. Successful long-term operation dictates that influent concentrations of Fe, Al and dissolved oxygen be less than 1 mg/L. More recently the use of Oxic Limestone Drains (OLDs), for generation of alkalinity *and* removal of metals, has been investigated, but their long-term effectiveness is unclear.
4) The Successive Alkalinity Producing System (SAPS) is a development of the ALD. Water flows downwards through a layer of compost, encouraging anoxic conditions, and then through a layer of limestone to generate alkalinity. These units are purported to require far less land than alternative passive treatment systems.

5) Anaerobic (compost) wetlands are appropriate for net-acidic waters. The key objective is to encourage dissimilatory sulphate reduction, which serves the dual roles of removing metals as sulphides under anaerobic conditions, and generating alkalinity. Whilst the important role of sulphate reducing bacteria (SRB) is in little doubt there have been few attempts to quantify differences in wetland system performance in terms of SRB populations and numbers. In addition the significance of other microbial groups, such as the iron reducers, is poorly understood.
6) Monitoring the performance of operational passive treatment systems is crucial for effective future design. The most common measures of performance are treatment efficiency and area-adjusted removal. The latter is the basis for the commonly applied empirical design formula of Hedin *et al.* (1994a). The research of Tarutis *et al.* (1999) suggests that the oxidation and precipitation of iron, and the removal of iron as a metal sulphide, are both first-order reactions. However, area-adjusted removal is based on zero-order kinetics. As a consequence sizing of wetlands based on the commonly applied formula of Hedin *et al.* (1994a) may result in undersizing or oversizing, depending on the absolute contaminant load and influent concentration. Tarutis *et al.* (1999) argue that knowing a value for the first-order removal of contaminants would enable the development of more effective design tools for wetland treatment systems.
7) Most common amongst the active treatment options is alkali dosing and settlement. Other processes, such as sulphidisation, sorption and ion exchange, and membrane processes, have been reviewed by Younger (2000d).
8) If they are properly constructed passive treatment systems cost less than active treatment options, mainly because the long-term operation and maintenance costs associated with passive treatment are much lower.

CHAPTER 4

DESIGN AND CONSTRUCTION OF THE QUAKING HOUSES COMMUNITY WETLAND

4.1 Introduction

Details regarding the design and construction of the wetland at Quaking Houses are described in this section. The final design of the wetland was strongly governed by two insurmountable design constraints, the nature of which are discussed below. In addition, however, the design of the constructed wetland was guided wherever possible by the desires of the local community, who were central to the entire project. Consequently, whilst effective mine water treatment was always the primary objective of all parties concerned, aesthetic considerations sometimes took priority over the need for the wetland to be a dedicated scientific research resource. It is for this reason that the wetland is not rectangular, even though such a shape would have made the calculation of such variables as areal removal rates far simpler.

The detailed design of both the pilot-scale and full-scale wetlands at Quaking Houses was undertaken by this author under the direction of Dr. Paul Younger (University of Newcastle upon Tyne). The author undertook all of the site engineering for the full-scale wetland, including site surveys, materials procurement and contractor supervision. The design and construction process, including details of construction materials and costs are described in this chapter.

4.2 Origins of the Quaking Houses mine water

The Morrison Busty Colliery, sited above the head of the Stanley Burn, won coal between 1927 and 1973 (Kemp and Griffiths, 1999). One of the most obvious legacies of the Morrison Busty workings is a 35 hectare spoil heap which is clearly visible around the former colliery (see Figure 1.1, Section 1.4), and this is the source of the mine water which now decants into the Stanley Burn (Younger *et al.*, 1997). However, according to local residents pollution of the Burn did not begin at the time of mine closure in 1973 (Kemp and Griffiths, 1999). Rather, it is thought that pollution began in 1986-87 during construction of the cutting that now carries the A693 road. Recent open-casting of the shallowest seams in the area has revealed that these are all dry. This is because when the Morrison Busty colliery was closed it was ensured that water would flow eastwards to the Kimblesworth mine water pumping station (Younger *et al.*, 1997), which is still operational at the time of writing (see Chapter 6). Therefore the mine water discharge to the Stanley Burn cannot originate from the deep workings. It appears that the construction of the road encouraged infiltration into the spoil, which led to the development of a perched aquifer within the heap. Simultaneously disturbance of the spoil led to oxidation of sulphide minerals in the spoil heap generating ferruginous and acidic waters, which continue to migrate via a road drainage system ultimately into the Stanley Burn. Figure 4.1 is a typical photograph of the mine water discharge during the mid-1990s, when aluminium hydroxide precipitates and 'froths' were common sights around the area of the discharge. Further downstream deposits of orange iron oxyhydroxides were also evident during this period.

4.3 The Quaking Houses Community wetland

4.3.1 Pilot-scale investigations into treatment feasibility

The predecessor of the present Environment Agency in England (the National Rivers Authority) instigated a feasibility study for treatment of the Stanley Burn in 1995, following persistent lobbying by the residents of the village of Quaking Houses. The outcomes of this investigation (which was undertaken by Nuwater Consulting Services Ltd., in association with Newcastle University) are reported in full by Jarvis *et al.* (1995), and more concisely by Younger *et al.* (1997). A key objective of the feasibility study was to design a treatment system that would be inexpensive in terms of both initial installation costs and long-term operating and maintenance costs. For this reason the investigative team adopted passive treatment technology as the preferred option, following recent successes with such systems in the USA. Much of the early work at

Figure 4.1 **The Quaking Houses mine water discharging from a surface drainage system into the Stanley Burn in November 1994.** The white discolouration of the streambed and unsightly 'froths' are aluminium hydroxide precipitates (photograph by Paul L. Younger, University of Newcastle upon Tyne).

Quaking Houses was based on research in the USA led by the now-defunct United States Bureau of Mines (USBOM), especially the synthesis of Hedin *et al.* (1994a).

In accordance with the design principles detailed in Chapter 3 a compost wetland system was viewed as the most appropriate type of passive technology. Two key findings emerged from the feasibility study (Younger *et al.*, 1997):

1) Laboratory microcosm studies using a variety of substrates (horse manure, cow manure and soil from the proposed site for a treatment system) suggested that the horse manure substrate in particular was capable of promoting bacterial sulphate reduction, a key process in compost wetlands.
2) A pilot-scale compost wetland ($45m^2$ area) was constructed, using the horse manure as a substrate. It should be noted that the term 'compost' wetland is applied here in a generic sense to all anaerobic constructed wetlands. In fact the horse manure used here, and the horse and cattle manure used in the full-scale wetland (see below), were not composted but fresh. Figure 4.2 illustrates the layout of this system. This system was monitored for a period of 12 months, and the results demonstrated that significant reductions in concentrations of iron, aluminium and acidity were occurring. Acidity was removed in the pilot-scale wetland at a rate of 9 $g/m^2/d$, which compared well with the rate of 7 $g/m^2/d$ which the work of Hedin *et al.* (1994a) had led the team to expect.

4.3.2 Full-scale treatment system design and construction.

Design of a full-scale system at Quaking Houses began at the outset of this PhD project in 1996, when an area of land of approximately 500 m^2 was made available by British Coal Property. Clearance of a dense stand of willow and birch on the site enabled a thorough site survey to be undertaken. Two critical design constraints were revealed by this site investigation:

i. It would not be possible to construct a vertical flow Successive Alkalinity Producing System (SAPS) at the site (cf. Section 3.2.4) because only 1.0m of hydraulic head was available across the site. Consequently a horizontal flow compost wetland, very similar to the pilot-scale wetland, was designed.

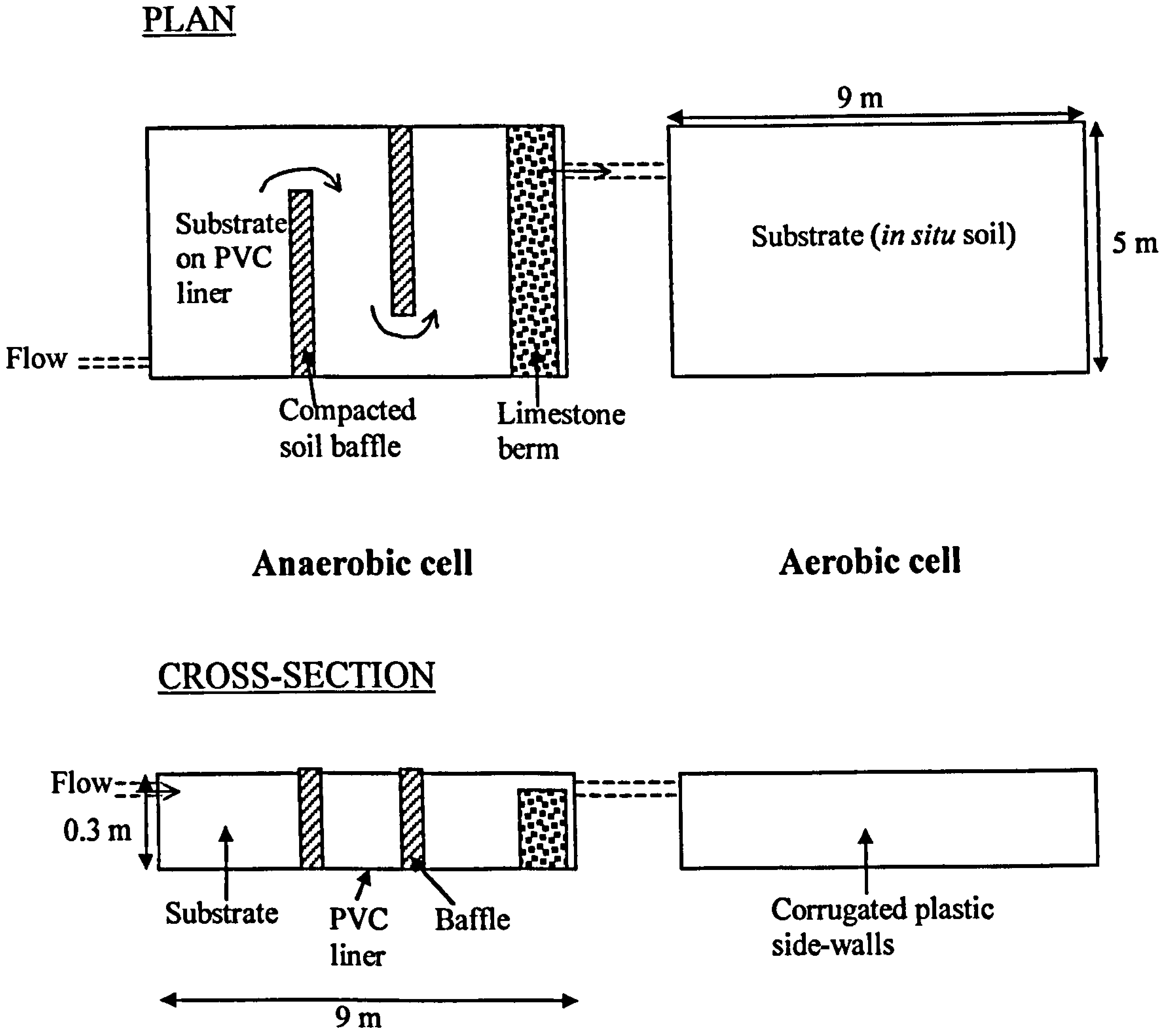


Figure 4.2 **Layout of the pilot-scale constructed wetland at Quaking Houses in plan and cross-section.** The system comprised of a horse manure substrate anaerobic cell, and an *in situ* substrate aerobic cell (after Younger *et al.*, 1997).

ii. The *in situ* soil proved to be contaminated with iron and aluminium, which was found to be because the site was formerly the location of an unrecorded coal washery associated with the Morrison Busty colliery. Excavation of the soil would lead to leaching of these metals, and therefore all construction works had to be located at or above ground level.

Several other key issues emerged which also shaped the design of the wetland and the manner in which it was constructed:

a) To satisfy the local residents and maximise ecological integration, the wetland should be designed to be as in keeping as possible with the local countryside. This meant that angular structures and 'concrete boxes' should be avoided, and slopes should be 3:1 (length:height) or less in order to encourage pond margin wildlife (Hawke and José, 1996).
b) The wetland was to have a nominal design life of 15 - 20 years, and therefore the design had to be robust. In particular the retaining embankments had to be designed to a suitable width, and there had to be sufficient freeboard to allow for substantial accumulation of solids and detritus on the substrate surface.
c) Vandalism is a problem at the site, and therefore exposed sections of pipe-work were to be avoided.

Construction of the wetland began in late August 1997. In total construction of the wetland took 8 weeks, although for approximately 2 of these weeks progress unavoidably ceased due to inclement weather conditions. The wetland was commissioned on 10th November 1997, and the first influent and effluent samples were collected on 14th November 1997.

Taking the advice of the Geotechnical Engineering group at Newcastle University retaining embankments were designed to have a minimum crest width of 1.5 m, and slope angles were designed with a minimum length:height ratio of 2:1. In order to minimise expenditure on materials pulverised fuel ash (PFA) was selected as the material for embankment construction. Once compacted PFA is highly impermeable, but costs less than half the price of clay. To avoid toe drainage, which may have affected the integrity of the structures, the base of the embankment was sunk approximately 0.2 m into the *in situ* soil. Figure 4.3 shows the retaining embankment under construction.

Because the site slopes downwards slightly (away from the proposed influent point to the wetland), a central weir was incorporated in the design in order that the wetland could be constructed on two levels, the second cell being 0.4 m lower than the first cell. In this way savings were made in terms of both materials costs and land area used for the embankment. Baffles and islands were also constructed from PFA. These features were incorporated in an attempt to minimise the potential for hydraulic short-circuiting through the wetland but they also served to improve the appearance of the wetland and diversify habitats within it. Figure 4.4 illustrates the as-built plan of the Quaking Houses wetland. The width of the embankment, the location of the central weir, and the locations of baffles and islands can be clearly seen on this plan.

Because the horse manure used in the pilot-scale wetland was not available in sufficient quantity, additional sources of compost were sought. The horse manure was therefore combined with cattle manure and municipal waste compost. The approximate ratio of horse manure to cattle manure to municipal waste compost in the completed wetland is 30:40:30. Additionally 30 tonnes of limestone were deposited at the far end of the wetland, to facilitate final pH adjustment if it should be required. Figure 4.5 shows placement of limestone at the far end of the treatment system. The system was designed such that the compost depth in the wetland would be 0.30 - 0.50m. An additional 0.30m of freeboard was allowed for accumulation of material on the substrate surface. The total area of substrate surface is 440m^2.

To generate additional hydraulic head a concrete wall was constructed across the culvert from which the discharge emanates. Two sections of 100mm diameter pipe were built into this wall. The first carries water underground to the influent point of the wetland, discharging into a basin from where the water is distributed across the wetland. The second section of pipe allows overflow back into the original watercourse when flow-rates exceed approximately 400 L/minute. Because pollutant concentrations are lower at higher flow-rates due to dilution, and because of further dilution of the overflow water by the effluent from the wetland, the impact of this water on the receiving watercourse is minimal.

Figure 4.3 **The pulverised fuel ash retaining embankment at Quaking Houses wetland under construction in the Summer of 1997** (photograph by the author).

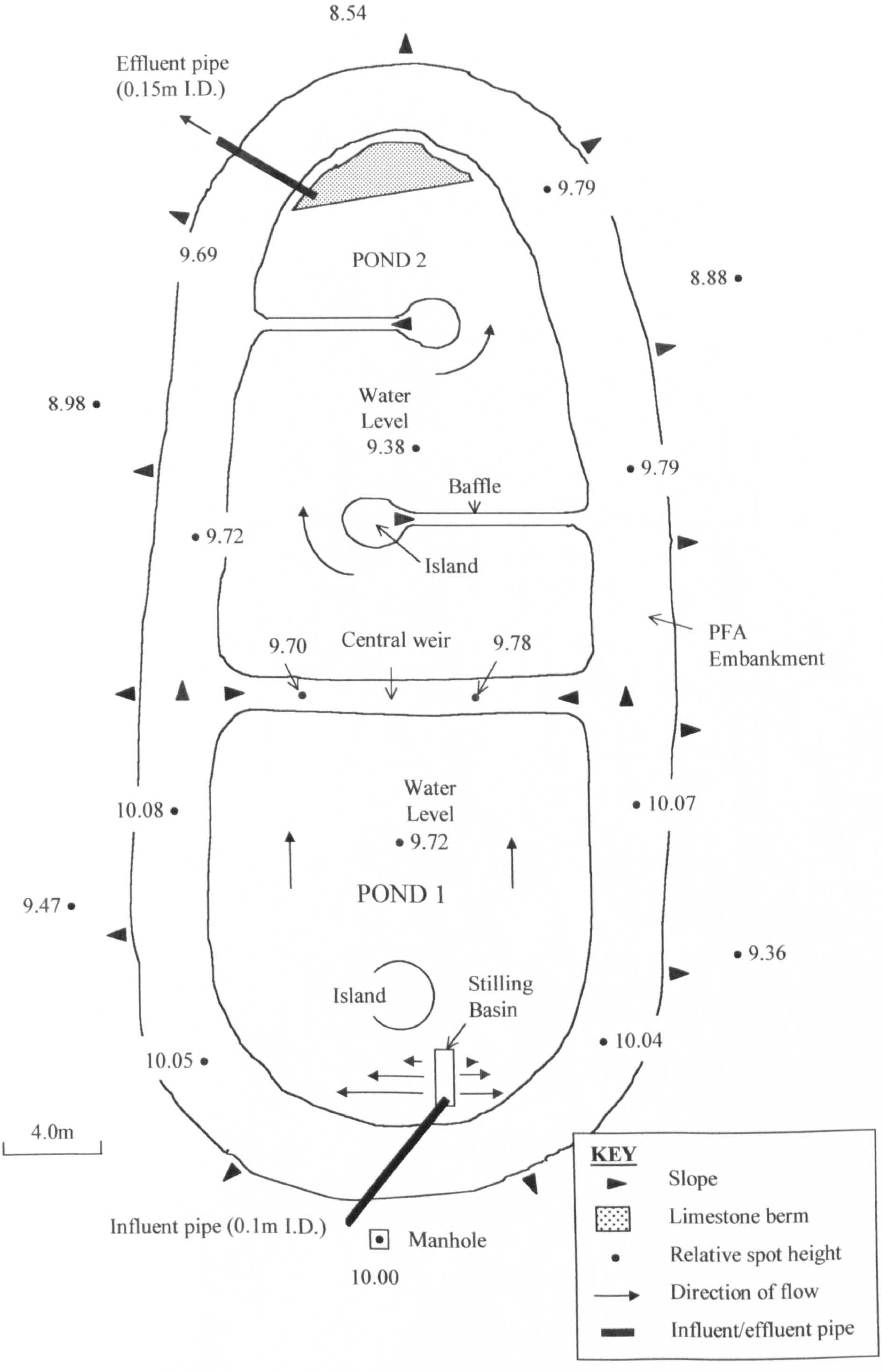


Figure 4.4 **As built plan of the Quaking Houses Community wetland for spoil heap drainage remediation.** The overall area of the wetland substrate is 440 m^2.

Figure 4.5 **Limestone, for final pH adjustment, being placed at the far end of the Quaking Houses wetland in the Summer of 1997** (photograph by the author).

The water outlet structure was originally a section of 150mm diameter plastic pipe buried into the retaining embankment. A movable 90° bend on the wetland-side of this pipe allowed the water level in the wetland to be adjusted (although typically the water level has been maintained approximately 50 - 100mm above the surface of the substrate). In June 1999 this effluent pipe was replaced with an open channel by members of the Quaking Houses Environmental Trust to avoid blockage problems. Figures 4.6 and 4.7 illustrate the completed, and operational, wetland.

4.3.3 Materials quantities and overall costs

The quantities of materials used, and the overall costs of the Quaking Houses constructed wetland are summarised in Table 4.1. The wetland cost just under £18 000 to construct in total. By far the greatest costs were associated with payment of designers and engineers, and plant hire and operation.

Materials	Quantity/Duration	Cost (£)
Pulverised fuel ash (PFA)	614 t	2511
Cattle manure[a]	60 t	295
Municipal waste compost	49 t	235
Horse manure[a]	50 t	245
Limestone	31 t	258
Pea gravel	11 t	110
Broken stone	10 t	129
Pipe-work/building materials	-	955
Top soil	64 t	370
Design/engineering consultation	6 months (50% time)	4000
Plant hire and operation	7 weeks	8880
Total		17 988

[a] These costs were solely for transport

Table 4.1. Construction materials quantities and costs for the Quaking Houses constructed wetland.

Figure 4.6 **The footbridge and central weir of the Quaking Houses Community wetland (just in front of the footbridge) during its early operation** (photograph by the author).

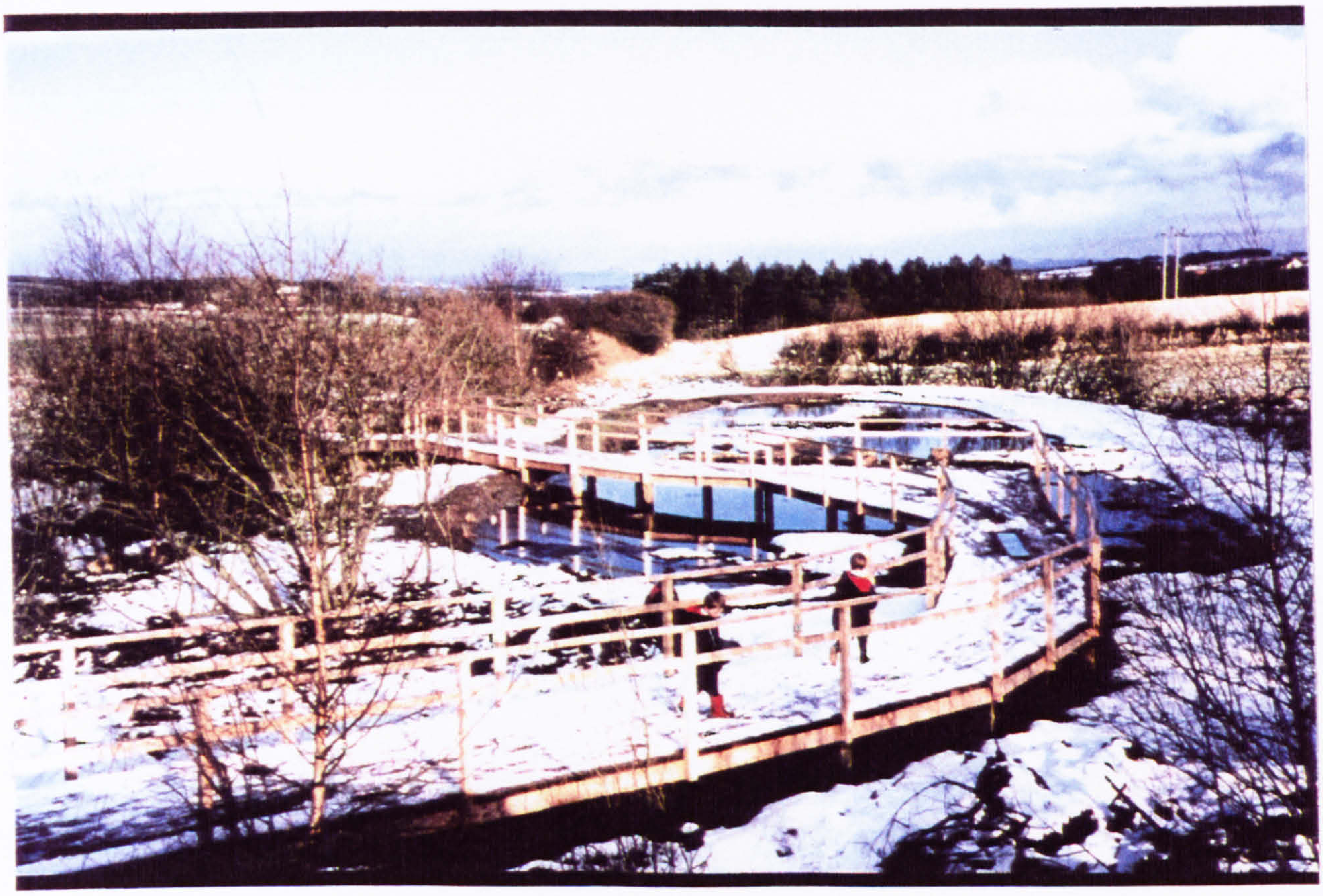


Figure 4.7 **The Quaking Houses community wetland viewed from above (the effluent point is at the far left of the wetland) in January 1998** (photograph by Dr Paul L. Younger, University of Newcastle upon Tyne, UK).

Using examples from around the UK Younger and Harbourne (1995) calculated the average cost of passive treatment systems to be £51/m^2. The Quaking Houses wetland cost £41/m^2, and therefore compares favourably with this national figure. Furthermore it is felt that future systems may be constructed at a lower cost, since this was the first wetland of its particular kind in the UK. Since its completion in November 1997 the maintenance costs associated with the wetland have been no greater than £250 - £500 / annum.

4.3.4 Legal obligations

Despite having been constructed under charitable status, under the England and Wales Water Resources Act 1991 (as amended by the Environment Act 1995) the outlet water from the wetland at Quaking Houses was legally required to have a consent to discharge when the wetland was completed in 1997. This consent stipulated the quality and quantity of water that could be discharged from the wetland. However, the initial application for a consent cost in excess of £500, and there was an additional annual fee of £250/year, which constituted a significant proportion of the overall maintenance costs of the wetland. Given the charitable nature of the project the Environment Agency recognised this to be a rather unfair imposition in this unusual case. As a consequence the consent was revoked in August 1998, and was replaced with a conditional prohibition notice, which has no charges associated with it. However, under the terms of the prohibition notice it is still a legal requirement that the wetland discharge meets certain water quality standards, although they are less stringent than those enforced by a full consent. Under the current agreement the operators of the wetland (i.e. the University of Newcastle upon Tyne) are obliged to monitor the quality of the discharge, and furthermore must ensure that the discharge quality does not breach the following standards:

a) The discharge shall have a pH value of not less than 6 nor greater than 9.
b) The discharge shall not contain more than 15 mg/L of dissolved iron.
c) The discharge shall not contain more than 5 mg/L of total aluminium.

In the following chapter it is shown that the wetland has consistently out-performed these requirements.

CHAPTER 5

RESULTS AND DISCUSSION: QUAKING HOUSES CONSTRUCTED WETLAND

5.1 Introduction

Sampling of the influent and effluent waters of the Quaking Houses Community Wetland began on 14th November 1997. At the time of writing this weekly sampling programme is ongoing, but for the purposes of this work only data collected up to and including the 11th February 2000 are reported here. Although the frequency of sampling has been predominantly weekly there have been periods where more intensive sampling has been undertaken, such as from 6/7/98 to 12/7/98 when samples were collected daily.

In February 1999 a small (approximately 10 m^2) aerobic pond was constructed downstream of the compost wetland. Outlet water from the main compost wetland now feeds through this unit prior to its discharge into the Stanley Burn. Since February 1999 effluent samples have been collected both from the compost wetland and from the additional aerobic cell. However, the discussion here is limited to the performance of the compost wetland only, for the following reasons:

1. The aerobic pond was built in an *ad hoc* fashion (by local volunteers) simply to occupy the small area of land available. It is so small that even minor fluctuations in flow-rates severely affect its performance. Meaningful interpretation of results is therefore almost impossible.
2. The objective with the Quaking Houses wetland data is predominantly to investigate the nature of anaerobic passive treatment processes. The Kimblesworth data are used, in conjunction with other sources, for a discussion of aerobic processes (Chapter 6).

In total 17 physicochemical variables have been measured at the Quaking Houses wetland, which may be broken down into physical and chemical determinands as follows:

- Physical: flow rate (L/minute), suspended solids (mg/L).

- Chemical (field measurement): temperature (°C), pH, conductivity (µS/cm), alkalinity (mg/L as $CaCO_3$).

- Chemical (laboratory measurement): acidity (calculated) (mg/L as $CaCO_3$), iron (total) (mg/L), aluminium (mg/L), manganese (mg/L), zinc (mg/L), calcium (mg/L), magnesium (mg/L), sodium (mg/L), potassium (mg/L), sulphate (mg/L), and chloride (mg/L).

In addition selected data from the automatic weather station (see Section 2.5) within the grounds of the Waste Transfer Station above the wetland (see Figure 1.1) are included. Specifically, air temperature (°C) and rainfall depth (mm) are included.

The number of pairs of influent / effluent measurements for each of these determinands varied over the 27 month sampling period from 21 (temperature, suspended solids) to 108 (iron, manganese) (excluding weather data variables). This variance is due largely to logistical and financial considerations that are beyond the control of the current work. For example 'field' measurements have not always been made in the field because it has not been possible for the author to make regular site visits due to other work commitments. These measurements have invariably been made on the same day as sample collection however. In other cases there are gaps in the data because of the cost of analysis of some determinands (such as calcium, magnesium, sodium and potassium).

Complete data tables for the wetland influent and effluent water quality are given in Appendices 2-5. These are ordered as follows:

Appendix 2: contains the raw water quantity and quality data.

Appendix 3: contains treatment efficiency values for iron and acidity, influent and effluent iron and acidity loads, and area-adjusted removal rates for iron and acidity (not dilution-adjusted).

Appendix 4: contains treatment efficiency values and area-adjusted removal rates (not dilution-adjusted) for manganese, aluminium and zinc.

Appendix 5: contains area-adjusted and dilution-adjusted removal rate values for all of the key pollutants above, and values for first-order removal constants for all of these variables.

Appendix 6: contains results of analyses of surface water and sediment water from the wetland, which are discussed in Section 5.6.

In addition Appendix 8 contains formulae for, and descriptions of, all of the statistical techniques used during the discussion of the Quaking Houses data.

5.2 Quaking Houses mine water quality characteristics

The mean values and ranges of physicochemical variables measured during the course of the investigation are shown in Table 5.1. Maximum influent flow-rate to the wetland is restricted by the capacity of the 100 mm internal diameter influent pipe. Measurements indicate that the maximum possible influent flow-rate is 420 L/minute. Maximum flow-rates have decreased recently (since around July 1999) because of sedimentation within the influent pipe. Indeed at the time of writing influent flow-rates had fallen to as low as 20 L/minute due to accumulation of debris within the pipe, and maintenance of this part of the wetland system was therefore undertaken on June 23rd 2000.

Measurements of pH, acidity$_{calc}$ and alkalinity reveal that the discharge over the 27 month sampling period has been only marginally acidic. This is contrary to historical measurements of this mine water, which showed the discharge to be strongly acidic (Younger and Bradley, 1994; Younger, 1995a; Younger *et al.*, 1997). The reason for this apparent improvement in quality is unclear, though it seems most likely to be due to the clay capping of the spoil heap along the embankments of the A693 road, which was undertaken in 1998 by the local council at the prompting of the research team.

Nevertheless the discharge remains net-acidic, particularly during the summer months when less dilution occurs.

In terms of metal ions the discharge is contaminated with iron, manganese, aluminium, and zinc (see Table 5.1), all of which are mobilised under acidic conditions within the spoil heap.

Determinand	Mean	Range (number of values, n)
Flow-rate (L/minute)	98.1	13.9 - 420.0 (79)
Temperature (°C)	11.8	8.0 - 13.8 (21)
pH	6.06	4.20 - 7.10 (83)
Conductivity (µS/cm)	7466	660 - 14030 (66)
Acidity$_{calc}$ (mg/L as $CaCO_3$)	51.8	11.8 - 107.4 (80)
Alkalinity (mg/L as $CaCO_3$)	49	0 - 107 (69)
Iron (total) (mg/L)	5.36	0.54 - 20.50 (104)
Manganese (mg/L)	3.57	0.08 - 6.94 (104)
Aluminium (mg/L)	6.18	1.22 - 11.82 (100)
Zinc (mg/L)	1.39	0.12 - 3.47 (50)
Calcium (mg/L)	233	101 - 408 (50)
Magnesium (mg/L)	73.9	20.9 - 141.0 (50)
Sodium (mg/L)	1489	380 - 3251 (50)
Potassium (mg/L)	185	36 - 505 (49)
Sulphate (mg/L)	796	120 - 1541 (97)
Chloride (mg/L)	2207	440 - 4535 (78)
Suspended solids (mg/L)	86.4	29 - 473 (20)

Table 5.1 Quaking Houses mine water quality (mean and ranges) from 14/11/97 to 11/2/00.

The mechanisms of sulphide mineral dissolution within spoil heaps, leading to the generation of acidity and mobilisation of metal ions, have been discussed in the Chapter 1 and will not be repeated here. The same processes result in the high concentration of sulphate in the discharge from the spoil heap (a mean concentration of 796 mg/L).

Figure 5.1 illustrates how the iron concentration in particular varies considerably from week to week. This can be attributed largely to fluctuations in flow-rate caused by surface runoff. There is a strong inverse correlation between iron concentration and flow-rate (r = -0.723; $p < 0.001$). There are also significant inverse correlations between flow-rate and manganese and aluminium concentrations (r = -0.637; $p < 0.001$, and r = -0.225; $p < 0.05$ respectively). Since the changes in flow-rate are caused by variations in the volume of surface runoff it is no surprise that the concentrations of all of these metals are also inversely correlated with weekly rainfall depth at a significance level of at least $p < 0.05$.

Clearly the changes in flow-rate caused by rainfall events affect all ions to some degree. As with Fe, Mn, and Al, typically these changes are characterised by decreasing concentrations as flow-rates increase. pH increases with increasing flow-rate, as would be expected (r = 0.562; $p < 0.001$). There are significant inverse correlations between pH and iron, manganese (all $p < 0.001$) and aluminium ($p < 0.01$) concentrations. The relationship is most striking when pH and manganese concentrations are illustrated graphically (Figure 5.2). However, the strong correlations between influent flow-rate and influent metal ion concentrations, coupled with the highly variable flow-rate, make it difficult to assign metal ion concentration fluctuations to variations in pH using simple correlation alone. Therefore partial correlation coefficients have been calculated. Using this technique it has been possible to correlate water quality variables whilst effectively holding influent flow-rate steady. The partial correlation coefficient between influent pH and influent manganese concentration is -0.672 ($p < 0.001$), apparently confirming the role of pH in controlling manganese concentrations. Interestingly neither iron or aluminium partial correlations with influent pH are statistically significant, suggesting that pH is not a major control in the concentrations of these two metal ions at this site. However, there is little doubt that pH is an important rate-determining control in the precipitation of both Fe^{3+} and Al (see for example Millero, 1990; Nordstrom and Ball, 1986; Stumm and Morgan, 1996). What might be the reason for the poor correlations between pH and iron and aluminium concentrations of the influent water? pH has a controlling influence on the rate of dissolution of minerals such as pyrite in the spoil heap (cf. Nordstrom and Alpers, 1999). Both the pH and the metal ion concentrations of the wetland influent water will

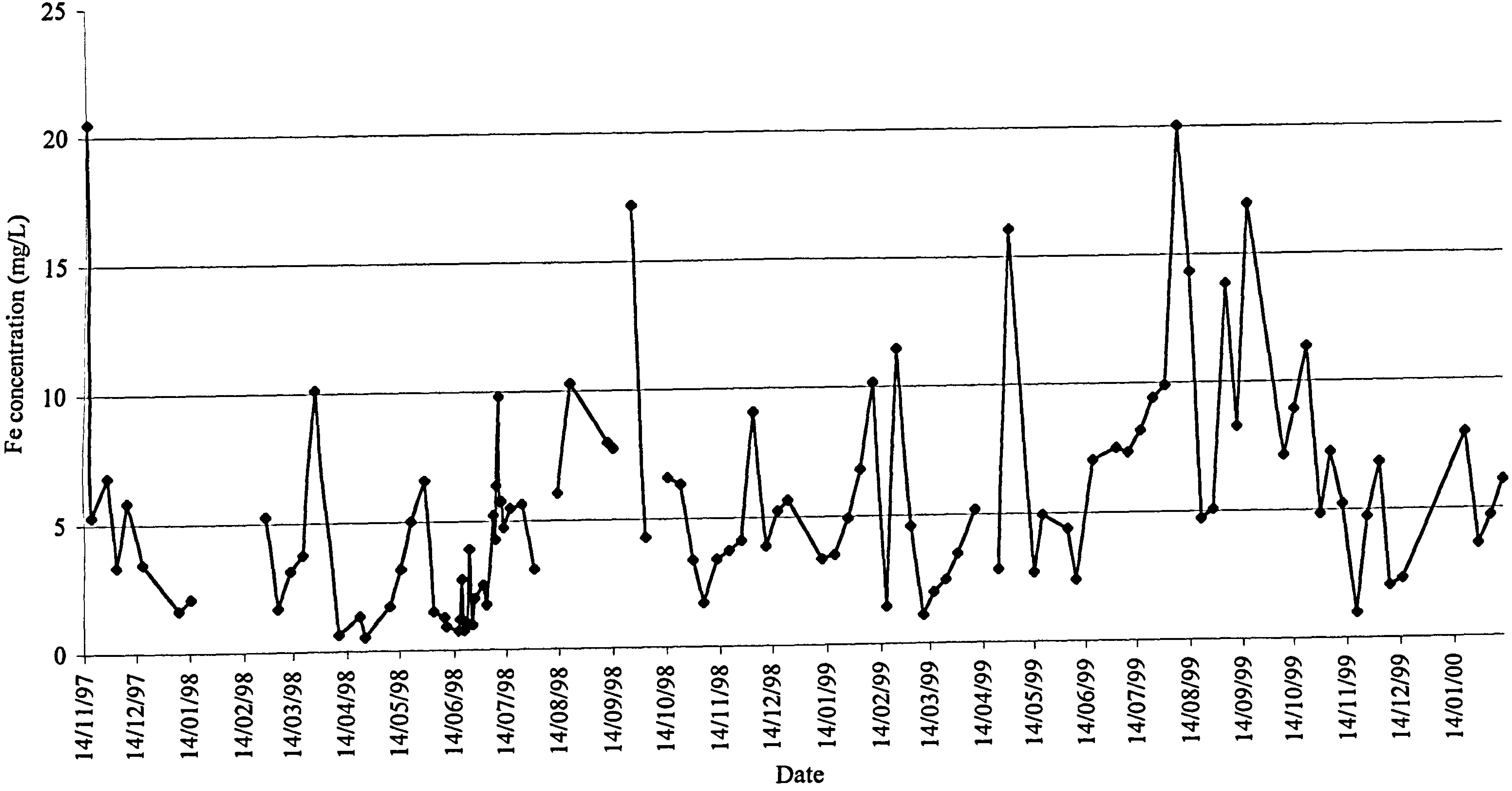


Figure 5.1 Variation of Quaking Houses spoil drainage iron concentrations from 14/11/97 to 11/2/00. Variation of the Fe concentration is largely due to dilution by surface runoff.

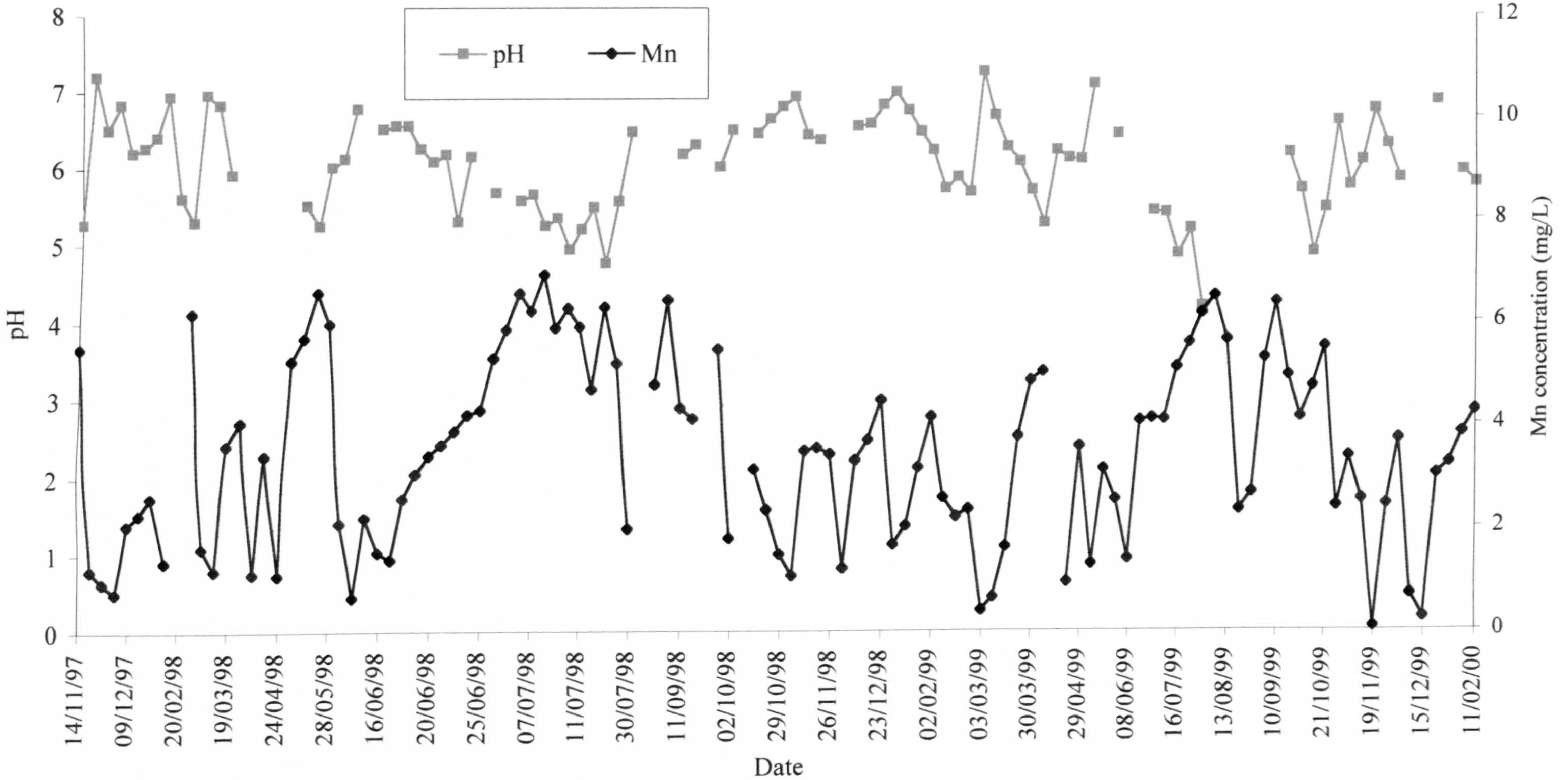
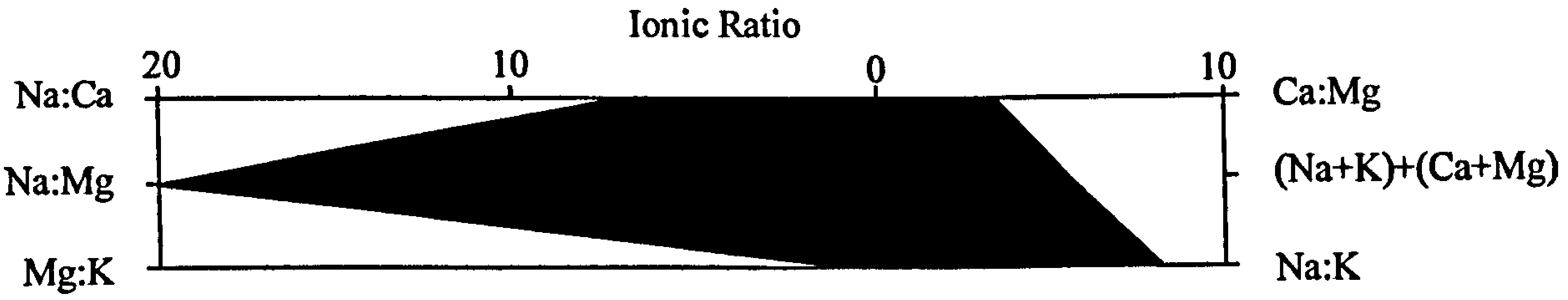


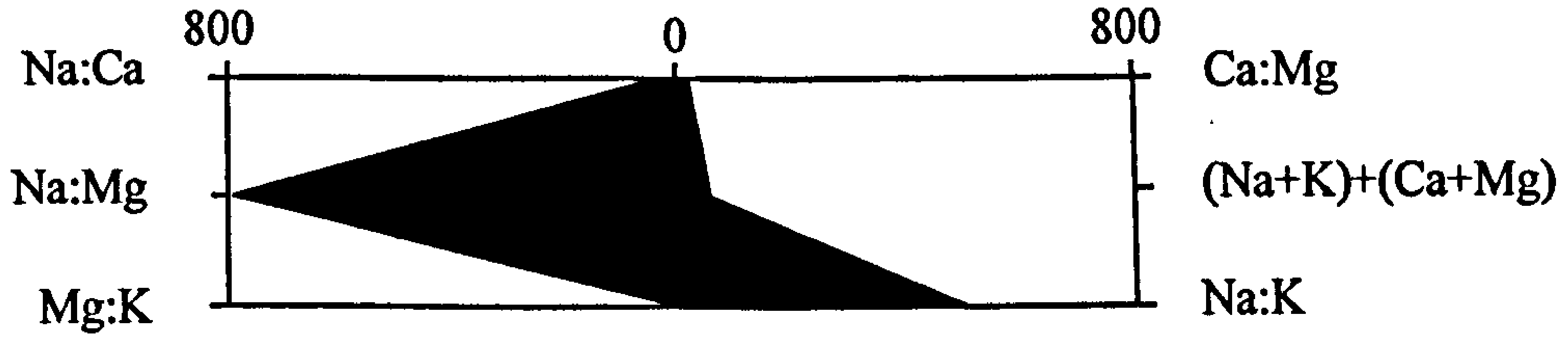
Figure 5.2 Relationship between pH and Mn concentration in the spoil drainage at Quaking Houses. There is a statistical relationship between these two variables, even after the fact that both are influenced by fluctuations in flow is taken into account.

be governed by the extent of this dissolution (ignoring dilution effects for the moment). However, at the pH range of the influent water (4.2 to 7.1) attenuation of both iron and aluminium may occur (e.g. Nordstrom and Ball, 1986; Stumm and Morgan, 1996). It is therefore conceivable that iron and aluminium are attenuated to a degree between the source of the pollution and the influent to the wetland without any measurable effect on the influent pH. Such removal processes may include adsorption processes (e.g. Chapman *et al.*, 1983) as well as the more obvious oxidation and precipitation reactions. In contrast manganese may remain in solution at a pH of up to approximately 8.5 (e.g. Diem and Stumm, 1984; Murray *et al*, 1985), and it would therefore appear plausible that Mn concentrations remain more closely linked with pH, thus explaining the correlation between pH and manganese concentration. An alternative explanation for the poor correlations between pH, iron and aluminium may be that the water entering the wetland has not reached equilibrium.

The mine water at Quaking Houses is characterised by very high concentrations of sodium and chloride (see Table 5.1). Deep coal measures brines may contain such elevated concentrations of these ions (Edmunds, 1975), but the Quaking Houses discharge evolves in the shallow subsurface (Younger *et al.*, 1997), and the overall geochemical signature of the water does not match that of a brine. Construction of Stiff diagrams in the manner proposed by Novak and Eckstein (1988) revealed that the cause of the elevated concentrations of sodium and chloride is in fact road salt. Figure 5.3 illustrates how the shape produced by plotting the ionic ratios of the mean concentrations of calcium, magnesium, sodium and potassium at Quaking Houses closely resembles the shape of the road salt signature given by Novak and Eckstein (1988). Subsequent investigations led to the discovery of a stockpile of road salt (unprotected from rainfall) in a nearby industrial yard. It appears that this road salt is rapidly dissolving and being washed into surface drains, leading to the high concentrations of sodium and chloride in the Quaking Houses discharge. If left unabated, this salt will hinder the recovery of invertebrate communities in the stream which would be expected as a result of the mine water treatment. At the time of writing the local district council is proposing to construct a warehouse in which to store the road salt stockpile, thus preventing dissolution of the salt.



(a) calculated from mean values of concentrations at Quaking Houses



(b) road salt (from Novak and Eckstein, 1988)

Figure 5.3 **Stiff diagrams illustrating the similarity between the geochemical signature of road salt (b) with that of the Quaking Houses mine water discharge (a).** Subsequent investigations confirmed that dissolution of a stockpile of road salt is responsible for the elevated concentrations of sodium and chloride at Quaking Houses.

The elevated concentrations of sodium and chloride strongly influence the conductivity of the water, which is typically very high (Table 5.1). Both sodium and chloride concentrations are strongly positively correlated with conductivity (r = 0.600 and r = 0.698 respectively; $p < 0.001$).

Since water quality data for the discharge at Quaking Houses are available for a period in excess of 2 years, time series analysis has been used to highlight any obvious trends in the data. Specifically, autocorrelation coefficients have been calculated for key water quality variables (influent and effluent pH, acidity, alkalinity, Fe, Al, Mn, and SO_4). The frequency of sampling has varied. For example occasionally frequency has been as high as daily (e.g. 6/7/98 - 12/7/98), whereas over the Christmas vacation periods the frequency has only been monthly. To maintain a constant lag period, therefore, certain data have been omitted. Time series analysis is performed only on data collected at weekly intervals between 20/2/98 and 15/12/99.

In Figures 5.4 and 5.5 the correlation coefficients for each lag period (r_k) are plotted against the lag (k). Such graphs are known as correlograms (Chatfield, 1989). Here the lag period is approximately 1 week (depending on the exact sampling date). Figure 5.4 shows the correlogram produced for influent pH with the maximum lag period set at 21 weeks (the default number used by Minitab for this number of observations, N). Both pH and all the other key influent water quality variables illustrate short-term correlation (Chatfied, 1989). In other words an observation of a high metal concentration one week, for example, is likely to be followed by high concentrations in the subsequent 1 - 2 weeks. In this case statistically significant short-term correlation is evident for values of k between 1 - 3 (or 1 to 3 weeks in this case).

Beyond the initial short-term relationship correlations are not statistically significant. However, there does appear to be a trend in the correlogram for influent pH (Figure 5.4), characterised by negative values of r_k at lag k of approximately 14 (equivalent to 16 weeks). On further inspection the same trend is evident for influent acidity, alkalinity, aluminium and sulphate concentrations. In other words increases in concentrations of these variables in week 1 are associated with decreases in concentrations in week 16 (or vice versa).

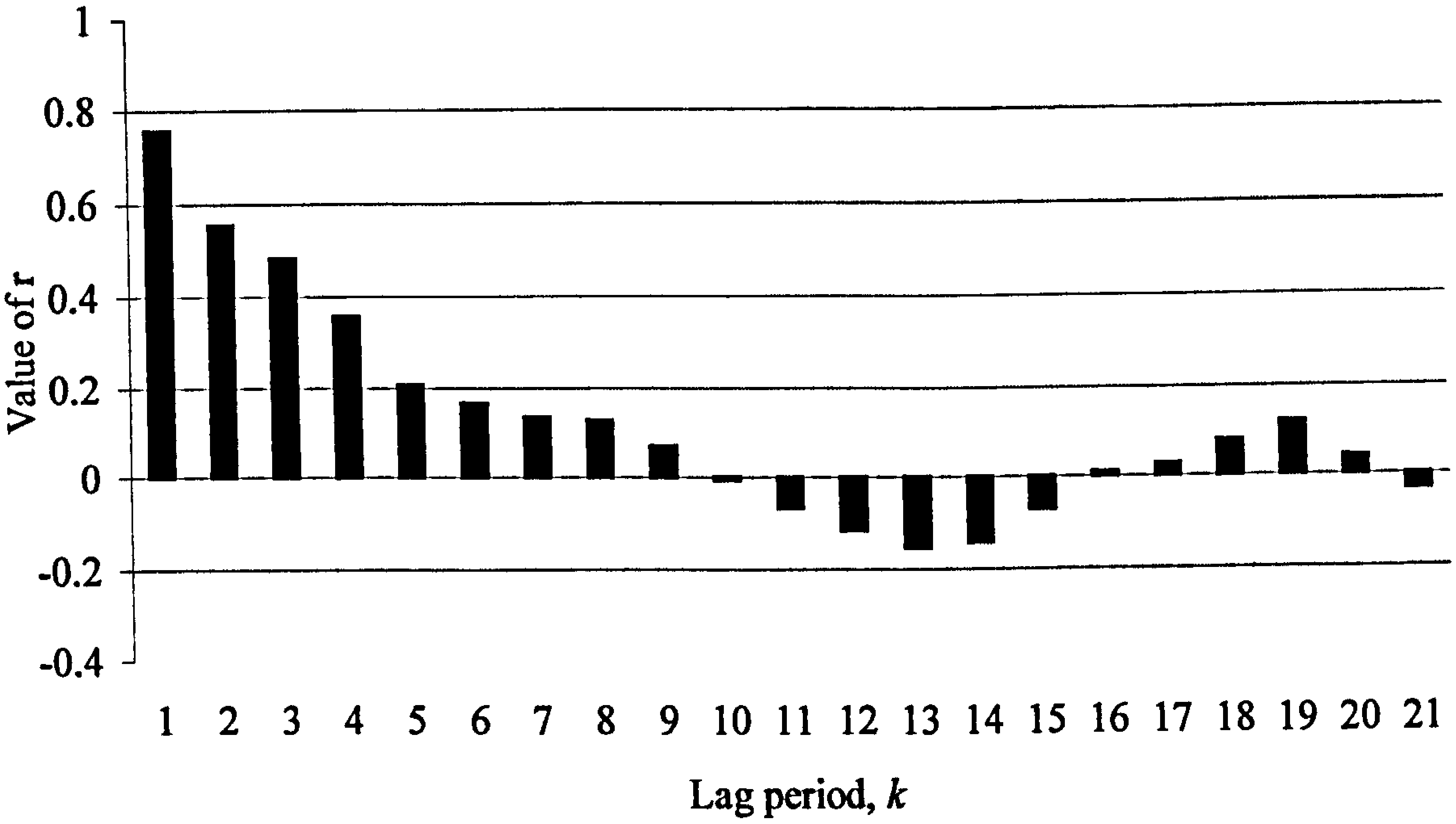


Figure 5.4 Correlogram of influent pH of spoil drainage at Quaking Houses (k= 21). The maximum lag period is 21, equivalent to approximately 24 weeks.

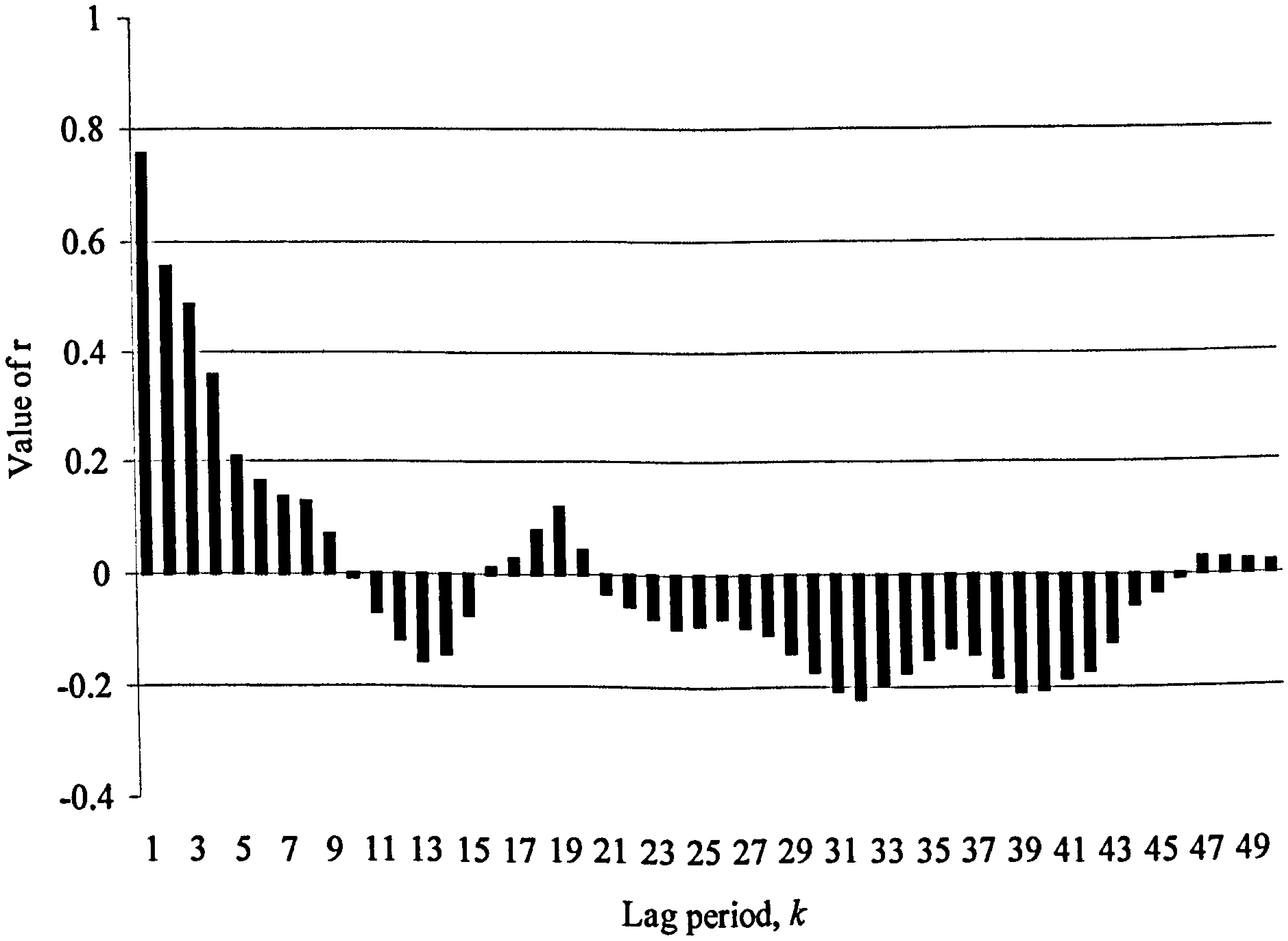


Figure 5.5 Correlogram of influent pH of spoil drainage at Quaking Houses (k = 50). The maximum lag period is 50, equivalent to approximately 57 weeks.

Although Chatfield (1989) notes that there is little virtue in calculating r_k for values of k above $N/4$, it is necessary to do this with the current data to examine the potential existence of a seasonal trend. Figure 5.5 therefore illustrates the correlogram for influent pH at $k = 50$. In addition to the negative values of r_k at approximately 16 weeks there also appear to be negative correlations around 32 - 45 weeks ($k = 30 - 40$). Again, the same pattern is evident in the correlograms of influent acidity, alkalinity, aluminium and manganese.

When the correlogram for air temperature is plotted (Figure 5.6) there is a very obvious sinusoidal pattern, typical of a seasonal trend. Inspection of Figure 5.6 illustrates that the points of inflection about the x-axis closely approximate the 16 and 40 week ($k = 10$ and 35 respectively) points identified above, suggesting that the water quality variables at Quaking Houses do exhibit a seasonal trend. Confidence in this assertion must be tempered by the fact that correlations at $k > 3$ are rarely statistically significant. Nevertheless identification of such trends has important implications for the calculation of any water quality prediction and/or wetland performance models, since such trends would need to be factored out for them to be accurate.

5.3 Residence time within the wetland

Robins (1998) has calculated the residence time of waters within the Quaking Houses wetland using tracer tests. Sodium chloride (NaCl) was selected as the most appropriate tracer, as it is highly soluble and analytical procedures are relatively straightforward. 5 kg NaCl were dissolved in 20 litres of water, providing a solution of sufficiently high concentration to be measurably greater in the effluent from the wetland than the already elevated background concentrations of Na and Cl (see below) (Robins, 1998).

Robins (1998) performed two tracer tests at Quaking Houses wetland. Meaningful results were only obtained from one of these however, due to unforeseen storm conditions during the first experiment. At an influent flow-rate of 66 L/minute Robins (1998) observed a distinct peak in Na and Cl concentrations at the effluent after 41 hours.

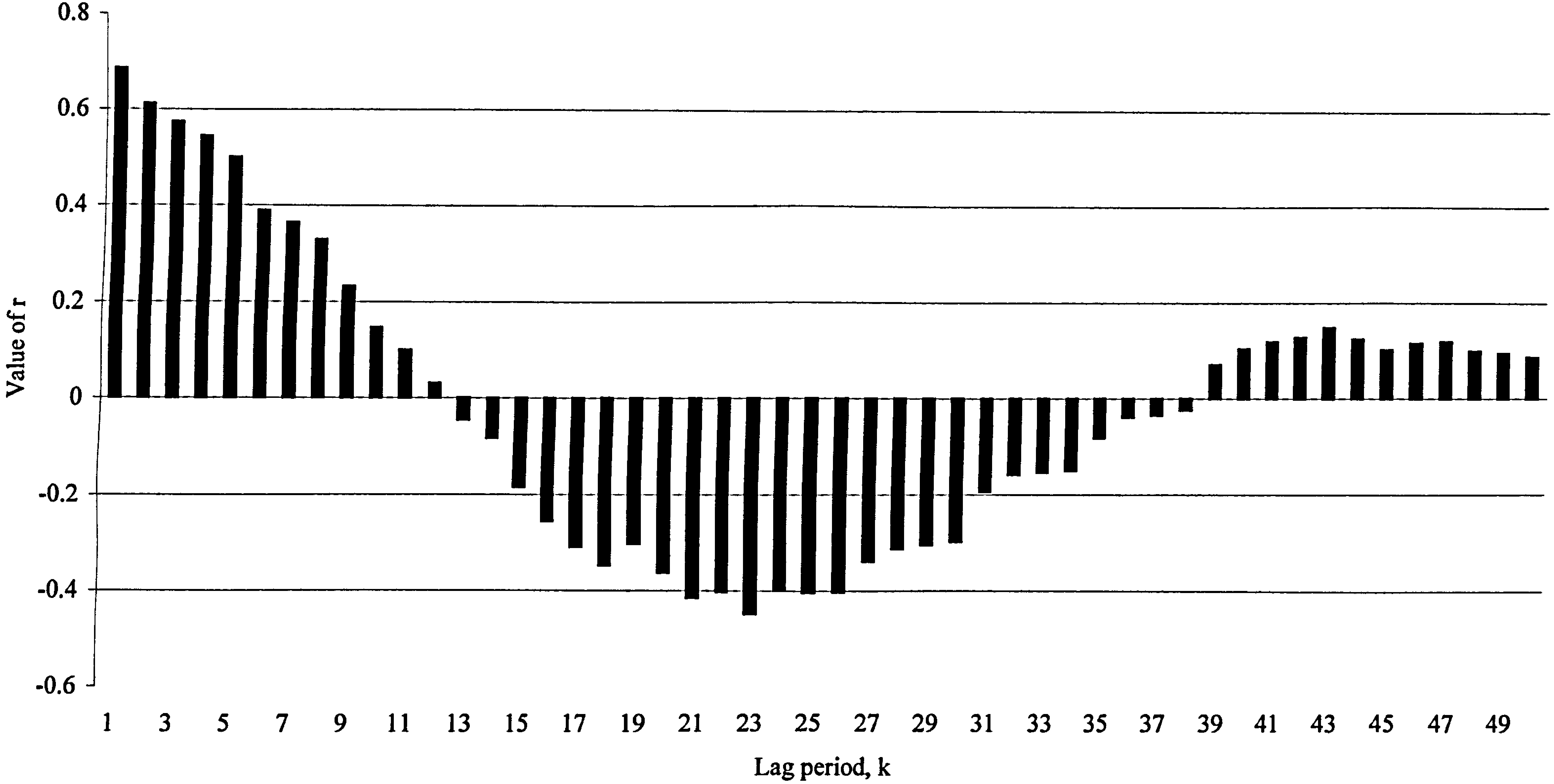


Figure 5.6 Correlogram of air temperature from Annfield Plain weather station. The maxumum lag period is 50, equivalent to approximately 57 weeks. The sinusoidal pattern is typical of a seasonal trend.

Nominal residence time is most easily calculated from the equation (from Kadlec, 1994):

$$\tau = V / Q$$

where, τ = nominal residence time (days)
V = volume of water in wetland (m^3)
Q = influent flow-rate (m^3/day)

For the Quaking Houses wetland, based on an absolute volume of 160 m^3, and media porosity of 50%, the nominal residence time at a flow-rate of 66 L/minute is 20.2 hours. Maximum and minimum influent flow-rates between 14/11/97 and 11/2/00 are 13.9 L/minute and 420 L/minute (see Table 5.1), and therefore nominal residence time theoretically varies between 3.2 hours and 96 hours. Actual residence time will vary accordingly, but it would require tracer tests at a range of flow-rates to determine the pattern of this variation. The critical significance of this is that routine influent and effluent samples for chemical analysis are collected almost simultaneously (a delay of no more than a few minutes). Samples collected at the effluent point may therefore be of water that nominally entered the wetland between 3.2 hours and 96 hours earlier. The result of the one tracer test at the wetland certainly confirms that actual residence times may be measurable on a scale of hours and days (Robins, 1998). Since the quality of the influent water is highly variable (see for example Figure 5.1, showing influent iron concentrations) serious questions must be asked about the validity of directly comparing influent and effluent water quality data with a view to assessing wetland performance on a daily basis.

Undertaking tracer studies at Quaking Houses has proved difficult because of the risk of vandalism at the site. Automatic sampling equipment can not be left on site unattended. To accurately quantify the actual residence time of water within the wetland at various influent flow-rates it would be necessary to perform numerous tracer tests, under a variety of flow conditions. The frequency of water sampling at the effluent would then be dictated by the flow-rate at the time the influent water sample was taken. Even if such an intensive programme of sampling were feasible (which to date it has not been) the very real possibility of influent flow-rates changing between collection of influent and effluent sampling would remain a problem.

For the reasons outlined above it has therefore been necessary to make the assumption that the time lag effect caused by the residence time of waters within the wetland does not invalidate comparisons of influent and effluent water quality variables. This assumption appears reasonable given the following facts:

i. Because the data cover more than 2 years of sampling the adverse effects of occasional storms should be far outweighed by the majority of data collected under more steady hydrological conditions.
ii. Plotting influent flow-rate against effluent flow-rate reveals that the two are in fact linearly related, supporting point (i) above. Not only are influent and effluent flow-rate highly correlated ($r = 0.827; p < 0.001$), but the equation describing the trend line illustrated in Figure 5.7 ($y = 1.0335x$) approximates a 1:1 relationship.
iii. Hedin and Nairn (1993) use a dilution factor (DF), based on magnesium concentrations, to correct for dilution and evaporation effects when comparing influent and effluent concentrations of pollutants (see Section 3.3 for further description). Because magnesium behaves conservatively in wetland environments (as long as they do not contain dolomite or Mg-rich limestone) changes in its concentration between influent and effluent ($DF = Mg_{effluent} / Mg_{influent}$) can be assigned to dilution and evaporation effects. When DF is equal to 1.0, influent and effluent Mg concentrations are equal, and there are no dilution / evaporation effects. Figure 5.8 graphically illustrates DF over the period of monitoring at Quaking Houses. On the majority of occasions it can be seen that $0.50 < DF < 1.50$. To avoid misinterpretation of pollutant removal rates data from the dates giving rise to the four obvious outliers in Figure 5.8 are not used in any of the statistical analysis contained here, although these data are used in graphs.

5.4 Constructed wetland effluent water quality

Table 5.2 summarises mean values and ranges of chemical quality variables for the effluent water from the Quaking Houses wetland. For comparative purposes the

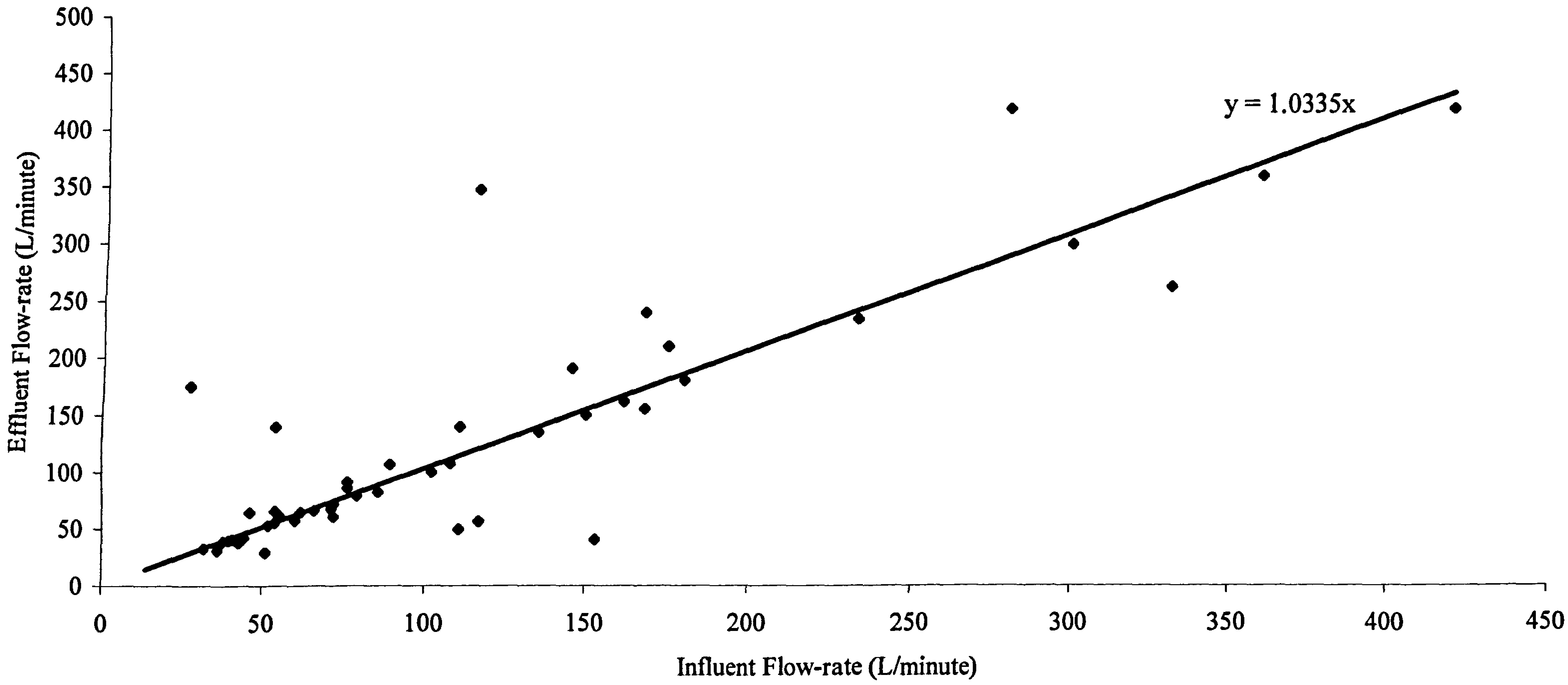


Figure 5.7 Relationship between simultaneously-measured influent and effluent flow-rates at Quaking Houses wetland. Discrepancies between flow-rates are due to short-term storm events.

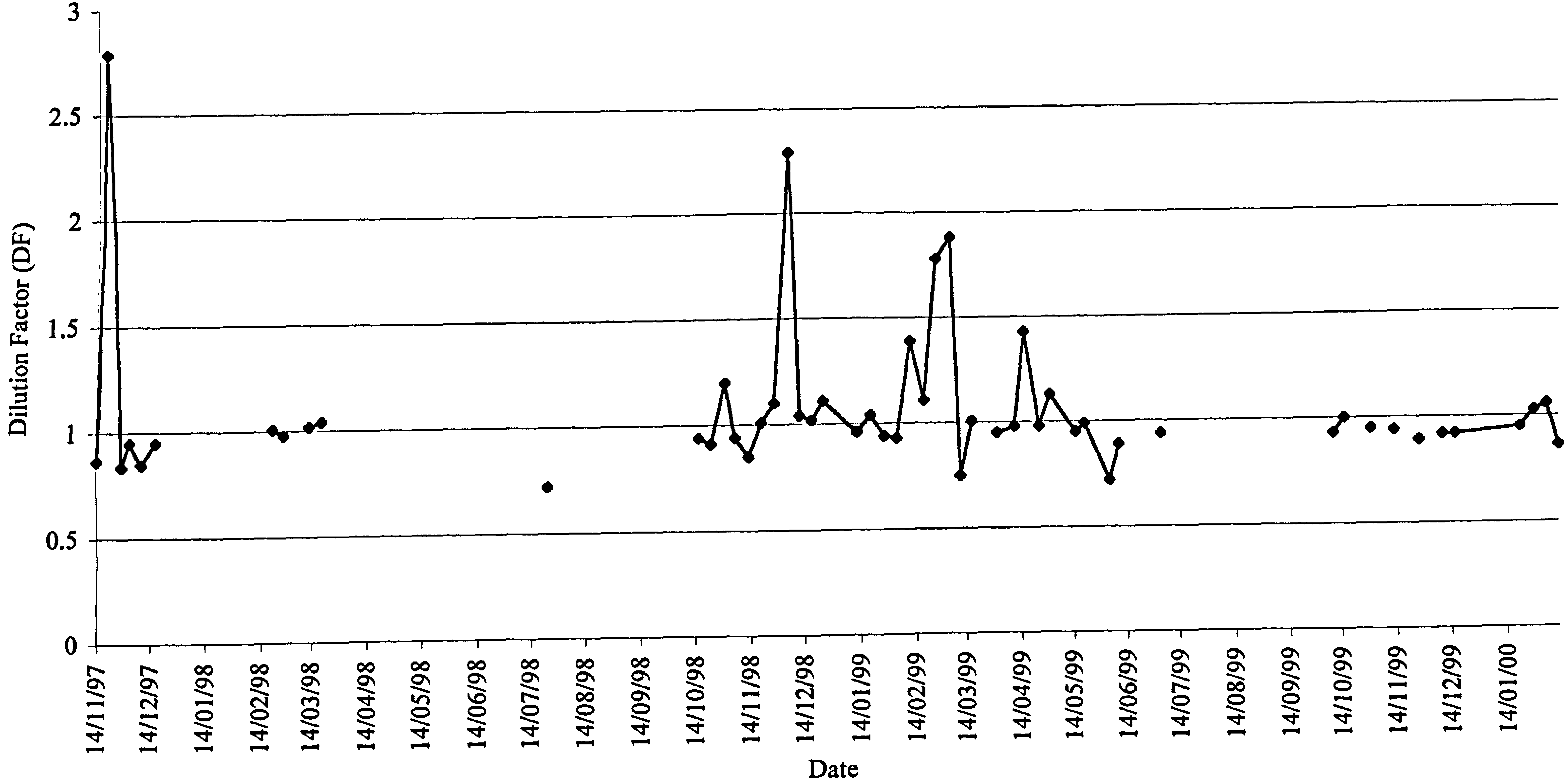


Figure 5.8 Dilution factors calculated from influent and effluent magnesium concentrations at the Quaking Houses wetland (see section 3.3 for details).

DETERMINAND	Influent mean	Range (number of values, n)	Effluent mean	Range (number of values, n)
Flow-rate (L/minute)	98.1	13.9 - 420.0 (79)	132.8	29.0 - 420.0 (20)
Temperature (°C)	11.8	8.0 - 13.8 (21)	14.1	8.0 - 13.8 (21)
pH	6.06	4.20 - 7.10 (83)	6.60	5.2 - 8.3 (83)
Conductivity (μS/cm)	7466	660 - 14030 (66)	7750	1548 - 19410 (66)
Acidity$_{calc}$ (mg/L as $CaCO_3$)	51.8	11.8 - 107.4 (80)	24.6	3.0 - 65.5 (80)
Alkalinity (mg/L as $CaCO_3$)	49	0 - 107 (69)	66.3	8 - 189 (69)
Iron (total) (mg/L)	5.36	0.54 - 20.50 (104)	2.40	0.1 - 7.3 (104)
Manganese (mg/L)	3.57	0.08 - 6.94 (104)	3.00	0.3 - 6.6 (104)
Aluminium (mg/L)	6.18	1.22 - 11.82 (100)	2.40	0.0 - 9.4 (101)
Zinc (mg/L)	1.39	0.12 - 3.47 (50)	1.10	0.2 - 7.2 (50)
Calcium (mg/L)	233	101 - 408 (50)	234	112 - 451 (49)
Magnesium (mg/L)	73.9	20.9 - 141.0 (50)	71.9	21 - 156 (49)
Sodium (mg/L)	1489	380 - 3251 (50)	1514	355 - 3929 (50)
Potassium (mg/L)	185	36 - 505 (49)	183	34 - 407 (50)
Sulphate (mg/L)	796	120 - 1541 (97)	766	111 - 1508 (97)
Chloride (mg/L)	2207	440 - 4535 (78)	2218	749 - 5039 (78)
Suspended solids (mg/L)	86.4	29 - 473 (20)	46.9	23 - 180 (20)

Table 5.2 Quaking Houses wetland effluent water quality compared to influent water quality.

influent water quality data from Table 5.1 are reproduced in Table 5.2. Because of changes to the effluent structure (see Section 4.3.2) it was only possible to measure effluent flow-rates during the early operation of the wetland (up until 18/6/99). Because influent flow-rates have decreased recently due to sedimentation within the influent pipe, *mean* effluent flow-rates are higher. However, had measurements of effluent flow-rate continued it is unlikely that this would have been the case.

Mean iron concentration is reduced from 5.36 mg/L in the influent water to 2.40 mg/L in the effluent water. Aluminium concentrations decrease to a similar degree, from 6.18 mg/L to 2.40 mg/L. Reductions in manganese and zinc concentrations are marginal (from 3.57 mg/L to 3.00 mg/L and 1.39 mg/L to 1.10 mg/L respectively). The lesser removal of manganese and zinc is of little surprise, given the slow rates of Mn (II) oxidation at circumneutral pH (Diem and Stumm, 1984) and the known mobility of zinc in the aquatic environment (Bodek *et al.*, 1988). Formation of manganese and zinc sulphides is also less likely than for iron, because of the relatively high solubility of MnS and ZnS (Hedin *et al.*, 1994a). Closer inspection of Table 5.2 reveals that the wetland is actually a source of Mn and Zn on some occasions. Significant increases in Mn concentration between influent and effluent only occur when influent Mn concentration is < 1 mg/L, perhaps suggesting that these increases may be at least partly due to analytical error. If desorption / resolubilisation of Mn does occur it is a rare event, since effluent Mn concentration is higher than influent concentration in only 4 out of 104 samples analysed. There is no seasonal pattern to the increases in effluent Mn concentrations, and it therefore seems unlikely that if Mn is accumulated in the wetland vegetation that it is subsequently released during winter die-back. In the case of Zn effluent concentration is higher than influent concentration on only one occasion (7.19 mg/L and 3.47 mg/L respectively). This effluent concentration is more than twice as high as any other Zn concentration measured, strongly implying that it is a result of sampling or analytical error.

Mann Whitney tests confirm that effluent metal ion concentrations are significantly less than influent concentrations. Effluent iron and aluminium concentrations are significantly less than influent concentrations ($p < 0.001$). Effluent manganese and zinc concentrations are significantly less than influent concentrations ($p < 0.05$ and $p < 0.01$ respectively). The overall reductions in metal concentrations, coupled with a mean rise in pH of 0.54 units, result in mean calculated acidity concentrations decreasing between influent and effluent points of the wetland (from 51.8 mg/L as $CaCO_3$ to 24.6 mg/L as $CaCO_3$). Effluent acidity concentration is significantly less than influent ($p < 0.001$), and effluent pH is significantly greater than influent pH ($p < 0.001$). Alkalinity concentration, which increases from 49.2 mg/L as $CaCO_3$ to 66.3 mg/L as $CaCO_3$ between influent and effluent (Table 5.2), is also significantly greater in the effluent water ($p < 0.01$).

There is little difference between the influent and effluent water quality in terms of the alkaline-earth and alkali metals (Ca, Mg, Na, K). Sodium concentrations remain high (mean effluent concentration of 1514 mg/L; see Table 5.2) due to the dissolution of the stockpile of road salt upstream of the discharge (effluent chloride concentrations are also very high - see Table 5.2). Since there are approximately 30 tonnes of limestone within the wetland increases in calcium concentration may be expected. Either significant dissolution of $CaCO_3$ is not occurring or there is an unidentified sink for calcium that counteracts any increases in calcium concentration due to limestone dissolution. Conceivably cation exchange reactions may mask increases in calcium concentration due to limestone dissolution (Hem, 1992). Magnesium is known to behave conservatively in wetland environments (Hedin *et al.*, 1994a). As previously noted Hedin *et al.* (1994a) use magnesium to calculate dilution effects in constructed wetlands since increases in its concentration are only likely to be due to evaporation, and decreases are only a result of diluting inputs (surface runoff and/or rainfall).

Despite the anticipated importance of bacterial sulphate reduction as a metal removal mechanism in anaerobic (compost) wetlands such as this (e.g. Hedin *et al.*, 1994a; Walton-Day, 1999) it is difficult to use reductions in sulphate concentrations as an indicator of such a process at this site. Mean reductions in sulphate concentration between influent and effluent are just 3.8% (from Table 5.2), and a Mann Whitney test reveals that there is no significant difference between influent and effluent sulphate concentrations. It is conceivable that residence times in the wetland may be insufficient to allow for significant sulphate reduction. Short residences time may be due to hydraulic short-circuiting, though further tracer tests would be required to ascertain whether this was the case. Installation of effective water distribution systems at the inlet of the wetland is likely to be crucial to avoiding short-circuiting problems. The role of sulphate reduction in pollutant attenuation at Quaking Houses is discussed at length in Section 5.5 below.

Time series analyses have been performed on the critical effluent water quality variables. As for the influent data, correlograms have been produced for effluent pH, alkalinity and acidity concentrations, and effluent Fe, Mn, Al and SO_4 concentrations. Unlike the influent data, however (see Section 5.2), in the majority of cases there is no consistent pattern or trend evident in the effluent data. A significant exception to this is the trend of the effluent aluminium correlogram. Specifically there is a striking relationship with ambient air temperature, which is illustrated graphically in Figure 5.9. The seasonal trend of air temperature is matched almost exactly by the effluent aluminium concentration. The pattern is reflected in the correlation coefficient between the two variables ($r = -0.611$; $p < 0.001$), and also in the partial correlation coefficient when influent flow-rate is held steady ($r = -0.612$; $p < 0.001$). This suggests that as ambient air temperature increases wetland effluent aluminium concentrations decrease. The strong implication that aluminium removal is controlled by temperature is discussed in detail in Section 5.5, below. Aluminium concentration is a major variable in the calculation of acidity concentration and consequently the relationship between air temperature and acidity concentration is also statistically significant ($r = -0.508$; $p < 0.001$). However, there is no such relationship between air temperature and any other variable used in the calculation of acidity (i.e. effluent Fe, Mn and pH).

5.5 Pollutant removal mechanisms and controls

Essentially there are two phases to successful operation of a compost wetland (Eger, 1994), and for each of these phases there are currently considered to be two mechanisms that are crucial (Hedin *et al.*, 1994a; Walton-Day, 1999):

1) Generation of alkalinity via	(a) dissimilatory sulphate reduction and / or
	(b) dissolution of carbonaceous material
2) Removal of metals via	(a) sulphate reduction sulphide precipitation and / or
	(b) adsorption (to mineral phases / organic matter)

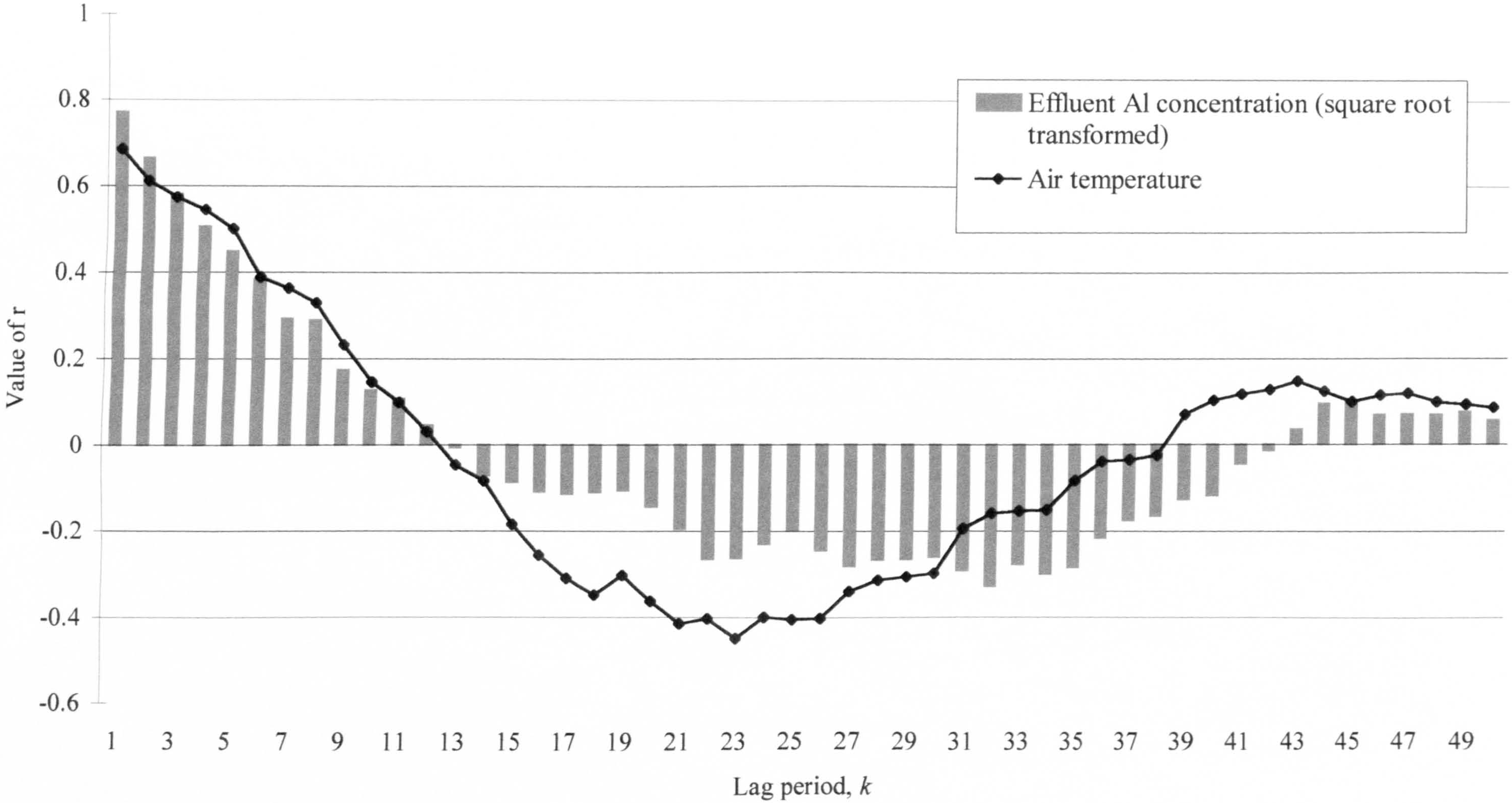


Figure 5.9 Correlograms of ambient air temperature and effluent aluminium concentration (square root transformed), demonstrating the close relationship between the two variables.

It was shown in Section 5.4 that there is no significant difference between influent and effluent sulphate concentrations. However, sulphate concentrations are typically at least two orders of magnitude greater than the concentrations of any of the metal contaminants that may be removed via dissimilatory sulphate reduction (i.e. iron, manganese and zinc). Therefore even if all of the metals were removed as monosulphides the measurable decrease in sulphate concentration would still only be minor. In fact, depending on the exact influent metal concentrations, the decrease would be typically less than 30 mg/L since the molar ratio of metal to sulphate in the relevant reactions (equations 3.11 and 3.12) is 1:1. Given the sample dilutions required to analyse sulphate concentration in the laboratory and the accuracy of the technique (see Chapter 2) it is questionable whether decreases in sulphate concentration due to bacterial sulphate reduction sufficient to precipitate the metals are actually detectable in this instance. Mitsch and Wise (1998) actually report increases in sulphate concentrations in a compost wetland in Ohio, USA. They attribute this to a lack of sulphate reduction due to unfavourable redox conditions, and possible oxidation of sulphur as it moves up into the water column. The intermittent appearance of a purple-coloured layer on the substrate surface at the Quaking Houses wetland has recently been suggested as an indication of the possible presence of sulphur-oxidising bacteria at this site (Barrie Johnson, University of Bangor, UK, personal communication, 2000). This lends support to Mitsch and Wise's (1998) suggestion of sulphur oxidation in the water column.

Table 5.3 reports results of recent analyses of surface water and pore water at the Quaking Houses wetland. Further results of such analyses are contained in Appendix 6. Sediment water was collected via a hypodermic needle from approximately 150 - 300 mm below the substrate surface. Interestingly sulphate concentrations are actually higher in the pore water (mean 544 mg/L) than the surface water (407 mg/L). Perhaps the most likely explanation for this is that accumulations of sulphur within the substrate are rapidly oxidised back to sulphate during sample collection and storage.

Although influent and effluent sulphate concentrations do not provide clear evidence of dissimilatory sulphate reduction there are other indications that suggest this process is occurring in the Quaking Houses wetland:

i. Gas bubbles can regularly be seen emerging from the wetland, particularly during the Summer months, and the strong odours indicate that at least a portion of this gas is hydrogen sulphide. It is possible for reduced sulphur to migrate to oxidising zones, which would result in no net increase in alkalinity. However, this degassing of H_2S is associated with permanent alkalinity generation (Mills, 1999). It is not possible here to quantify the relative proportions of reduced sulphur (a) forming insoluble metal precipitates, (b) being liberated to the atmosphere, and (c) being oxidised (and therefore effectively wasted).

ii. Visual signs and analytical results suggest that below the substrate surface anaerobic conditions certainly predominate. Anaerobic conditions are a necessary prerequisite for bacterial sulphate reduction (Hedin *et al.*, 1994a). The visual signs include the fact that deposits of orange and red iron hydroxide precipitates are only ever seen where water aerates as it cascades over the central bund between the two cells of the wetland and as it first enters the wetland via the stilling basin (see Figure 4.4). Clearly aerobic conditions exist in these areas, but there has never been any evidence of such ochre staining in any other part of the wetland, suggesting that even the water-substrate interface is under anaerobic or anoxic conditions. In addition recent (28/10/99) Eh measurements of water collected from 150 - 300mm below the sediment surface indicate strongly reducing conditions (-79 to -275 mV; see Table 5.3 for further results). In addition heavy black deposits within the substrate, and occasionally on the surface, resemble iron monosulphide precipitates.

iii. Early work on the pilot-scale wetland by Heasman (1996), and subsequently summarised by Younger (2000a), demonstrated that reduced sulphur species were a dominant component of the substrate. Three forms of sulphur were identified (with their relative proportions in parentheses): FeS (35%), FeS_2 (31%), S^0 (34%) (Younger, 2000a). In addition to indicating the presence of sulphate reducing bacteria in the pilot-scale wetland, Younger (2000a) argues that these observations suggest pH increases across the wetland were more due to consumption of protons (H^+) than the generation of bicarbonate alkalinity (HCO_3^-). The following reactions are consistent with the consumption of H^+, formation of S^0, and removal of Fe in this manner (Younger, 2000a):

$$5\,H^+ + 2FeOOH + HS^- \rightarrow 2Fe^{2+} + S^0 + 4H_2O \qquad (5.1)$$

$$Fe^{2+} + H_2S + 2HCO_3^- \rightarrow FeS + 2H_2O + 2CO_2 \qquad (5.2)$$

Since the pilot-scale wetland was very closely analogous to the full-scale wetland in its design and construction materials, it seems reasonable to conclude that similar processes may be operational in the full-scale system. Certainly there is evidence of both iron removal and an increase in pH across the wetland (Table 5.2).

iv. Recent work has demonstrated that there are quantifiable communities of sulphate reducing bacteria within the substrate (Unpublished data, Dr Mike Milner, University of Newcastle, UK, 2000). In particular the presence of *Desulfovibrio* within the wetland has been confirmed.

Although these strands of evidence are either anecdotal or based on only a few analytical results, when taken together they nevertheless strongly suggest when viewed together that sulphate reduction reactions are occurring within the wetland, despite the negligible absolute reduction in sulphate concentrations between influent and effluent. Mills (1999) has pointed out that iron reduction may also be an important process in anaerobic wetlands, although it has received little attention in research literature. It is unclear how this process may influence sulphate concentrations and sulphide generation in the Quaking Houses wetland however.

Walton-Day (1999) explains that at pH < 4.5 sulphate reduction may lead to a net consumption of protons (and therefore increase in pH) without a commensurate increase in alkalinity concentration, in accordance with the reaction (Walton-Day, 1999):

$$2\,CH_2O + SO_4^{2-} + 2\,H^+ \rightarrow 2\,CO_2 + H_2S + 2\,H_2O \qquad (5.3)$$

However at higher pH values bicarbonate, and therefore alkalinity, may be generated:

$$2\,CH_2O + SO_4^{2-} \rightarrow H_2S + 2\,HCO_3^- \qquad (5.4)$$

Location	pH	Eh (mV)	Fe (total) (mg/L)[a]	Mn (mg/L)[a]	Zn (mg/L)[a]	Al (mg/L)[a]	SO_4 (mg/L)	TOC (mg/L)[b]	IC (mg/L)[c]
Surface water, first cell	6.77	84	5.30 (6.30)	1.63 (2.02)	0.59 (1.30)	3.67 (6.04)	453	< 7	22
Pore water, first cell[d]	6.73	-109	601 (3368)	28.35 (42.52)	5.85 (125.30)	0.50 (4054)	661	22	130
Amongst reeds, surface water, first cell	7.2	-74	1.90 (2.54)	1.31 (1.81)	0.14 (0.94)	0.89 (3.77)	381	9.1	66
Amongst reeds, pore water, first cell[d]	6.52	-186	89.00 (323.4)	6.08 (6.32)	2.62 (31.15)	0.86 (425.4)	462	15	150
Surface water, second cell	7.11	-58	2.73 (3.05)	1.42 (1.81)	0.35 (1.78)	1.26 (4.23)	382	< 7	25
Pore water, second cell[d]	6.62	-275	105.2 (192.2)	7.28 (7.46)	8.77 (14.88)	8.87 (241)	529	8.2	130
Amongst reeds, surface water, second cell	6.99	-61	1.41 (1.62)	1.05 (1.39)	0.27 (0.91)	0.72 (3.28)	413	7.2	27
Amongst reeds, pore water, second cell[d]	7.39	-79	15.46 (945.4)	21.81 (37.46)	1.98 (17.89)	0.69 (959.4)	523	9.7	54

a Figures in parentheses are concentrations found following digestion of sample in concentrated nitric acid (see Section 2.3.1 for details of analytical procedure).

b TOC is Total Organic Carbon (analysed by Analytical and Environmental Services Ltd).

c IC is Inorganic Carbon (analysed by Analytical and Environmental Services Ltd).

d Pore water samples were collected from 150 - 300 mm below the substrate surface.

Table 5.3 **Comparison of chemical quality of surface water and pore water at various locations within the Quaking Houses constructed wetland.**

Concentrations in parentheses are for acid-digested samples (samples collected on 28th October 1999).

pH readings of the substrate pore water in the Quaking Houses wetland fall within the range 6.52 - 7.39 (see Table 5.3). Sulphate reduction may therefore be a mechanism through which alkalinity is generated in the Quaking Houses wetland.

The comparative significance of alkalinity generation via sulphate reduction versus dissolution of carbonaceous material is unclear. As detailed in Section 5.4 there is no evidence of an increase in calcium concentration between influent and effluent, which would be the most obvious indication of alkalinity generation via carbonate dissolution. Brodie *et al.* (1993) suggest that at pH > 6.4 (i.e. the pH range of the wetland water in this instance) the key reaction is:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad (5.5)$$

An increase in calcium concentration would therefore be anticipated. However, the mean increase in alkalinity concentration is only 17.1 mg/L as $CaCO_3$ (see Table 5.2). This equates to approximately 20.5 mg/L HCO_3^- (by multiplying by 1.2; APHA, 1998). The equivalent increase in calcium concentration is just 13.7 mg/L, which is within the range of analytical error at the mean effluent concentration of calcium (234 mg/L).

In aerobic wetland systems precipitation of metals as oxides and hydroxides is widely considered as the most significant metal attenuation mechanism (e.g. Eger, 1994; Hedin *et al.*, 1994a; Tarutis and Unz, 1990; Wieder, 1988). For removal of iron and manganese such a mechanism is not significant in the wetland at Quaking Houses because anaerobic conditions are encouraged. Iron hydroxide precipitates can be seen over the central bund of the wetland and as water enters the wetland, but in no other area is the easily identifiable orange precipitate consistently evident. Consistent net removal of iron within the confines of the wetland is most likely to be due to the two processes given above i.e. adsorption and precipitation as a monosulphide, FeS. Machemer and Wildeman (1992) suggest that adsorption is only a significant removal process in the first months of operation. Exhaustion of sorption sites limits further adsorption, and sulphate reduction becomes the dominant mechanism over the long-term. There has been no detectable improvement or deterioration in the iron removal rate at the Quaking Houses wetland site over the 27 months of monitoring (see Section 5.6), and so if sorption sites were exhausted it appears that it was either very early, before regular monitoring was in place, or else after sulphate reducing bacteria populations were well established.

Inspection of Table 5.3 reveals that most of the iron in the water column of the wetland is in the dissolved state (ferrous), because the concentration of total iron in the digested samples is only marginally greater than in the untreated samples. Since there is no evidence of hydroxide precipitates on the wetland substrate surface it seems apparent that the main sink for iron is *within* the substrate itself. Analyses of iron concentrations in the wetland pore water confirm this supposition. Filtered samples of pore water contain 15.46 - 601 mg/L of iron, whereas filtered surface water samples contain just 1.41 - 5.30 mg/L. Acid digestion of pore water samples (which are heavily laden with sediment) strongly suggests that iron is bound to organic and mineral surfaces within the substrate. Concentrations of iron in acid digested pore water samples range from 192 - 3368 mg/L (Table 5.3). Unfortunately the iron concentrations associated with acid digested samples of the wetland substrate *before* it was flooded with spoil heap drainage are unavailable. Nevertheless it seems unlikely that animal waste materials and municipal waste compost would contain such elevated concentrations of iron. If they had then at least some leaching of metals from the substrate might have been expected during the early operation of the wetland, but there is no evidence for this.

Hedin *et al.* (1994a) and Hedin and Nairn (1993) highlight the difficulties of manganese removal in constructed wetlands due to its mobility in aquatic environments. In aerobic wetlands Hedin and Nairn (1993) note that the rate of removal of manganese is some 20 - 40 times slower than that of iron removal. In anaerobic systems precipitation of MnS is also more difficult than formation of FeS because of the greater solubility of the manganese monosulphide (Hedin *et al.*, 1994a; see Table 3.2).

At Quaking Houses the mean wetland influent iron concentration is 1.5 times greater than manganese concentration (Table 5.1), but acid digestions of the pore water and associated sediment reveals that the ratio of iron to manganese within the substrate is far greater than this (Table 5.3). Acid digested samples of pore water contain iron concentrations an order of magnitude greater than manganese concentrations. In fact, even taking account of the greater influent iron concentration, the ratio of iron to manganese in the digested pore water is 40:1, implying that manganese removal is some

40 times slower than iron removal in this anaerobic wetland (cf. 20 - 40 times slower in aerobic wetlands according to Hedin and Nairn (1993)).

According to their solubility products (Table 3.2) the order of removal of metals as monosulphdes at Quaking Houses should be ZnS, FeS and then MnS. The extent of removal in the Quaking Houses wetland, according to the information contained in Table 5.3, is Fe ≈ Al > Zn > Mn. Aluminium does not form a sulphide in wetland environments, and possible mechanisms for its removal at Quaking Houses are discussed below. The fact that the other metals are not removed in the order expected according to their solubility products certainly implies that other processes influence metal removal. Although adsorption is not considered a viable long-term removal mechanism (Machemer and Wildeman, 1992; Walton-Day, 1999) it is possible that it still plays a role at Quaking Houses. Machemer and Wildeman (1992) found that competition for sorption sites favoured specific metals in the following order: Fe = Cu > Zn = Mn. Co-precipitation of Mn has been cited as an important mechanism in limestone drains (Cravotta and Trahan, 1999), and other investigators have achieved successful Mn removal using limestone systems provided that iron is removed first (e.g. Stark *et al.*, 1996; Brant and Ziemkiewicz, 1997). There are "pockets" of limestone within the substrate at Quaking Houses that may influence manganese removal, but detailed analysis of mineral composition would be necessary to confirm the existence of manganese precipitates and co-precipitates in these areas. Similarly the existence of ZnS and MnS precipitates could perhaps be established using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) techniques, although successful identifications might not be feasible until the cumulative Zn and Mn had reached g/kg levels. A natural progression from the work reported here would be to undertake such analyses in detail.

Table 5.4 is a correlation matrix that illustrates the close inter-relationships between the key influent and effluent water quality variables at Quaking Houses wetland. Many of the data have been transformed (either by taking the square roots or the natural logarithms of the original observations) in order to meet the requirement that the data to be correlated are normally distributed (see Figure A1 for an example of a normal distribution).

The magnitude of the increase in alkalinity and pH necessary to effect a measurable improvement in zinc and manganese remediation is still unclear. There is no correlation between effluent alkalinity concentration and effluent iron and aluminium concentrations (Table 5.4). This implies that the effective removal of these two metals is not limited by insufficient alkalinity generation through the wetland. Effluent aluminium concentration is not correlated with effluent pH, implying that its attenuation is limited neither by alkalinity or pH. Mean influent pH is 6.1, and mean effluent pH is 6.6. This is well within the range at which aluminium will begin to rapidly form a hydroxide precipitate (Lydersen *et al.*, 1991).

	Effluent Fe^a	Effluent Al^a	Effluent Mn^a	Effluent Zn^b	Air Temperature^c
Effluent Fe^a	-	0.113	***0.396***	0.171	-0.005
Effluent Al^a	0.113	-	0.073	*0.458*	***-0.619***
Effluent Mn^a	***0.396***	0.073	-	***0.639***	*0.309*
Effluent Zn^b	0.171	*0.458*	***0.639***	-	-0.084
Effluent pH^c	*-0.271*	-0.046	***-0.640***	***-0.610***	-0.153
Effluent alkalinity^a	-0.196	-0.116	***-0.508***	***-0.560***	-0.114
Effluent acidity^b	***0.400***	***0.847***	***0.455***	***0.592***	*-0.481*
Influent Fe^a	***0.644***	*-0.223*	***0.423***	0.030	***0.509***
Influent Al^a	*0.295*	***0.463***	***0.577***	***0.538***	-0.239
Influent Mn^c	***0.410***	-0.057	***0.885***	***0.594***	***0.536***
Influent Zn^b	0.168	*0.263*	***0.714***	***0.812***	0.236

a Data not normally distributed, therefore square root of original observations used.

b Data not normally distributed, therefore natural logarithm of original observations used.

c Original data normally distributed, therefore no transformation.

Table 5.4 Correlation matrix demonstrating the inter-relationships between key influent and effluent water quality variables and ambient air temperature at Quaking Houses wetland. Significance levels are as follows: ***$p < 0.001$***; *$p < 0.01$*; *$p < 0.05$*.

There is a strong positive correlation between effluent acidity concentration (calculated) and metal ion concentrations, but given that the acidity concentration is calculated from metal ion concentrations and pH (see Section 2.3.2), this is of little surprise.

One of the most interesting relationships illustrated in Table 5.4 is the inverse correlation between air temperature and effluent aluminium concentration ($p < 0.001$), which was mentioned in Section 5.4 and is illustrated in Figure 5.9. There is no correlation between influent aluminium concentration and air temperature. The conclusion therefore is that higher air temperatures result in more effective attenuation of aluminium within the wetland at Quaking Houses. In laboratory experiments Hem and Roberson (1990) and Lydersen *et al.* (1991) both report higher rates of formation of $Al(OH)_3$ at higher temperatures. Hem and Roberson (1990), for example, show that at pH 6.0 the solubility of microcrystalline gibbsite is greater at 5.0°C than at 35.0°C by a factor of 2. The difference in solubility as a function of temperature increases as pH decreases (Hem and Roberson, 1990). However, to the author's knowledge this is the first time such a relationship has been demonstrated for a constructed wetland system. Although the relationship between effluent water temperature and effluent aluminium concentration is an inverse one, the correlation is not statistically significant. However, only 19 paired observations are available for this test because it has not been possible to routinely measure temperature on site. 49 paired observations are available for the correlation of air temperature with effluent aluminium concentration. Although constructed wetlands are not typically designed specifically for aluminium removal (Hedin *et al*, 1994a), the identification of this relationship has implications for the design of units for treatment of aluminium-rich water, particularly in cold climates. On the basis of this relationship aluminium removal will be less effective under harsh climatic conditions, although further research would be required to confirm this hypothesis.

5.6 Performance assessment of the Quaking Houses constructed wetland

Three different measures have been used to assess the performance of the constructed wetland at Quaking Houses. The relevant figures for the key pollutants are given in Table 5.5. The three methods of assessing constructed wetland performance were detailed in Section 3.3. Treatment efficiency and contaminant load removal have been the most commonly employed. In addition Tarutis *et al.* (1999) have more recently proposed a new system based on the first-order reaction kinetics of iron. Complete listings of all the data on which these summary calculations are based are given in Appendices A2 to A4.

In terms of mean treatment efficiency approximately 50% reductions in the concentrations of acidity, iron and aluminium have been achieved over the 27 month study period. Mean efficiencies for manganese and zinc are lower, at 26.4% and 25.8% respectively. In all cases however treatment efficiencies are highly variable (see Table 5.5). On at least one occasion during the study period the wetland has actually been a source of each of the target metal contaminants. Conversely, treatment efficiency has been in excess of 95% for acidity and iron, up to 100% for aluminium and manganese, and over 80% for zinc on at least one occasion.

Area-adjusted acidity removal rates range from 1.3 - 46.1 g/m^2/d. However, 46.1 g/m^2/d is an extreme value associated with a very high influent acidity load. Excluding this value the mean area-adjusted acidity removal rate over 27 months is 5.6 g/m^2/d, based on influent flow-rates only, and 5.01 g/m^2/d if dilution effects are accounted for (see Section 3.3 for details). Figures for dilution-adjusted and unadjusted rates are given in Table 5.5 because there are twice as many observations available for the latter. Area-adjusted removal rates for the metal contaminants are much lower. Taking account of dilution effects area-adjusted removal rates range from 0.065 g/m^2/d for zinc, through 0.23 g/m^2/d for manganese, and up to 0.53 g/m^2/d and 0.60 g/m^2/d for iron and aluminium respectively.

First-order rate constants (k_1) (following the work of Tarutis *et al.*, 1999) are provided for acidity, iron, manganese, aluminium and zinc. k_1 is given in m/d, which is the unit of settling velocity (i.e. based on an areal model rather than a volumetric one) (Tarutis *et al.*, 1999). Tarutis *et al.* (1999) propose the use of this measure for constructed wetland performance assessment and design in preference to treatment efficiency and area-adjusted removal because:

i. Tarutis *et al.* (1999) believe that wetland performance is concentration-dependent, and yet treatment efficiency and area-adjusted removal fail to account for this.

ii. Treatment efficiency is a relative measure of performance, and therefore different wetlands cannot be easily compared in terms of performance. Treatment efficiency is also of minimal use for design purposes.

	Mean	Range (n)[a]
Acidity treatment efficiency (%)[b]	53.4	11.8 - 95.5 (80)
Area-adjusted acidity removal (g/m^2/d)[c]	5.6	1.3 - 16.3 (57)
Area-adjusted acidity removal with DF (g/m^2/d)[c,d]	5.01	1.33 - 15.67 (29)
First-order acidity removal (m/d)[e]	0.118	0.034 - 0.296 (29)
Fe treatment efficiency (%)[b]	46.4	-23.8 - 96.6 (104)
Area-adjusted Fe removal (g/m^2/d)[c]	0.58	-0.06 - 2.58 (76)
Area-adjusted Fe removal with DF (g/m^2/d)[c,d]	0.53	-0.10 - 2.58 (34)
First-order Fe removal (m/d)[e]	0.105	-0.013 - 0.322 (34)
Mn treatment efficiency (%)[b]	26.4	-13.9 - 100 (102)
Area-adjusted Mn removal (g/m^2/d)[c]	0.26	-0.03 - 1.18 (72)
Area-adjusted Mn removal with DF (g/m^2/d)[c,d]	0.23	-0.41 - 1.15 (34)
First-order Mn removal (m/d)[e]	0.061	-0.197 - 0.282 (34)
Zn treatment efficiency (%)[b]	25.8	-107.2 - 81.0 (49)
Area-adjusted Zn removal (g/m^2/d)[c]	0.090	-0.02 - 0.280 (39)
Area-adjusted Zn removal with DF (g/m^2/d)[c,d]	0.065	-0.047 - 0.230 (29)
First-order Zn removal (m/d)[e]	0.062	-0.040 - 0.322 (29)
Al treatment efficiency (%)[b]	51.2	-2.9 - 100 (99)
Area-adjusted Al removal (g/m^2/d)[c]	0.81	-0.02 - 8.76 (70)
Area-adjusted Al removal with DF (g/m^2/d)[c,d]	0.60	-0.01 - 2.17 (34)
First-order Al removal (m/d)[e]	0.161	-0.002 - 0.563 (34)

a n = number of observations b after Wieder (1989)

c after Hedin *et al.* (1994a)

d DF = dilution factor; see Section 3.3 for calculation (after Hedin and Nairn, 1993)

e after Tarutis *et al.* (1999)

Table 5.5 Measures of performance assessment for acidity, Fe, Mn, Zn and Al removal at the Quaking Houses constructed wetland.

iii. The area-adjusted removal method is based on zero-order kinetics, but Tarutis *et al.* (1999) argue that the removal of iron and manganese in constructed wetlands (irrespective of whether they be aerobic or anaerobic systems) more closely approximates first-order reaction kinetics.

The mean first-order rate constants for iron and manganese in the Quaking Houses wetland are 0.105 m/d and 0.061 m/d respectively. For 35 natural wetlands Tarutis *et al.* (1999) report mean values for k_1 of 0.29 m/d for iron and 0.057 m/d for manganese. Perhaps the difference in Fe removal rate relates to the ecological differences between constructed and natural wetlands identified by Webb *et al.* (1998). However, if this were the case a difference in the removal rate of manganese might also be expected, and yet the manganese removal rates are very similar. Calculation of values of k_1 for other constructed wetlands will be necessary to confirm whether these differences and similarities between constructed and natural wetlands are typical or simply coincidental.

For iron and acidity all three measures of wetland performance are significantly positively inter-correlated for the Quaking Houses data. This is to be expected since all three measures are essentially derived from the same operating data (Tarutis *et al.*, 1999).

Influent iron concentration has a strong statistical influence on treatment efficiency and area-adjusted removal rate. Specifically, as the influent iron concentration increases the percentage of iron concentration removed (i.e. treatment efficiency) increases, and so does the area-adjusted removal rate ($p < 0.001$). Table 5.6 illustrates the relevant correlation coefficients, and also demonstrates that the same pattern is evident for both acidity and for aluminium. However, there is no correlation between influent concentrations of iron, acidity and aluminium and their respective first-order removal rates (Table 5.6). This observation strongly supports the contention of Tarutis *et al.* (1999) that performance is concentration-dependent i.e. pollutant removal rate depends on initial pollutant concentration. It also suggests that their first-order model of wetland performance may be a more useful tool for making comparisons between systems, because the other measures will tend to give a more favourable indication of performance if influent contaminant concentrations are high. For the same reasons better design of passive treatment systems may be possible using a first-order model as opposed to the area-adjusted removal model commonly employed at present.

How does the Quaking Houses constructed wetland compare with other mine water treatment wetlands in terms of these various performance indicators? The wetland at Quaking Houses was designed on the basis of guidelines drawn up by the US Bureau of Mines (Hedin *et al.*, 1994a; see Section 3.3). Based on the performance of wetlands in the USA Hedin *et al.* (1994a) suggested that an acidity removal rate of 7 $g/m^2/d$ was appropriate for the design of compost wetlands. The operation of a pilot-scale wetland at Quaking Houses confirmed that this was a reasonable target removal rate, since in that system acidity removal was in the order of 9.0 $g/m^2/d$ (Younger *et al.*, 1997; see Section 4.3.1). After 27 months of operation the actual area-adjusted acidity removal rate at Quaking Houses is 5.01 $g/m^2/d$ however (see Table 5.5). The full-scale wetland therefore appears to be under performing in terms of area-adjusted removal. But the correlations in Table 5.6 demonstrate that area-adjusted removal is strongly influenced by influent contaminant concentrations (and by association influent flow-rate, since influent contaminant concentrations are significantly inversely correlated with influent flow-rate - see Section 5.2). By contrast first-order removal constants for the Quaking Houses wetland do not correlate with influent pollutant concentrations (Table 5.6), demonstrating that the Tarutis *et al.* (1999) model does appear to be concentration-independent. Table 5.7 shows wetland data collected by Hedin *et al.* (1994a) which were used in the calculation of average acidity removal rates (i.e. 7.0 $g/m^2/d$), and also reports the area-adjusted removal rate for each of the three wetlands. Using the data of Hedin *et al.* (1994a) this author has calculated values of first-order rate constants for the systems. Values for area-adjusted removal rate and first-order removal constants for the Qauking Houses wetland are included for comparative purposes. What Table 5.7 reveals is that in terms of first-order removal rates the wetland at Quaking Houses compares very favourably with the examples from the USA.

By keeping influent loading rate constant but varying influent flow-rate and concentration Tarutis *et al.* (1999) illustrate that predictions of wetland area required for a given combination of flow-rate and concentration vary, despite the steady loading rate. This has been illustrated graphically in Figures 3.6 and 3.7. Specifically *"...area-adjusted removal will always predict smaller wetland areas for higher flows and lower*

	Influent [Fe]	Influent [acidity]	Influent [Al]
Treatment efficiency	***0.526***	***0.566***	***0.498***
Area-adjusted removal rate	***0.677***	*0.548*	*0.441*
First-order removal rate	0.143	0.097	-0.022

Table 5.6 **Correlation coefficients showing the strength of relationships between influent iron, acidity and aluminium concentrations and their respective constructed wetland performance measures.** There is no statistical relationship between first-order removal rate and influent iron, acidity and aluminium concentrations. Significance levels are as follows: ***$p < 0.001$***; *$p < 0.01$*.

concentrations..., and larger wetlands for lower flows and higher concentrations..." (from Tarutis *et al.*, 1999). It is apparent from Table 5.7 that the Quaking Houses wetland receives a high flow and low concentration discharge when compared to the examples from the USA. This is exactly why the Quaking Houses wetland compares unfavourably in terms of area-adjusted removal rates.

It should be pointed out that Hedin *et al.* (1994a) always recognised concentration-dependence as a possibility, stating that *"it is possible that Fe removal rates are a function of Fe concentration; i.e., as concentrations get lower, the size of system necessary to remove a unit of Fe contamination...gets larger"*. It was for this reason that they included in their design guidelines more conservative removal rates (see Table 3.3). The important conclusion from this is that if an area-adjusted removal approach is to be used to design constructed wetland systems then it is not sufficient to simply look at contaminant loading rates; the individual components of the load must also be assessed. This situation will obtain until such time as it is possible to use a first-order removal approach for design, which does separate the concentration and flow-rate components. However, to calculate wetland areas in this way it is first necessary to know the value of the first-order removal constant (k_1). Tarutis *et al.* (1999) highlight this as a pressing need for constructed wetland systems. Given the increasing volume of historical data available from constructed systems this should be an easily achievable, albeit time-consuming task, at least for aerobic systems. For anaerobic systems (compost wetlands) calculation of values of k_1 may take longer, simply because there are fewer of these systems. In the UK, for example, at the end of 1999 there were 13 operational aerobic wetlands, but only 3 anaerobic systems (Younger, 2000a). Furthermore, SAPS are the main treatment units in 2 of these 3 cases (the other case being Quaking Houses).

	Emlenton		Somerset		Latrobe		Quaking Houses	
	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.
Flow-rate (m^3/d)	79.2		67.7		123.8		141.3	
Surface area (m^2)	643		1005		2800		440	
Acidity (mg/L)	320	271	373	69	617	343	52	25
Fe (mg/L)	89	15	162	18	125	56	5.4	2.4
Mn (mg/L)	77	73	50	33	32	29	3.6	3.0
Area-adjusted removal ($g/m^2/d$)	3.1		9.9		6.9		5.0	
k_1 Acidity (m/d)	0.020		0.114		0.026		0.118	
k_1 Fe (m/d)	0.219		0.148		0.036		0.105	
k_1 Mn (m/d)	0.007		0.028		0.004		0.061	

Table 5.7 **Values of area-adjusted removal rates and first-order removal constants for Quaking Houses wetland compared with values from analogous systems in the USA** (USA data from Hedin *et al.*, 1994a).

5.7 Quaking Houses wetland performance prediction

Being able to predict effluent contaminant concentrations from influent variables at constructed wetlands that have been operational for several years, such as the Quaking Houses system, would be of considerable use. Ideally it would be desirable to first understand the exact processes operational within a constructed wetland, and especially to be able to quantify the relative importance of these mechanisms. However, achieving such an understanding currently seems to be some years away. Predicting effluent pollutant concentrations, even within generous margins of error, would perhaps help to focus attention on particular mechanisms operational within wetland systems, and would certainly appear to be a more immediately achievable goal in research terms, even if it is only possible on a system-by-system basis.

The preceding discussion has revealed much about the critical controls on effluent water quality at the Quaking Houses wetland. Effluent concentration is strongly positively correlated with influent concentration for many contaminants (acidity, Fe, Mn, Al) (see Table 5.4), and therefore the influent concentration must be included in any predictive algorithm. The work of Tarutis *et al.* (1999), which is strongly supported by this research, indicates that influent flow-rate is also an important control on wetland performance. Calculated acidity concentration (Hedin *et al.*, 1994a) may be a useful component of a predictive algorithm too, since it includes many of the most important water quality variables in the Quaking Houses mine water (i.e. Fe, Mn, Al and pH).

As a first step in producing a predictive equation for the removal of pollutants within the Quaking Houses constructed wetland linear multiple regression has been undertaken using Minitab software. Effluent iron concentration has been selected as the response variable, since its removal has been a central theme of this research, and also because removal of iron is often the main focus of regulatory standards, in the UK at least. This is largely because (a) iron is the main contaminant in mine waters and (b) iron causes highly visible staining problems in receiving watercourses. The predictor variables selected are influent iron concentration, acidity concentration and flow-rate, for the reasons discussed above. The regression equation calculated is (maintaining transformed variables where applicable):

$$\sqrt{Fe_{out}} = 1.10 + 0.00038\ Acid_{in} - 0.09\ \log_e Q_{in} + 0.383\ \sqrt{Fe_{in}} \qquad (5.6)$$

The value of R^2 (the coefficient of determination; see Appendix 8) is 53.5%. In other words 53.5% of the variation in effluent iron concentration is explained by the influent flow-rate, the influent iron concentration and the influent acidity concentration. Using a variety of combinations of other key influent variables as the predictors reveals that this is the highest value of R^2 obtainable using multiple regression. This certainly suggests that the predictor variables chosen are the most influential in terms of governing the effluent iron concentrations at the Quaking Houses wetland. Nevertheless 46.5% of the variance in effluent iron concentration remains unexplained by this equation. Figure 5.10 is a plot of the actual effluent iron concentrations versus the iron concentrations predicted by equation 5.6. The line $y = x$ is drawn on the graph. It is apparent from Figure 5.10 that equation 5.6 over-predicts effluent iron concentrations, particularly at actual iron concentrations of less than approximately 4 mg/L. This perhaps implies that an important predictor variable, which assists iron removal within the wetland, is missing from the equation. What this variable might be is open to conjecture, although the rate of hydrolysis of organic carbon is one possibility.

Whether it would be possible to significantly increase the value of R^2 by using a non-linear regression technique is unclear, but researching this possibility would certainly be a worthwhile endeavour. Whatever statistical techniques are used it seems unlikely, given the complexity and uniqueness of constructed wetland systems, that a *universally* applicable predictive equation will ever be an achievable goal. However, the generation of predictive algorithms for *individual* systems may be possible, and would unquestionably assist in discerning the key contaminant removal mechanisms in these constructed wetlands.

At the time of writing the constructed wetland at Quaking Houses has proved a success in many respects. From an engineering point of view the wetland is a success for a number of reasons:

- It was constructed at low cost (less than £20 000; Table 4.1)
- The materials used during construction were all low cost, and predominantly waste materials.
- There is no evidence at present that the retaining embankments are either eroding significantly or allowing toe drainage.
- The wetland successfully ameliorates the pollution from the spoil heap.

There are however some aspects where engineering improvements may be made, depending on the outcomes of future research. In particular it is possible that hydraulic short-circuiting is limiting residence time to the detriment of the effectiveness of treatment. On a related matter the baffles constructed to encourage circuitous flow

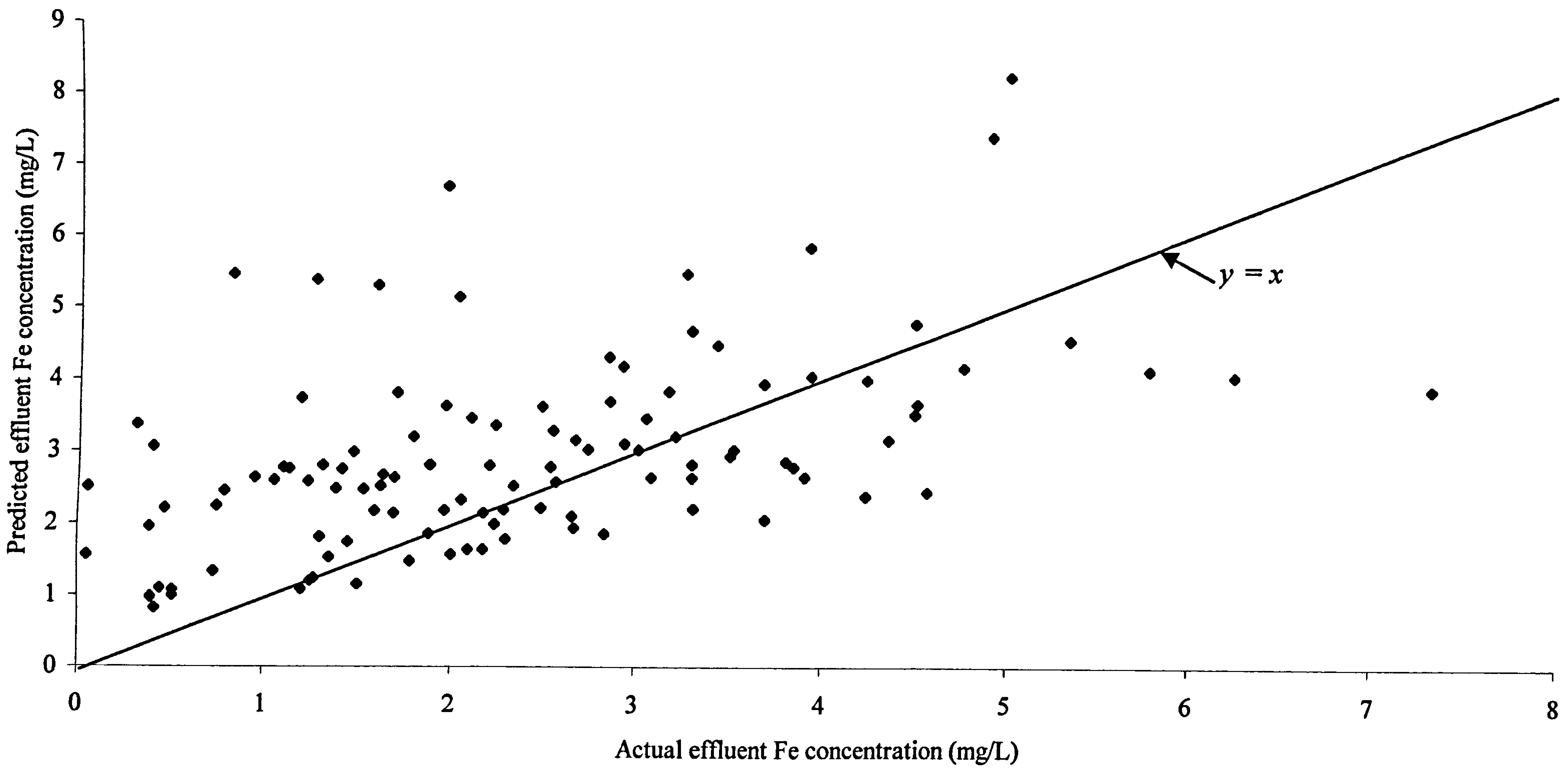


Figure 5.10 Actual effluent concentration versus predicted effluent Fe concentration (by multilinear regression) for the Quaking Houses wetland, using the equation: sqrt eff Fe = 1.10 + (0.00038*Inf acid) - (0.09 * loge inf flow) + (0.383*sqrt Inf Fe)

paths could possibly be higher because at present they are slightly submerged below the water surface.

From an ecological viewpoint extensive stands of *Typha latifolia* and other wetland plants have successfully colonised the wetland, although in some areas, especially in the lower pond, the water depth appears to be too great to allow successful early growth of plants (Dr Lesley Batty, University of Newcastle, UK, personal communication, 2000). Ecological assessments of the receiving watercourse have not been undertaken since the wetland was commissioned. However, it seems unlikely that significant improvements would be evident. This is not indicative of ineffective treatment by the wetland, but a consequence of the continued pollution of the Stanley Burn by road salt (see section 5.2).

From a social point of view the wetland continues to be a great success. The significant improvement in the visual appearance of the Stanley Burn was always a key objective of the residents of Quaking Houses village, and this has been achieved. Many of the residents of the village (of all ages) have been involved with the wetland since the inception of the project, and continue to play a vital role (voluntarily) in the routine maintenance of the system. In addition the Quaking Houses Environmental Trust have hosted many other community groups planning similar environmental restoration projects.

CHAPTER 6

PILOT-SCALE TREATMENT OF KIMBLESWORTH PUMPED MINE WATER DISCHARGE

6.1. Introduction

This chapter discusses an investigation into the feasibility of treatment of a marginally ferruginous, strongly net-alkaline mine water in County Durham, UK. This research was independent of the project at Quaking Houses. The chemical quality of the mine water addressed here is very different to that at Quaking Houses, and the approach to passive treatment adopted is unique. It is for these reasons that the research at Kimblesworth pumped mine water is introduced, discussed and concluded within this single chapter (with the exception of analytical methods, which are covered in Chapter 2). Many of the methods employed to illustrate both the processes involved in, and the effectiveness of, passive treatment systems are the same as those used in the discussion of the performance of the Quaking Houses wetland (see Chapter 5). However, the most significant connection between the two investigations can only be appreciated with a knowledge of the results of both investigations. Specifically, it appears as though the two treatment systems would operate very effectively in series. This issue is discussed in detail in Chapter 7, when the results of both investigations have been detailed.

Despite the well documented acid-generating reactions involved in pyrite oxidation and dissolution (e.g. Stumm and Morgan, 1996) many mine waters emerging at the surface are in fact net-alkaline (i.e. alkalinity > acidity) (Hedin, 1997; NRA, 1996), due to the presence of calcareous minerals in the vicinity of the reacting pyrite (Hedin, 1997). The main objective of passive treatment of these net-alkaline waters is the removal of metal contaminants, which are typically limited to iron and manganese (see Section 3.2.2 for a complete discussion of aerobic metal removal processes). Thick deposits of iron oxyhydroxide on streambeds, and the relative clarity of waters affected by ferruginous, net-alkaline discharges, provide clear evidence that the iron present in such discharges is rapidly oxidising and accreting on the stream bed. The overall objective of this research project was to investigate whether harnessing such chemical reactions within a reactor containing high surface area media may provide an effective treatment option for ferruginous, net-alkaline discharges arising in areas of difficult terrain and/or limited land availability.

6.2 Study site characteristics

Kimblesworth mine water, County Durham, is one of nine pumped mine waters in the region (Figure 6.1). These nine stations lower the water table over an area of approximately 600 km^2, discharging a total of over 100000 m^3/d (of which Kimblesworth contributes 9100 m^3/d) (Younger, 1993). Chemically these discharges are typified by high alkalinity (550 - 1050 mg/L as $CaCO_3$) and marginally elevated total iron concentrations (0.5 - 6.0 mg/L) (Younger, 1998a). At Kimblesworth mine water is pumped to the surface from old coal workings 150 m below ground level. The water quality of the discharge at the surface has been monitored from February 1998 to February 1999. The mean values and ranges of chemical determinands are given in Table 6.1.

The discharge is highly mineralised and strongly net-alkaline. Although the mean concentration of iron is low compared to many of the uncontrolled discharges in the region (see NRA, 1996), the loading of iron is nevertheless high enough to cause severe ochre staining of the receiving watercourse (a tributary of the River Wear) for some distance downstream. Mine waters of this chemical nature are ideal candidates for rapid oxidation and accretion of ochre on high surface area media, mainly because the high alkalinity serves to buffer the acidity generated by the precipitation of iron, as illustrated by the reaction (from Hedin *et al.*, 1994a):

$$Fe^{3+} + 2\,H_2O \rightarrow FeOOH + 3\,H^+ \qquad (6.1)$$

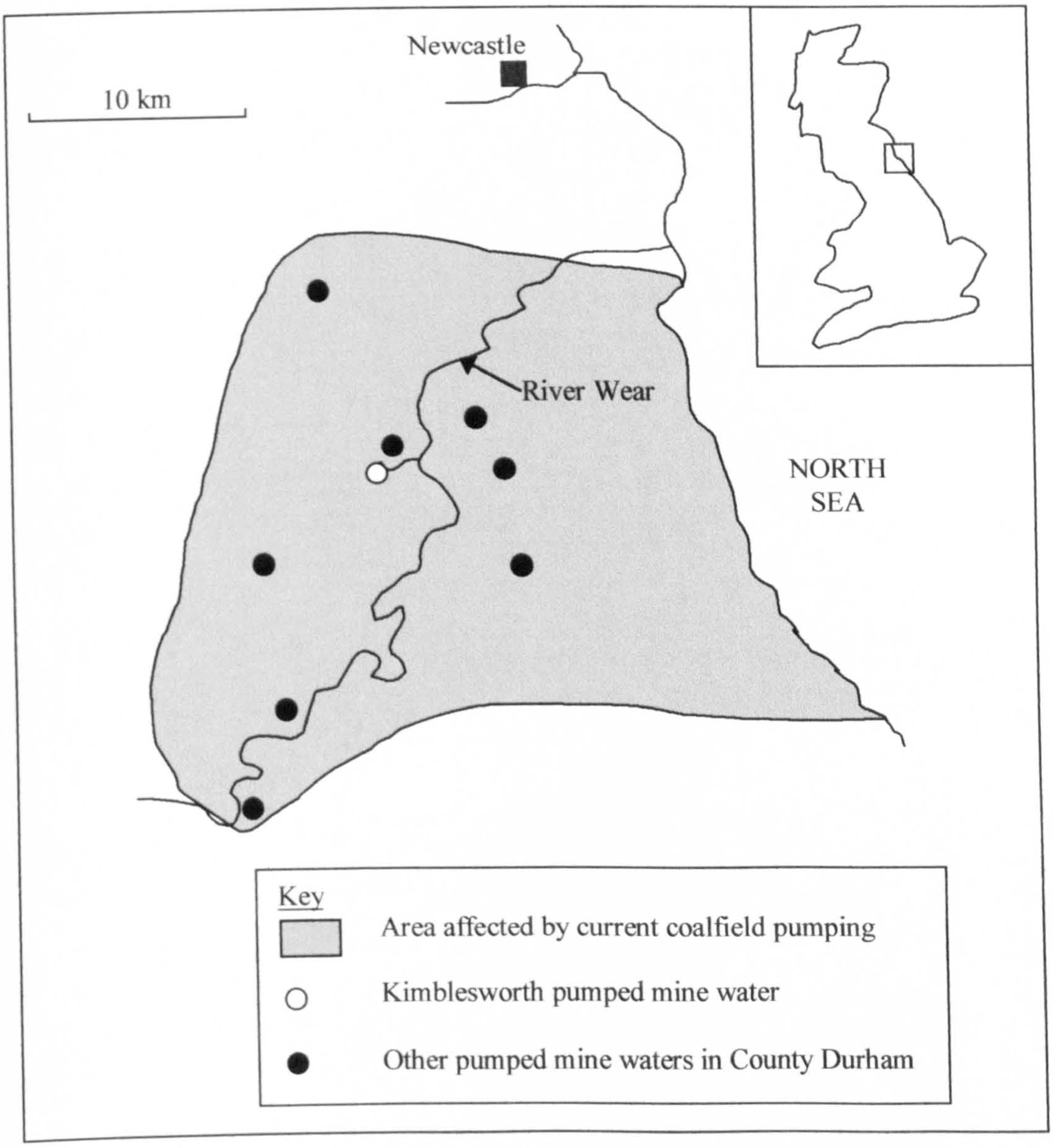


Figure 6.1 **Location of Kimblesworth mine water and other pumped mine waters in County Durham, UK** (adapted from Younger, 1993).

Determinand	Mean	Range (total number of values)
Temperature (°C)	14.5	11.7 - 15.2(n=17)
pH	6.95	6.85 - 7.09 (n=17)
Eh (mV)	-18	-6 - -28 (n=5)
Conductivity (μS/cm)	2163	1600 - 2490 (n=16)
Alkalinity (mg/L as $CaCO_3$)	758	692 - 857 (n=16)
Acidity$_{calc}$ (mg/L as $CaCO_3$)	5	2 - 8 (n=16)
Ca (mg/L)	98.3	92.5 - 106.1 (n=14)
Mg (mg/L)	37.9	36.0 - 43.8 (n=14)
Na (mg/L)	356.9	268.6 - 471.3 (n=14)
K (mg/L)	19.2	11.0 - 37.6 (n=14)
Fe (total) (mg/L)	1.87	0.82 - 3.47 (n=21)
Mn (mg/L)	0.63	0.34 - 0.78 (n=21)
SO_4 (mg/L)	307.7	261.9 - 331.9 (n=19)
Cl (mg/L)	188.3	95.6 - 433.8 (n=19)

Table 6.1 **Kimblesworth pumped mine water quality, February 1998 to February 1999.**

6.3 Pilot-scale reactor development

Two pilot-scale reactors have been constructed adjacent to the Kimblesworth pumping station. Figure 6.2 illustrates the dimensions and layout of the reactors, which are constructed from pre-cast concrete. A metal framework and ladder provides access to the tops of the 2 m high reactors. Both reactors are fed with mine water via a 20 mm internal diameter PVC flexible pipe which carries mine water, under pressure, directly from one of the rising main pipes. Circular sections of PVC pipe perforated with 5mm holes at 8 evenly spaced locations facilitate even distribution of mine water into the reactors. Mine water flows downward over the high surface area media and is collected in a drain which carries the water back into the original channel. Ball valves enable flow control at the influent points of the reactors.

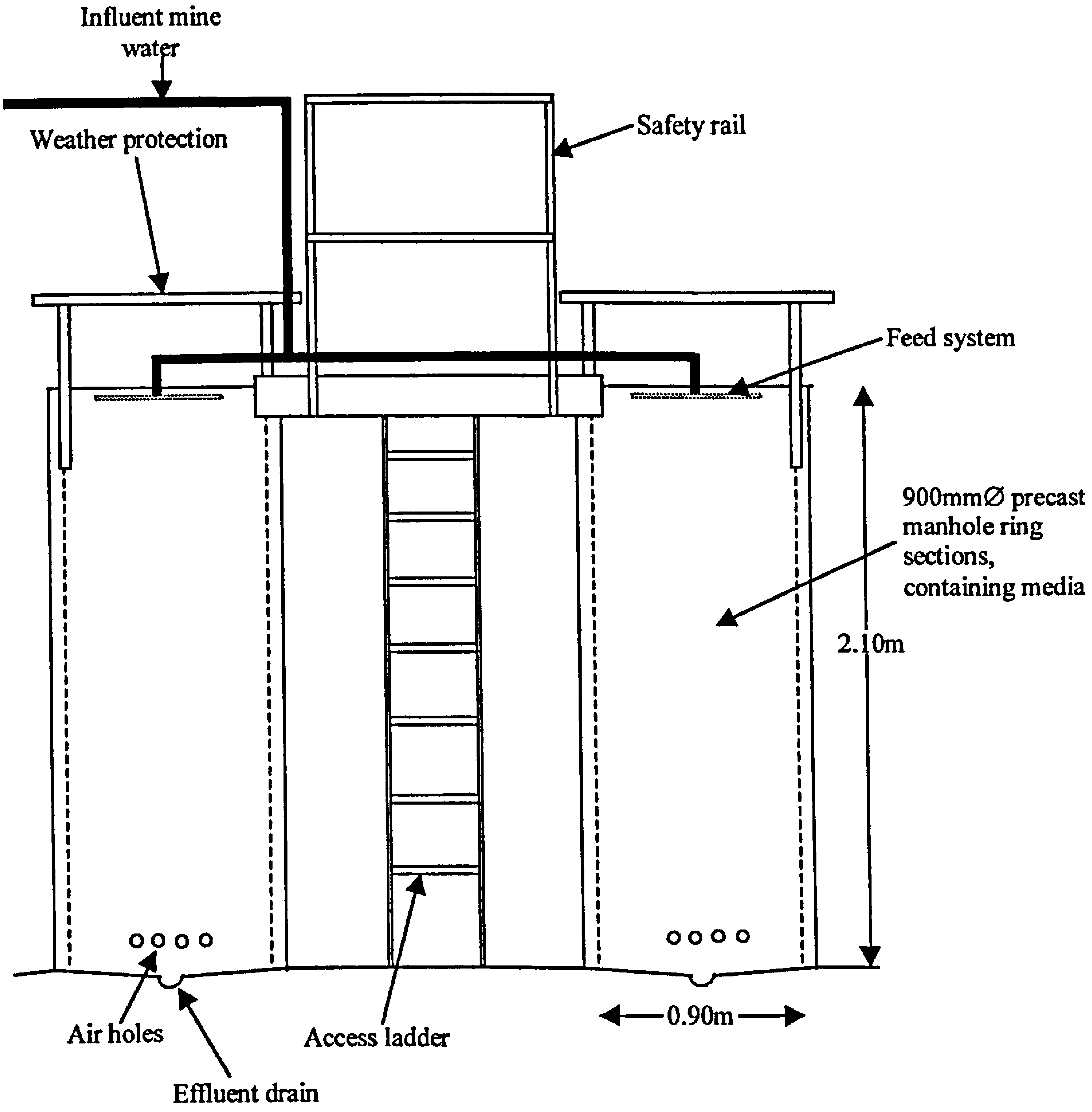


Figure 6.2 **Schematic diagram of Kimblesworth pilot-scale reactors (not to scale).** Water is fed from the main discharge to the top of the reactors. From there it is distributed evenly across the reactor media, trickling downwards to the effluent drains.

Throughout the duration of the experiments presented here the media used were commercially available plastic trickling filter media (Table 6.2). Technical data for such media (widely used in the water industry) include specific surface area figures, which are a distinct advantage for these pilot-scale investigations. Table 6.2 details the reactor dimensions, media types, and total surface areas within each reactor.

PARAMETER	Reactor A	Reactor B
Height of media within reactor (m)	2.00	
Internal diameter (m)	0.90	
Reactor volume (m^3)	1.27	
Media type	PVC Cascade Filterpak YTH 1120	PVC Cascade Filterpak YTH 1150
Quoted specific surface area (m^2/m^3)	100	200
Porosity (%)	94.4	93.1
Media surface area within reactor (m^2)	127	254

Table 6.2 **Operating parameters for Kimblesworth pilot-scale reactors, indicating both the dimensions of the reactors and the surface areas of the media.**

6.4 Results and Discussion

Between April 1999 and August 1999 the reactors were fed continuously with minewater, and samples were taken at approximately weekly intervals. Complete results tables can be found in Appendix 7. Both reactors achieved significant reductions in iron and manganese concentrations. Mean influent iron concentration is 1.43 mg/L, while mean effluent iron concentrations are 0.41 mg/L and 0.38 mg/L for reactors A and B respectively. Influent iron concentrations are significantly greater than effluent concentrations ($p < 0.001$).

Manganese concentrations also decrease. Mean influent manganese concentration over the sampling period was 0.67 mg/L, compared to effluent concentrations of 0.53 mg/L and 0.47 mg/L for reactors A and B respectively. At low loading rates (approximately 0.50 - 0.90 g/d) effluent manganese concentrations are 50% less than influent concentrations in reactor B. Effluent Mn concentration is significantly less than influent concentration in reactor A ($p < 0.01$) and reactor B ($p < 0.001$).

The flow-rate to the reactors has been intentionally varied over time to assess the influence on removal efficiencies of varying loading rates. Because influent Fe and Mn concentrations vary very little the loading rate (in g/day) is strongly governed by the flow-rate (influent flow-rate and loading rate are strongly positively correlated; $r > 0.99$, where r = correlation coefficient). Fe and Mn removal rates (in g/m^3/d) for both reactors increase with increasing loading rate ($p < 0.001$). Using data from both reactors Figure 6.3 demonstrates that at loading rates of less than 14 g/d the relationship between loading rate and removal rate is a linear one, and can be described by the equation:

$$RR = 0.8557LR - 0.0369$$

where, RR = Fe removal rate (g/m^3/d)
LR = Fe loading rate (g/d)

The slope of this trend line suggests that at loading rates up to 14 g/d the systems can remove 85% of the influent iron. The linearity of the relationship becomes less clear as the loading rate increases above 14 g/d, although insufficient removal rate values at the higher loading rates are currently available to ascertain the exact nature of the relationship. The percentage of the Fe load removed with increasing loading rate does not show this linear relationship (Figure 6.4). Indeed, at loading rates below 14 g/d there is no significant correlation between loading rate and percentage Fe load removed ($r = -0.208$). From Figures 6.3 and 6.4 it can be tentatively concluded that loading rates of up to 14 g/d may be applied to the reactors without any noticeable deterioration in treatment performance. Above 30 g/d there does appear to be some decrease in performance efficiency (although 50% of the iron load is still removed), but it is

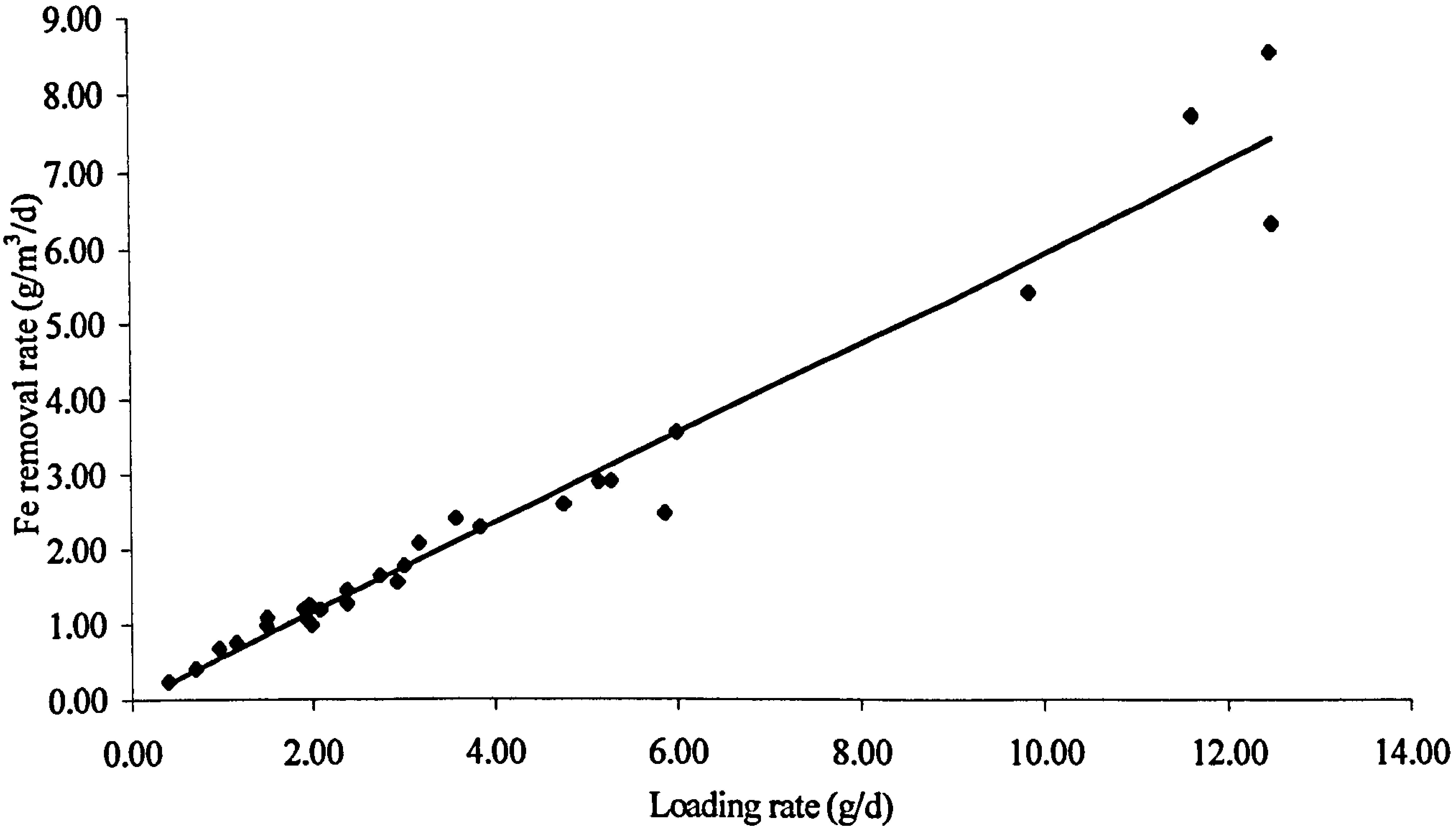


Figure 6.3 Iron removal rate as a function of loading rate at Kimblesworth pilot-scale system (data from both reactors used).

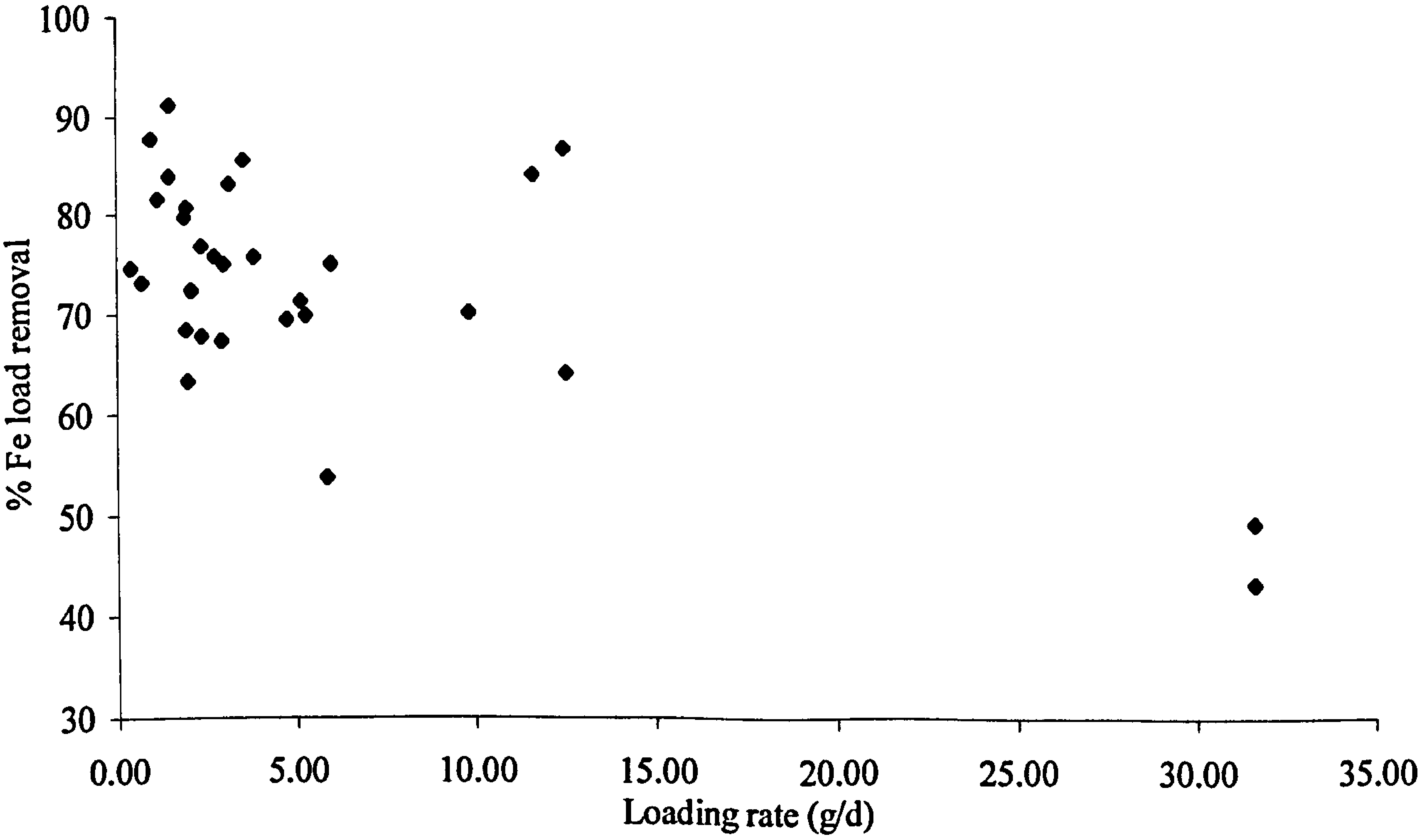


Figure 6.4 Percentage iron load removal as a function of loading rate at Kimblesworth reactors (data from both reactors used).

currently unclear what the optimum loading rate is for these systems with regard to iron removal.

Figures 6.5 and 6.6 present the same graphical representations for manganese loads and removal rates. The relationship between loading rate and removal rate is less clear for manganese (Figure 6.5), although a statistically significant positive correlation still exists ($p < 0.001$). In this case the relationship between loading rate and manganese removal is a non-linear one, and can be described by the equation:

$$RR = -0.0196(LR^2) + 0.2611LR$$

where, RR = Mn removal rate ($g/m^3/d$)

LR = Mn loading rate (g/d)

Figure 6.6 illustrates that the percentage of Mn load removed decreases sharply with increasing loading rate. Clearly therefore if manganese was to be the focus of treatment loading rates would have to be kept low or treatment system size would have to be substantially greater.

Patterns of metal removal within the two reactors with increasing loading rate are similar for both reactors but reactor B, with the higher total surface area, is more effective in removing manganese. Effluent manganese concentrations for reactor B are significantly lower than those for reactor A ($p < 0.001$). Lithium tracer tests have revealed that the peak residence time of water in reactor B is slightly higher than that of reactor A. For reactor A peak residence times range from 70 seconds (at 12 L/minute flow-rate) to 170 seconds (1.48 L/minute), whereas in reactor B times range from 110 seconds (12 L/minute) to 300-460 seconds (0.80 L/minute). Figure 6.7 compares the tracer graphs for the two reactors at a flow-rate of 12 L/minute. The shape of the graph for reactor B (i.e. a flatter curve) implies that this reactor may be better mixed. It is therefore difficult to ascertain whether the better performance of reactor B with regard to manganese is a function of the higher surface area *per se*, or the consequently longer residence time, or both.

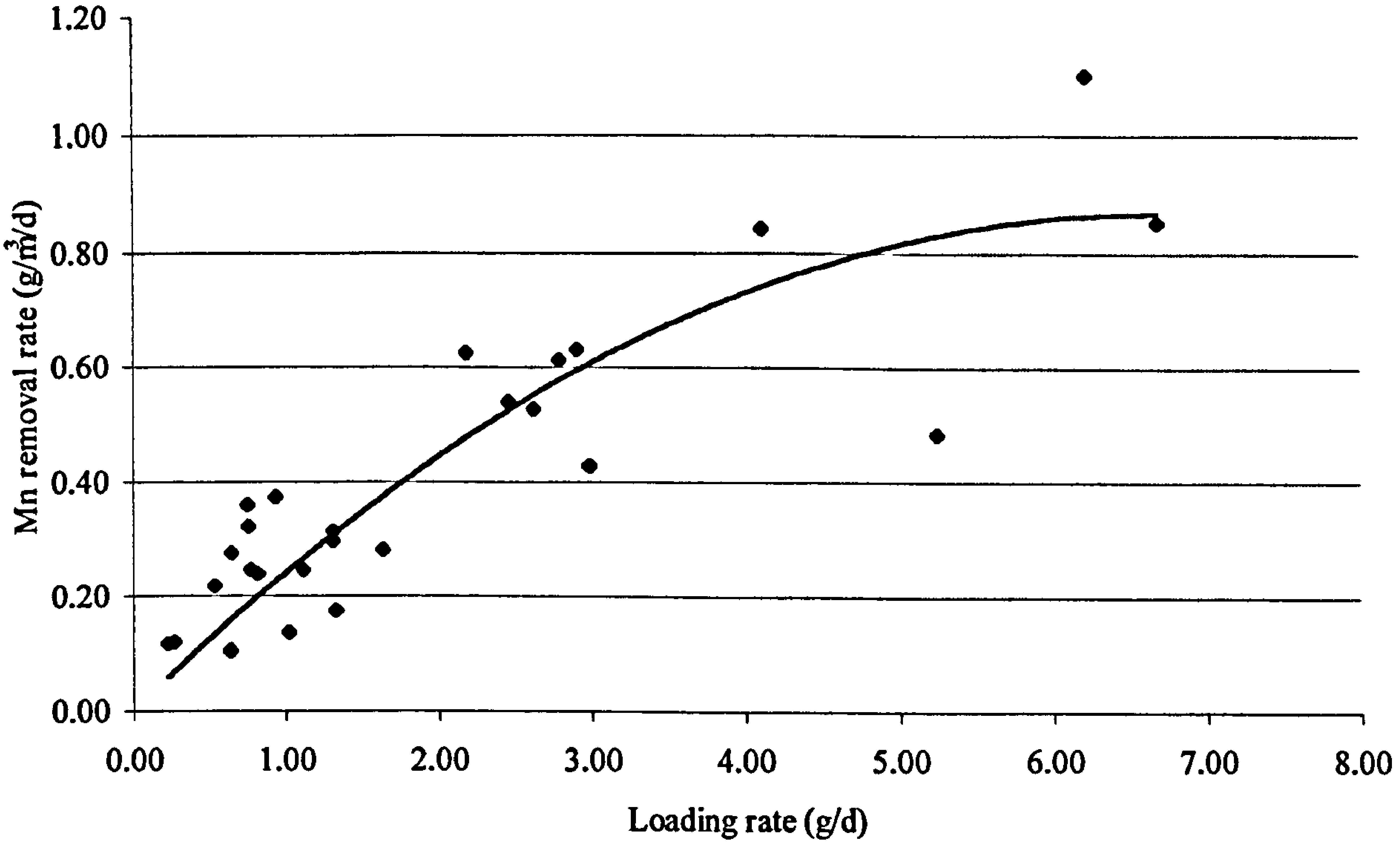


Figure 6.5 Manganese removal rate as a function of loading rate at Kimblesworth reactors (data from both reactors used).

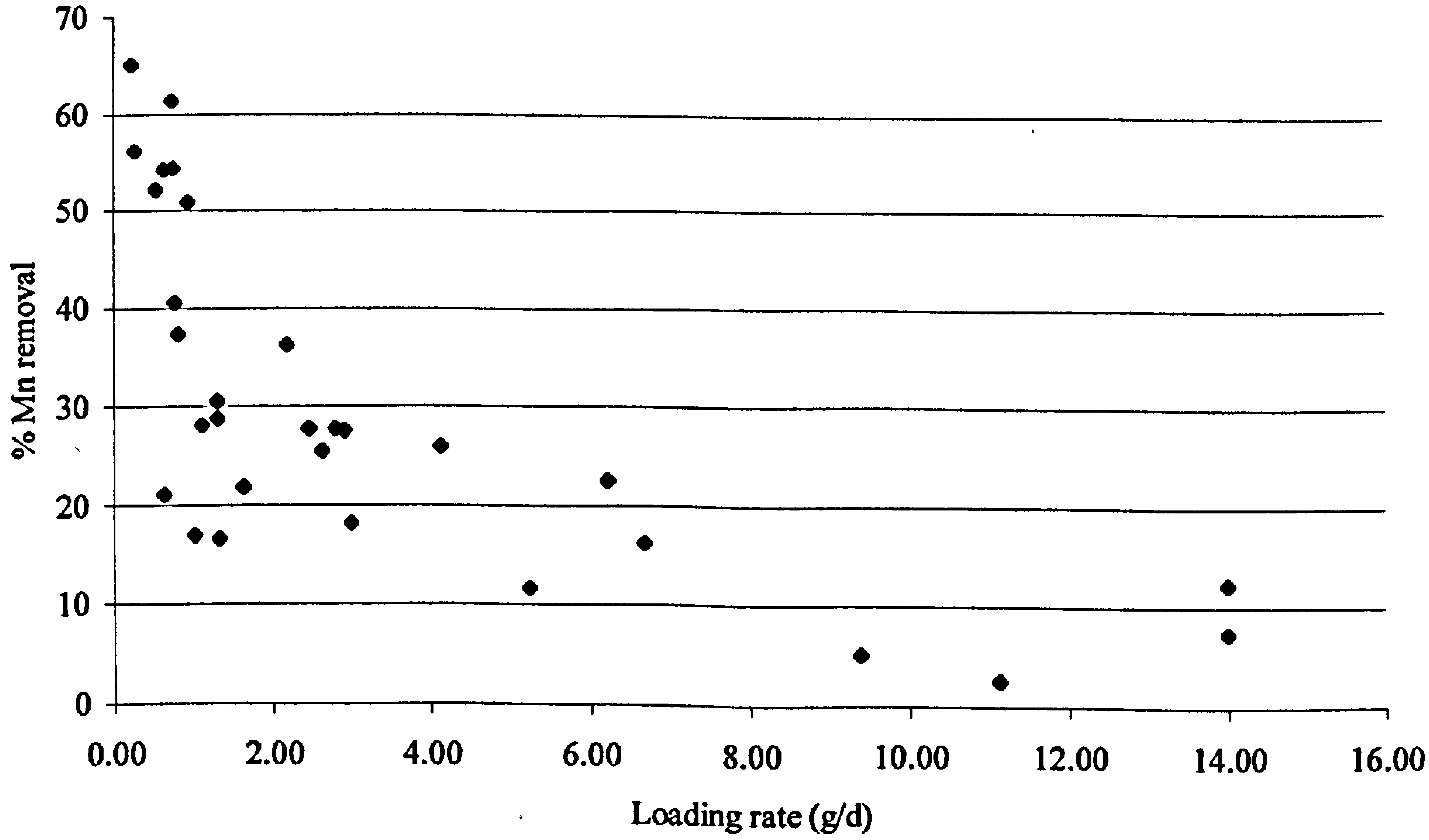


Figure 6.6 Percentage manganese load removal as a function of loading rate at Kimblesworth reactors (data from both reactors used).

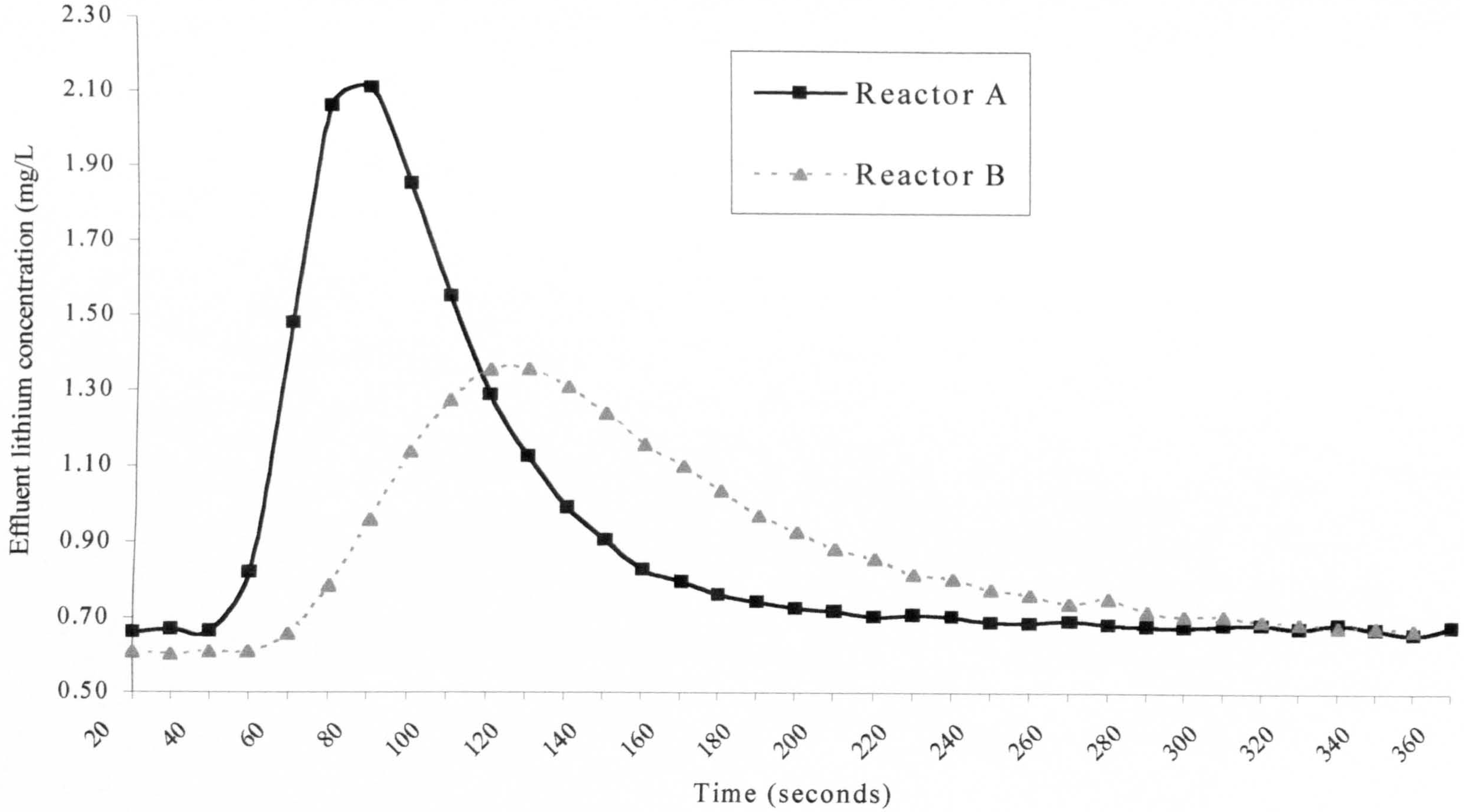
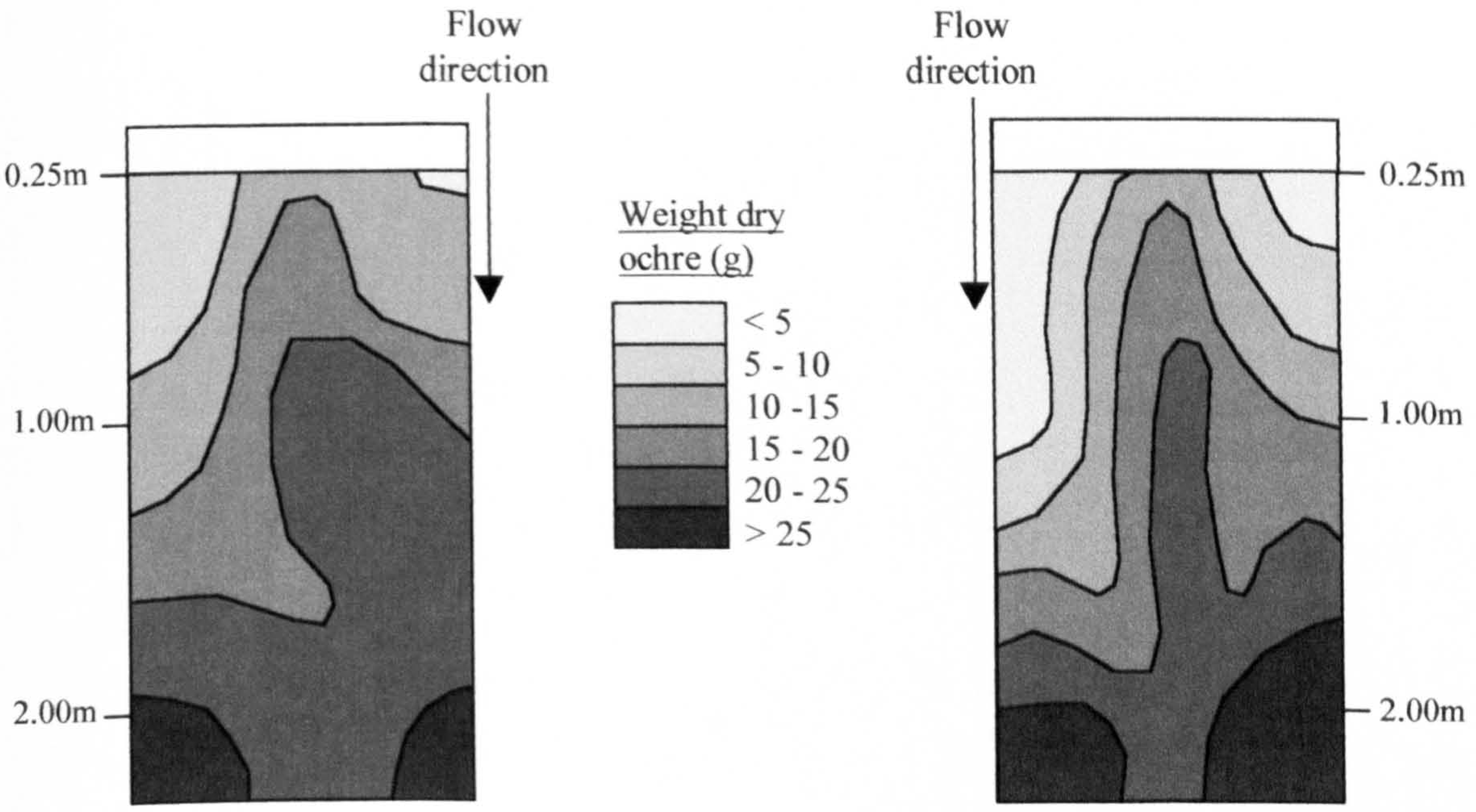


Figure 6.7 **Lithium tracer test results for Kimblesworth reactors A and B at 12 L/minute flow-rate.** The results illustrate that residence time within the reactors is as low as 80 seconds.

These results clearly suggest that oxidation of ferrous iron is occurring rapidly as the water trickles over the media. Measurements of dissolved oxygen (DO) concentrations at the influent and effluent points of the reactors confirm that oxygenation of the water is occurring. Influent DO is approximately 2 mg/L, whilst effluent DO values for both reactors are consistently greater than 8 mg/L. Laboratory investigations have suggested that ferrous iron oxidation may occur in a matter of minutes at pH 7 (Tamura *et al.*, 1976; Stumm and Lee, 1961). The autocatalytic effect of the oxidation product, ferric hydroxide, is thought to be negligible at initial ferrous iron concentrations of < 3 mg/L (Tamura *et al.*, 1976). However, the reactor media were heavily coated with ochre at the end of these long-term experiments, and therefore adsorption of ferrous iron to this ferric hydroxide, and subsequent oxidation, during the course of the experiments cannot be ruled out as a significant removal mechanism. The bicarbonate ion (HCO_3^-) has been identified as a catalyst to the reaction (Millero, 1990; Stumm and Lee, 1961), since it encourages the formation of $FeCO_3$. This may be a significant catalyst at the Kimblesworth site, where alkalinity concentrations are on the order of 760 mg/L as $CaCO_3$.

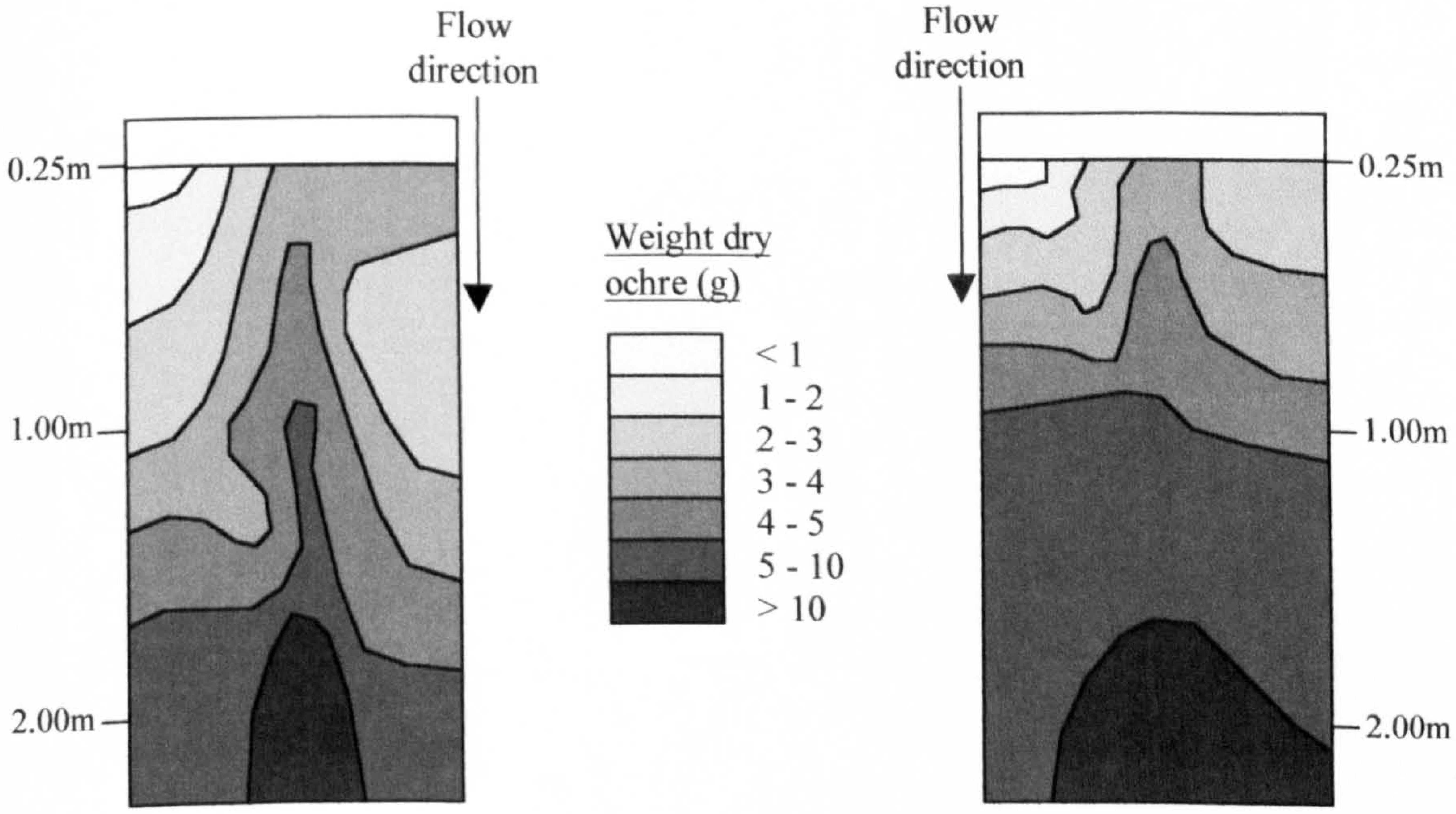
At the pH of the influent waters at Kimblesworth, Diem and Stumm (1984) suggest that abiotic rates of oxidation of Mn are very slow. Given the very short residence time of water within these reactors it can only be concluded that Mn is removed by adsorption to ferric hydroxide precipitates or co-precipitation with Fe.

Visually there is clear evidence that accretion is occurring in the form of extensive coatings of ochre on the reactor media. Careful removal of the media at the end of the experiments enabled individual sections of medium to be dried and weighed, in order to assess the distribution of ochre accretion through the two reactors. Figure 6.8 illustrates the results of this investigation. It is apparent that the greatest mass of ochre accretes towards the bottom of the two reactors (note that the mass of ochre on reactor A media is greater because *individual* sections have a greater surface area). The reason(s) for this is presently unclear, because it was not possible to sample waters at various depths through the media. Possible explanations include flushing of ochre through the media, insufficient reaction time for ochre to accrete near the top of the reactors, and reaction-limiting dissolved oxygen concentrations near the top of the reactors.



(a) Reactor A (large media)

(b) Reactor A (90° rotation)



(a) Reactor B (small media)

(b) Reactor B (90° rotation)

Figure 6.8 **Mass distribution of ochre (dry weight) in Kimblesworth reactors (not to scale).** Greatest ochre accretion is towards the base of the reactors (there is a greater mass of ochre on the media in reactor A only because *individual* sections are larger).

It is difficult to directly compare these results with those of aerobic wetland treatment systems, because the performance of the latter are invariably based on areal removal rates (Hedin *et al.*, 1994a), whereas these reactors are more appropriately assessed by volumetric means. At the highest loading rates reactors A and B remove 10.8 g/m^3/d and 12.3 g/m^3/d respectively. Dividing by the surface area of each reactor (Table 6.2) gives areal removal rates of 0.085 g/m^2/d and 0.048 g/m^2/d. Compared directly with typical Fe removal rates for aerobic wetlands (Hedin *et al.*, 1994a) of 10 - 20 g/m^2/d the new reactors do not appear efficient. However, this area-adjusted removal rate takes no account of residence time, and yet it is the residence time required for effective treatment that critically determines the overall size of the treatment system. Residence times of the wetland systems from which the Fe removal rates above were determined range from 0.3 - 33.9 days (Hedin *et al.*, 1994a). Ignoring the exceptionally long residence time of 33.9 days, the mean residence time in the wetlands is 3.5 days (n=12). By contrast residence time of water within the high surface area media reactors discussed here have a residence time of only 90 - 120 seconds at the highest flow-rate, several orders of magnitude less than an effective aerobic wetland. Dividing the area-adjusted removal rate by the residence time of each system provides a more realistic guide to the comparative efficiency of the different types of system. Using the mean figure of 3.5 days, removal rates for the wetland systems calculated in this manner are 2.9 - 5.7 g/m^2. The reactors currently under investigation have removal rates of 34.6 - 81.6 g/m^2. Thus, in terms of Fe removal and reaction rates these high surface area media reactors appear to be an order of magnitude more effective than aerobic wetland systems.

These removal rates are particularly impressive given the comparatively low influent iron concentration. Because the oxidation and precipitation of iron is a first-order reaction the removal rate of iron in aerobic wetlands is lower when the influent iron concentration is low (Tarutis *et al.*, 1999; see Section 5.7), and therefore wetlands have to be a relatively greater size. As a consequence there has been some difficulty attempting to remove low concentrations of iron using an aerobic wetland. Reactors such as those described above may therefore represent a significant addition to the list of passive treatment technologies currently in use.

Design of a full-scale system would almost certainly be based on loading rate, since this appears to govern the effectiveness of treatment (see Figures 6.3 and 6.4). Assuming for the moment that the topography at a hypothetical site allowed for a reactor 2.0 m high to be installed, then the pilot-scale reactors at Kimblesworth could effectively be enlarged areally to meet the requirements of the particular discharge. Perhaps the most difficult part of such a full-scale design would be ensuring very efficient distribution of water onto the surface of the media. A rotating or travelling arm, such as those commonly used in water and wastewater treatment plants, would be one option. However, considerable maintenance problems have been encountered at currently operational full-scale mine water treatment systems due to ochre accretion within pipes, ultimately leading to complete blockage (Adrian England, IMC Consulting Engineers Ltd., UK, personal communication, 2000). Careful consideration would therefore have to be given to this issue.

What size of full-scale reactor would be required to treat the entire discharge at Kimblesworth? The total volume of water discharged is 9100 m^3/d (see Section 6.2). Using the mean influent iron concentration of 1.4 mg/L (Appendix 7), the total iron load is 12740 g/d. At the highest loading rate reactor A removed iron at a rate of 10.8 $g/m^3/d$. The volume of reactor needed to treat the Kimblesworth discharge is then easily calculated by dividing the load by the removal rate (cf. Equation 3.23). The necessary volume of reactor calculated in this way is 1180 m^3 (and therefore an area of 590 m^2). If the treatment unit was circular (to accommodate a rotating arm distribution system), the reactor would have a diameter of approximately 27.5 m (assuming a depth of 2.0 m). Using the design criteria of Hedin *et al.* (1994a) (Table 3.3) the size of an aerobic wetland to treat this discharge would be 1274 m^2 (using the compliance criteria, since complete iron removal is the target). Thus, the new technology may enable considerable savings in land area requirements where topography allows the installation of such systems.

Unless the influent water pressure could be used to drive a rotating / travelling arm the need to ensure very efficient water distribution over the media may dictate that systems such as this require mechanical flow distribution systems, and thus they would not be 'passive' systems in the strictest sense i.e. they would require energy inputs, but no chemical inputs (cf. definition in Section 1.1). In addition such a system would certainly require concrete structures to accommodate a mechanical distribution system. If mechanical devices were included then maintenance requirements would be considerably greater than those of a constructed wetland system.

Eventually the media would need replacing as they became coated in ochre. Only very first approximations of the effective lifetime of the reactive surfaces can be made at this stage. Assuming for the moment that all of the amorphous iron precipitated within the reactors ultimately formed goethite (FeOOH) (see Section 3.2.2), then an estimate can be made of the time it would take to completely clog such a reactor. If the hypothetical full-scale system above was installed, and filled with the same media as was used in reactor A at pilot-scale, then the volume available for accumulation of ochre would be 1114 m^3 (because the media porosity is 94.4%; Table 6.2). Assuming treatment efficiency was the same in the full-scale system as it was in the pilot-scale system, then the iron retained within the system would amount to approximately 7.3 kg/d. Taking into account the molecular weight of goethite compared to the atomic weight of iron, this equates to 11.6 kg/d of goethite. The specific gravity of goethite is approximately 4 (i.e. 4000 kg/m^3). The reactor volume available is 1114 m^3, and therefore the reactor would have the capacity to accommodate 4460 tonnes of goethite. In theory therefore it would take the reactor 1050 years to completely plug with goethite. This, of course, is a very preliminary approximation, which takes no account of deterioration in performance over time, or of the potential for accumulation of more voluminous precipitates. Nevertheless, it indicates that such systems should be easily comparable to constructed wetlands in terms of operational lifetime.

6.5 Conclusions

1. High surface area plastic media contained in down-flow pilot-scale reactors have strongly suggested that rapid oxidation and accretion of ochre is a key removal mechanism for a pumped mine water discharge at Kimblesworth, County Durham, UK.

2. Two reactors have been used during these experiments. Reactor A has a larger media, with an approximate surface area of 124 m^2, whilst reactor B has a smaller

media with total surface area of approximately 178 m^2. Both reactors achieve a significant reduction in iron and manganese concentrations. Mean influent iron concentration is 1.43 mg/L, while mean effluent iron concentrations are 0.41 mg/L and 0.38 mg/L for reactors A and B respectively. Manganese concentrations also decrease. Mean influent manganese concentration over the sampling period was 0.67 mg/L, compared to effluent concentrations of 0.53 mg/L and 0.47 mg/L for reactors A and B respectively.

3. Iron removal rates increase linearly with loading rate up to 14 g/day. Although the linear relationship does not appear to continue at higher loading rates, even at a loading rate of nearly 32 g/day load removal is approximately 50% for iron. It is currently unclear what the optimum loading rate for these reactors is.

4. Manganese concentrations may be decreased by as much as 50% when loading rates are low (0.50 - 0.90 g/d). Reactor B, with the higher surface area, performs significantly better than reactor A in terms of manganese removal.

5. Residence time in these reactors is as little as 70 seconds. The combination of short residence time and efficient removal of iron at low influent concentrations (approximately 1.5 mg/L) strongly suggests that these reactors may be an effective passive alternative to aerobic wetlands, particularly at sites where topography and / or land area are restrictive. In terms of reaction rates these preliminary results suggest that such reactors may be as much as an order of magnitude more efficient than aerobic wetlands.

6. Full-scale development of treatment systems such as these may well be feasible. Although land requirements may be less than for an equivalent aerobic wetland, these systems may require inputs of energy for effective flow distribution. The systems might therefore be considered as "semi-passive". Preliminary approximations suggest that high surface area media reactors may have very long lifetimes, at least for waters of relatively low iron concentration as at Kimblesworth.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

7.1.1 Quaking Houses constructed wetland

This thesis has focused on the design, construction and operation of two contrasting (but potentially complementary) passive treatment systems for mine water pollution remediation. Greatest emphasis has been placed on work undertaken at the more complex of the two systems, at Quaking Houses, County Durham, where a full-scale compost wetland has been designed, built and operated over a period of 27 months (14/11/97 to 11/2/00). At this site an acidic spoil heap drainage, containing elevated concentrations of iron, aluminium, manganese and zinc, discharges via a road drain into the Stanley Burn (a third order tributary of the River Wear). Following the lead of Hedin *et al.* (1994a) a pilot-scale compost wetland was installed at the site in 1995 (Younger *et al.*, 1997). This system effectively removed the pollutants over an 18 month period. Following this success a full-scale wetland system was designed for the site. Initial plans to install a Successive Alkalinity Producing System (SAPS) (as described by Kepler and McCleary, 1994) were thwarted due to insufficient hydraulic head across the site, and consequently a compost wetland, closely analogous to the pilot-scale system, was designed and built.

Key elements in the functioning of a compost wetland are widely regarded to be:

i. generation of alkalinity via carbonate dissolution and dissimilatory sulphate reduction (Hedin *et al.*, 1994a) and
ii. immobilisation of metal contaminants within the wetland substrate by adsorption and precipitation as metal sulphides and oxides / hydroxides (Walton-Day, 1999).

The objectives of the research at Quaking Houses Community wetland (for the local community were a major catalyst in its creation) were:

1) Evaluate the design and engineering aspects of the constructed wetland at Quaking Houses, with a view to assisting the design and construction of future projects.
2) Through regular monitoring of the wetland water quality, produce a detailed and relatively long-term set of data characterising the performance of the system.
3) Investigate which pollutant removal mechanisms are most important in this wetland.
4) Assess the performance of the wetland using a number of measures in order to ascertain which is the most appropriate measure in terms of comparing wetland systems.
5) Attempt to generate an algorithm for predicting effluent water quality at the Quaking Houses constructed wetland.

In the following paragraphs the degree to which these objectives have been realised will be examined:

1) The constructed wetland at Quaking Houses is comparatively small in engineering terms (cf. the Woolley Colliery constructed wetland for example; Laine, 1998), and is unique in the sense that the local community played an important role in guiding the design of the system. The wetland built is an anaerobic (compost) surface flow system. In engineering terms the decision to construct such a system was based on the limited hydraulic head available across the site. The surface area of the compost in the system is 440 m^2. At the request of the local community the wetland was not built in an angular manner, despite the fact that this might make future research more difficult (e.g. for hydraulic studies). 640 tonnes of pulverised fuel ash (PFA) were used for the construction of the retaining embankments, which are keyed into the *in situ* soil to a depth of approximately 0.2 m. Extensive excavation of the *in situ* soil was not possible as it was found to be heavily contaminated with metals from former mining operations. Once compacted the PFA formed a highly impermeable barrier, and there has been no evidence of toe drainage since the commissioning of the wetland. The substrate of the wetland is a combination of horse manure, cow manure and municipal waste.

The wetland took 8 weeks to construct, although during 2 of these weeks construction was halted due to inclement weather conditions. The total cost of construction was just under £18000. Just under 50% of the total capital outlay went on plant hire and operation.

2) The compost wetland does remove pollutants from the spoil drainage, as illustrated in Table 7.1, below.

Determinand	Influent	Effluent
pH	6.06	6.60
Acidity (calculated) (mg/L as $CaCO_3$)	51.8	24.6
Alkalinity (mg/L as $CaCO_3$)	49.2	66.3
Fe (total) (mg/L)	5.35	2.37
Al (mg/L)	5.32	2.11
Mn (mg/L)	3.78	2.67
Zn (mg/L)	1.40	1.12
SO_4 (mg/L)	801	768

Table 7.1 **Mean concentrations and values of the wetland influent and effluent water at Quaking Houses Community wetland.**

Even a cursory inspection of the data in Table 7.1 illustrates that the wetland improves the water quality. The water is net-acidic when it enters the wetland but net-alkaline when it leaves, and there are significant reductions in metal ion concentrations, especially those of iron and aluminium.

3) The discharge emanates from a surface drainage system and consequently contaminant concentrations are highly variable because of dilution by surface runoff. This has made interpretation of the data more complicated, because it is difficult to differentiate between changes in wetland performance resulting from dilution and changes resulting from variations in the effectiveness of removal mechanisms. Whilst it has not been possible to assign strictly quantitative proportional significance to each of the various contaminant removal mechanisms

within the scope of this project, there are some indicators as which are the pre-eminent processes:

- recent work has demonstrated that there are quantifiable communities of sulphate reducing bacteria within the wetland. Furthermore gas bubbles, odours of hydrogen sulphide, and black deposits within the substrate, all suggest that sulphate reduction, and precipitation of metal sulphides, is an active process within the wetland.

- the main sink for metals appears to be within the substrate, though it is unclear what role the sediment-water interface plays in metal attenuation. Of particular interest is that aluminium, the removal of which is commonly assumed to be by precipitation as $Al(OH)_3$ on the wetland surface (e.g. Younger *et al.*, 1997), is closely associated with the pore water / sediment of the wetland. Acid-digestions indicate Al concentrations as high as 4 g/L within the pore water / sediment. Since there is strong evidence to suggest that anaerobic conditions exist below the water-sediment interface, it seems likely that there are other important removal mechanisms for aluminium, such as complexation with organic matter and / or adsorption.

- removal of manganese and zinc is less effective than for iron and aluminium. Evidence for this comes not only from analyses of influent and effluent water quality, but also from analyses of acid-digested pore water samples. There is approximately 40 times more iron within the substrate than manganese (accounting for differences in influent concentrations), suggesting that removal of manganese is 40 times slower than iron removal. This is a similar differential to that suggested by Hedin and Nairn (1993) for removal of these metal ions in aerobic wetland systems.

Ambient air temperature and rainfall data are available for the period of monitoring of the influent and effluent water quality at the Quaking Houses wetland. Statistical analysis suggests that effluent aluminium concentrations (and acidity concentrations) are strongly controlled by ambient air temperature. Specifically, the higher the ambient air temperature the lower the effluent aluminium concentration. Hem and Roberson (1990) and Lydersen *et al.* (1991) both demonstrate increased rates of precipitation of aluminium (as a hydroxide) at higher temperatures under laboratory conditions, but to the author's knowledge this is the first time such a relationship has been demonstrated for a constructed wetland system. Irrespective of whether the predominant solid phase sink for aluminium is the hydroxide, the evidence clearly implies that temperature is an important control in aluminium removal. It is unclear whether temperature is the direct cause of changes in removal efficiency, or whether perhaps temperature changes influence microbial activity, which in turn affect metal removal efficiency. In either case this observation has some important implications. In particular, it suggests that wetland systems operating under cold climate conditions may be less effective, at least in terms of aluminium removal.

4) Three methods are currently in use for assessing constructed wetland performance:

   a) treatment efficiency (%)
   b) area-adjusted removal rates ($g/m^2/d$)
   c) first-order removal constants (m/d)

   To make useful comparisons between constructed wetland systems a performance indicator must be independent of differences in influent pollutant concentration (Tarutis *et al.*, 1999). In this regard the fluctuating flow-rates at Quaking Houses are useful. By assessing the wetland using all three measures it has been shown that both treatment efficiency and area-adjusted removal rate are strongly influenced by influent contaminant concentrations. A new method of wetland performance assessment proposed by Tarutis *et al.* (1999), based on first-order removal of contaminants, appears to be a far better method of assessment. Using this method at Quaking Houses there is no correlation between the first-order rate constant and influent pollutant concentrations (Table 5.6), suggesting that the first-order rate constant is indeed concentration-independent. This method also gives a better representation of the kinetics of removal of iron and manganese in wetland systems (i.e. first-order removal rather than zero-order removal) (Tarutis *et al.*, 1999).

Area-adjusted removal has been the basis of design of many constructed wetlands (including the one at Quaking Houses). The system is relatively robust and easily applied. Using this method to compare the system at Quaking Houses with some of those from the USA suggests that the Quaking Houses system is under performing. The rate of area-adjusted acidity removal is 5.01 $g/m^2/d$ at Quaking Houses, compared with an average figure for 6 systems in the USA of 7.00 $g/m^2/d$ (Hedin *et al.*, 1994a). However, when compared on the basis of first-order removal the Quaking Houses wetland compares well with these systems. The apparent reason for this is identified by Tarutis *et al.* (1999). Specifically, discharges typified by high flow-rate and comparatively low metal concentrations require a relatively greater wetland area for effective treatment than systems treating an equal contaminant *load* but with low flow-rate and high contaminant concentrations. Evidence from the Quaking Houses constructed wetland strongly supports such a pattern of wetland performance - the systems from the USA, compared above with that at Quaking Houses, all have lower flow-rates and higher contaminant concentrations. It therefore appears that performance assessment of constructed wetlands would be better based on the first-order removal model proposed by Tarutis *et al.* (1999).

5) Using some of the key wetland influent variables it has been possible to generate an equation for predicting effluent iron concentrations at Quaking Houses. Using linear multiple regression the following equation is derived:

$$\sqrt{Fe_{out}} = 1.10 + 0.00038\ Acid_{in} - 0.09\ \log_e Q_{in} + 0.383\ \sqrt{Fe_{in}}$$

Fifty-three percent of the variation in effluent iron concentration is described by this equation (i.e. $R^2 = 0.535$). No other combination of influent variables resulted in such a high value for R^2, suggesting that influent iron concentration, influent acidity concentration, and influent flow-rate are key variables in determining the effluent iron concentration from the Quaking Houses wetland. The fact that 46.5% of the variation remains unexplained is testament to the complexity of compost wetland systems.

It seems unlikely that a universally applicable predictive equation will ever be generated, but the calculation of reasonably accurate predictive algorithms for individual systems may be feasible. Although, ultimately, understanding the type and quantitative importance of removal mechanisms within wetlands will result in the most accurate design formulae, it seems that achieving this goal is still some years away. Producing predictive equations such as the one above will undoubtedly help to focus attention on what might be the most important removal mechanisms within these systems however.

7.1.2 Kimblesworth pilot-scale system

At Kimblesworth, also in County Durham, a pilot-scale reactor was designed and built to investigate the potential utility of a novel passive treatment technique for iron-rich, alkaline mine waters. The approach entails encouraging the rapid oxidation and accretion of ochre to high surface area media. The research objectives for this second element of the work were as follows:

1) Through regular monitoring of the influent and effluent water quality from two reactors over the course of 4 months ascertain whether this novel passive treatment technology might be applicable at full-scale.
2) Measure residence times of water within the reactors and calculate metal loading rates in order to establish the most efficient operating conditions for such systems.
3) Compare performance of this novel treatment system with other passive technologies.

The degree to which these objectives have been met is discussed below:

1) The operation of two pilot-scale reactors containing high surface area media, over the course of 4 months, has successfully demonstrated that rapid oxidation and accretion of ferrous iron may be a very useful technology for treatment of net-alkaline waters at full-scale. Reactor A contains media with an approximate total surface area of 124 m^2, and reactor B has a total surface area of approximately 178 m^2. Both reactors have achieved significant removal of iron (mean concentrations are reduced from 1.43 mg/L to 0.40 mg/L). Visually obvious accretions of iron

precipitates on the media, and measurable increases in dissolved oxygen concentrations, suggest that rapid oxidation and accretion of iron is the key removal mechanism.

Preliminary calculations suggest that high surface area media reactors could successfully remediate the Kimblesworth mine water discharge at full-scale. Furthermore, when compared with the area of land required for an aerobic wetland, considerable savings may be made in land area requirements for such a full-scale system at this site. First approximations suggest that a full-scale system would have a lifetime at least as long as an equivalent wetland system. To operate efficiently it would be necessary to ensure very effective distribution of mine water over the media. Mechanical systems, such as rotating or travelling arms, might be required to achieve this. Since this would necessitate inputs of energy, such a system would not be a passive unit in the strictest sense, but may be described as "semi-passive".

2) Peak residence times at the highest flow-rate (12 L/minute) are just 80 seconds and 120 seconds for reactors A and B respectively (see Figure 6.7). At the same influent flow-rate, residence time in reactor B is slightly greater than that in reactor A, and metal removal is marginally more efficient. It is unclear whether the improved iron removal in reactor B is due to the higher surface area of the reactor or the increased residence time, or both.

   Iron removal rates increase linearly with loading rate up to 14 g/day (Figure 6.3). Although the linear relationship does not appear to continue at higher loading rates, even at a loading rate of nearly 32 g/day load removal is approximately 50% for iron. Unfortunately it is currently unclear what the optimum loading rate for these reactors is because no data are available for loading rates in the range 15 - 30 g/d (Figure 6.4).

3) It is difficult to compare the performance of the Kimblesworth reactors directly with the performance of aerobic wetlands because it is more appropriate to measure the former on a volumetric basis, whereas the latter are typically assessed on an areal basis. However, by dividing area adjusted removal (in $g/m^2/d$) by residence time the Kimblesworth reactors can be compared to aerobic wetlands, in terms of the rate of

iron removal per unit area (in g/m^2). In this manner it appears that the reactors investigated here are an order of magnitude more effective than aerobic wetland systems.

7.1.3 Conceptual links between the Quaking Houses and Kimblesworth systems

Within the field of passive treatment of mine waters the work at Kimblesworth contrasts sharply with that at Quaking Houses. The mine water at Kimblesworth is net-alkaline, and is only marginally polluted with iron (mean 1.43 mg/L) and manganese (0.67 mg/L). In addition the novel treatment system at Kimblesworth is designed to actively encourage oxidising conditions, whereas at Quaking Houses the intention is to promote a reducing environment. However, viewing the performance of these two systems together it appears that they complement each other well. The effluent water from the Quaking Houses wetland still contains marginally elevated concentrations of iron (2.37 mg/L; see Table 7.1), but it is net-alkaline. The water entering the Kimblesworth pilot-scale reactors has a similar iron concentration, but mean effluent concentration is 0.62 mg/L. The systems could therefore complement each other. High surface area media reactors such as those at Kimblesworth could potentially be effective polishing systems, following a compost wetland such as that at Quaking Houses. Tarutis *et al.* (1999) implicitly state that it is more difficult to remove low-level iron contamination, and the reactors at Kimblesworth are therefore an important advance. In addition the very short residence time of water within the reactors at Kimblesworth suggests that such systems may be usefully employed in their own right at sites where topography restricts land availability.

7.2 Recommendations

1) Much can be drawn from the design and construction experiences at Quaking Houses, and these lessons may be of considerable use for future constructed wetland projects:

   - A thorough characterisation of the quantity and quality of mine water to be treated proved essential in this project. There is no doubt that a similar familiarity should be encouraged for all such projects, since mine waters commonly exhibit fluctuations in both quantity and quality.
   - The available hydraulic head and the nature of the *in situ* soil crucially determined the final design of the wetland. A considerable period of time (and capital) was spent at the inception of the project on a variety of preliminary designs, many of which subsequently proved to be unfeasible. In particular initial designs focused on the use of a Successive Alkalinity Producing System (SAPS) (see section 3.2.4), which subsequently proved unfeasible. Thus, establishing the physical constraints of the site should be the top priority in projects of this sort. Specifically this should include a thorough topographical survey and detailed ground investigations. Based on the experiences of the work at Quaking Houses Figure 7.1 summarises the key considerations, in chronological order, when undertaking mine water assessment and remediation projects.
   - All of the materials used in the construction of the wetland were sourced locally, making substantial financial savings since transport costs were considerable. Cost savings were also made by using materials such as pulverised fuel ash (PFA) in preference to more obvious (though no more effective) alternatives. Investigation of the variety of construction materials available is therefore to be encouraged.
   - Almost 50% of the total expenditure of this project was on plant hire and operation. Typically costs are incurred even when machinery is not operating due to inclement weather conditions. By definition wetlands are suited to low-lying areas which are susceptible to flooding. It is therefore strongly advisable to undertake construction of wetlands during the driest months of the year, even

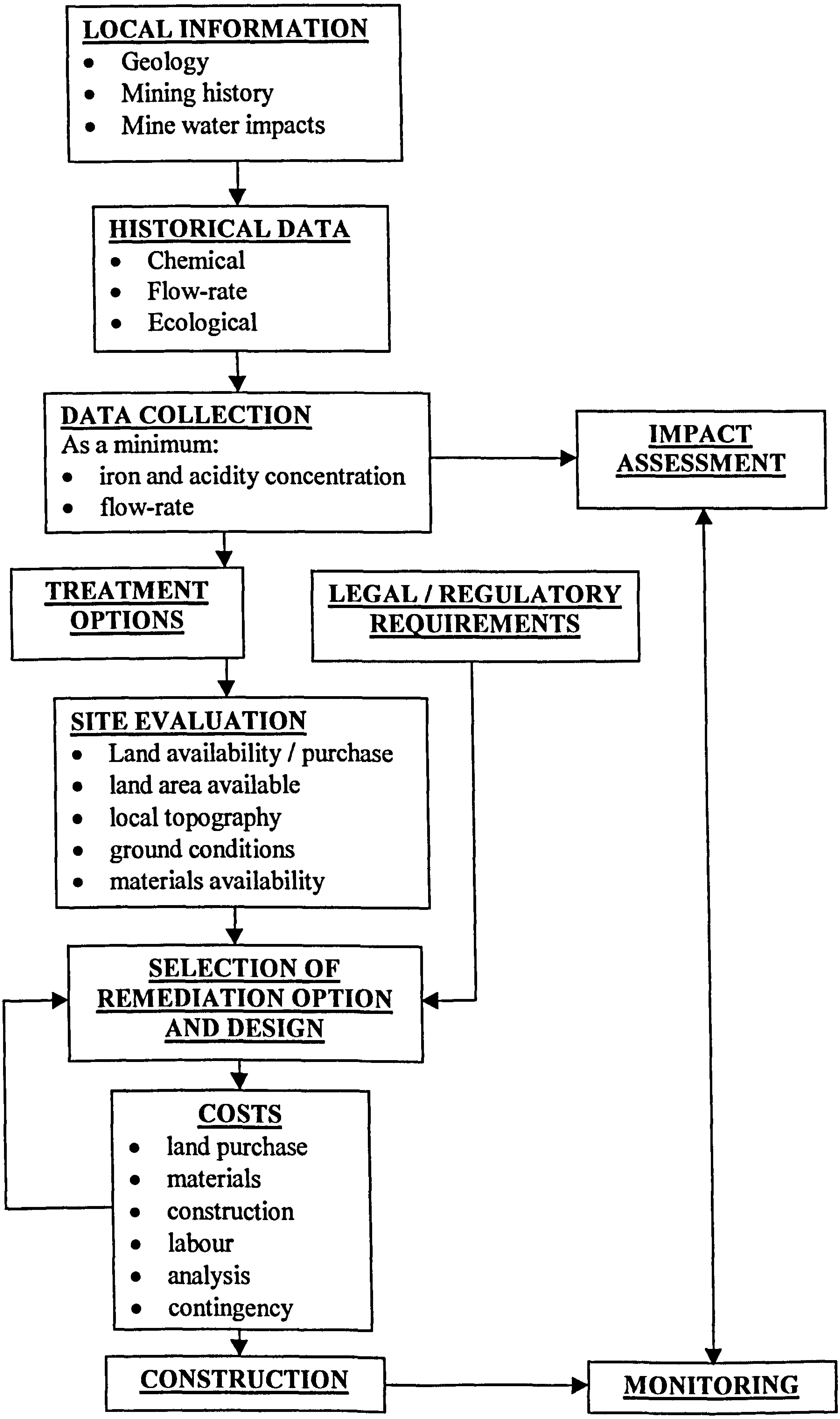


Figure 7.1 **Site assessment and remediation methodology flow chart**

if this entails delays of up to 6 months. Environmental regulatory authorities in the UK usually have no powers of prosecution in relation to discharges arising from mines abandoned prior to 31/12/2000. Consequently these authorities are typically sympathetic to schemes aimed at remediating such discharges, and construction delays such as these are usually acceptable. Future mine abandonments might result in legal action being taken however, in which case delaying construction of treatment schemes may not be possible.

2) Establishing the exact removal mechanisms operational within the Quaking Houses wetland will require detailed and long-term biogeochemical research, which was beyond the scope of this particular study, and is already planned for subsequent studies (Dr Paul Younger, University of Newcastle upon Tyne, UK, personal communication, 2000). From the results of this work it would seem that particular emphasis needs to be placed on establishing the main mineral phases within the wetland substrate, and ascertaining the role of iron and sulphur cycling in the vicinity of the water-sediment interface.

3) The hydraulics of the wetland at Quaking Houses, and particularly the residence time of water within the wetland, are poorly understood. If contaminant removal is rate dependent, as the weight of evidence suggests it is, then it is crucial to have accurate indications of residence times to properly understand the removal mechanisms operating within constructed wetlands. Tracer tests, using a conservative ion such as lithium, should be undertaken to achieve this. However, multiple tests would be required to establish residence times at different influent flow-rates. The use of automatic sampling equipment would be of great use in this regard, if it could be securely protected from vandals.

4) The first-order removal model of assessment proposed by Tarutis *et al.* (1999) appears to be the most appropriate method for comparing wetland performance. This being the case, future constructed wetlands may be more effectively designed on the basis of the first-order removal model. However, as Tarutis *et al.* (1999) point out, if this is to be possible future research must be undertaken to gather values for the first-order removal constant at constructed wetlands already operational.

5) No work has been done here on the rate of accumulation of material within the wetland. Similarly, no research has yet focused on carbon cycling within the wetland. In particular the potential for exhaustion of carbon sources should be investigated. Such work is necessary if an accurate lifetime for the wetland at Quaking Houses is to be calculated. Properly assessing constructed wetland lifetime may require long-term research (10 - 20 years). Although constructed wetland systems have been shown to be generally more financially attractive than equivalent active treatment systems, lifetime predictions are necessary if accurate cost-benefit analyses for mine water clean-up programmes are to be made. Such cost-benefit analyses should be based not only on the chemical and ecological impacts of mine waters (such as undertaken by NRA, 1996), but also on water resource and socio-economic impacts (see Jarvis and Younger, 2000b, for example). In calculating the costs of such schemes the significantly lower maintenance costs of passive treatment systems compared to active treatment systems (see Section 3.6) must be accounted for.

6) The pilot-scale reactors at Kimblesworth appear to be a very promising new treatment technology, particularly for remediation of marginally polluted mine water discharges. However, only first approximations of the optimum loading rates to such systems have been established to date. For application at full-scale more accurate indications of loading rates would be advisable. In addition no research has been undertaken to determine the mineral phases accreting to the media within the reactors. Such work would certainly assist in ascertaining the exact removal mechanisms operational in these treatment units. It appears that at full-scale a very efficient water distribution system would be required for the system to operate effectively. If mechanical units were required to do this then such treatment systems could only be described as "semi-passive". Designing water distribution systems which can operate passively (e.g. rotating arms driven by water movement), and do not rapidly block due to ochre accretion, is an important topic for engineering research.

7) Wetland / passive treatment of other waste streams may be feasible, and in some cases has been successfully undertaken. Elements of the research presented here

may be applicable to other water pollution issues, and an investigation of such possibilities might prove fruitful. In particular the following types of wastes may be suitable for passive treatment:

- landfill drainage
- airport / runway drainage
- sewage effluent (wetlands are already employed as tertiary treatment units in some parts of the UK)
- railway runoff

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APPENDIX 1

Bibliography of publications by Adam P. Jarvis

BIBLIOGRAPHY OF PUBLICATIONS BY ADAM P. JARVIS

Some of the work presented in this thesis was successfully submitted for publication during the period of study. Of the following journal and conference articles numbers 4, 6 and 9 arose from work presented here. Of the others, numbers 7, 8, 11, 12 and 13 all relate to passive treatment of mine waters, but arose from projects other than that reported in this thesis.

1) Firth, S., Jarvis, A.P. and Urbanski, I. (1995) Impact assessment of pre-selected abandoned minewaters within the Northumbria & Yorkshire Region. Interim report by the National Rivers Authority, December 1995.

2) Jarvis, A.P. (1997) Towards a Complete Methodology for Mine Water Impact Assessment and Site Remediation, *Minewater Treatment Using Wetlands* (Edited by Younger, P.L.). Proceedings of a CIWEM National Conference held 5th September 1997, University of Newcastle, Newcastle Upon Tyne. NE1 7RU. pp.165-177.

3) Jarvis, A.P. (1997) Critical Issues in Minewater Impact Assessment and Site Evaluation: The Way Forward, *Journal Annales Geophysicae*, **15**.

4) Jarvis, A.P. and Younger, P.L. (2000) Rapid Removal of Iron From Net-Alkaline Mine waters Using High Surface area Media. *South African Journal of Science*. In Press.

5) Jarvis, A.P. and Younger, P.L. (2000) Broadening the Scope of Mine Water Impact Assessment - a UK perspective. *Environmental Impact Assessment Review*, **20(1)**, 85-96.

6) Jarvis, A.P. and Younger, P.L. (2000) Passive Treatment of Ferruginous Mine Waters Using High Surface Area Media. *Water Research*. In Review.

7) Jarvis, A.P. and Younger, P.L. (2000) Passive Treatment of Net-Acidic Mine Waters: Field Experiences in the UK. *Proceedings of International Mine Water Association Congress.* Poland, September 2000. In Press.

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12) Younger, P.L., Curtis, T.P., Jarvis, A.P. and Pennell, R. (1997) Effective Passive Treatment of Aluminium-Rich, Acidic Colliery Spoil Drainage Using a Compost Wetland, at Quaking Houses, County Durham, UK, *Journal of the Chartered Institution of Water and Environmental Management,* **11**(3), 200-208.

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APPENDIX 2

Quaking Houses wetland data:
raw water quality and quantity - all variables

Note:

In this appendix, to save space, some measurement units are omitted. The relevant units are as follows:

Temperature (°C)
Conductivity (μS/cm)
Acidity (calc) (mg/L as $CaCO_3$)
Alkalinity (mg/L as $CaCO_3$)

DATE	Temperature		pH		Conductivity		Acidity (calc)		Alkalinity (mg/L)		Flow (L/minute)	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
14/11/97			5.27	6.75			107	20	32	100		
28/11/97			6.50	6.84			37	17	85	97		
02/12/97	9.0	3.7	6.83	7.13	9700	6600	33	20	70	97		
09/12/97			6.20	6.80	8200	8000	49	16	56	60		
17/12/97			6.27	6.94	660	6610	67	3				
07/01/98	8.6	6.2	6.41	6.68			38	21				
14/01/98	8.0	6.9	6.94	7.17			28	17	87	105	300	
20/02/98	11.0	10.9	5.61	6.50								
26/02/98	11.1	7.2	5.30	6.10	7100	7200	80	29				42
05/03/98			6.96	7.33			30	15				168
12/03/98			6.83	7.25			27	16				65.6
19/03/98			5.92	6.41			48	15	40	40		
26/03/98												53.6
09/04/98											115	348
21/04/98												
24/04/98												
08/05/98												
14/05/98			5.52	6.12	5960	6040	69	33	40	50	46	64.6
20/05/98	10.7	14.9	5.25	5.65	5850	6510	67	29	15	23		
28/05/98	10.7	16.3	6.02	5.72	5720	4500	84	25	80	185	38	38.8
02/06/98	10.9	16.0	6.13	6.50	5080	5030	26	17			180	180
08/06/98	13.5	13.6	6.78	6.38			53	6	43	67	300	300
09/06/98												262.5
16/06/98			6.52	6.72			16	11	91	88	360	360
17/06/98			6.56	6.90			15	9	92	97	420	420
18/06/98			6.56	6.83			44	17	79	82		300
19/06/98			6.26	6.61			24	14	74	71	150	150
20/06/98			6.09	6.43			30	16	70	72	180	180
21/06/98			6.19	6.72			29	17	58	72	150	150
22/06/98	13.6	17.6	5.31	6.48	4350	4150	38	22	58	68	135	135

DATE	Temperature		pH		Conductivity		Acidity (calc)		Alkalinity (mg/L)		Flow (L/minute)	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
24/06/98	12.0	16.3	6.16	6.49			40	22	58	61		
25/06/98												131
30/06/98			5.69	6.09	5690	5990	54	30	33	43	72	72
02/07/98											79.2	79.2
06/07/98	12.7	16.6	5.59	5.16	5590	5160	67	42	24	32	66	66
07/07/98	11.9	17.2	5.67	6.06	5260	5260	74	46	21	33		
08/07/98	12.5	14.3	5.26	6.04	5260	6040	52	18	23	31	66	66
09/07/98	13.1	17.4	5.36	6.20	5360	6200	68	27	32	63	60	57.5
10/07/98	12.8	17.9	4.95	5.82	4950	5820	62	20	19	30	66	66
11/07/98	13.0	17.7	5.22	6.35	5220	6350	63	26	28	45	66	66
12/07/98	13.3	19.0	5.50	6.53	5500	6530	41	10	33	50	66	66
16/07/98	13.0	18.6	4.78	5.80	5130	4830					42.8	38.1
23/07/98			5.58	6.52	4050	3660	57	22	19	38	53.8	55.3
30/07/98	13.8	16.3	6.48	7.19			27	18	40	49	280	420
06/08/98											36.2	31.1
13/08/98											37.2	36.5
20/08/98											27.2	175
11/09/98			6.19	6.91	5664	5618	46	15	58	189	44.2	42
14/09/98	12.4	11.8	6.31	6.93	5300	5048	50	22	66	162		
17/09/98											31.9	32.3
24/09/98			6.02	6.60	5705	6005	90	23	49	70		
02/10/98			6.50	6.94	1906	1548	31	19				
08/10/98											116.6	56.7
15/10/98			6.46	7.29	5765	5131	36	12	77	90	55.2	61.7
22/10/98			6.65	7.33	5589	5496	34	15	91	98		
29/10/98			6.81	7.36	5380	5060	22	12	96	91	168	155.5
04/11/98			6.94	6.94	5970	7719	17	15	93	88	420	420
12/11/98			6.44	6.71	7550	7866	40	22	59	70	110.5	49.4
19/11/98			6.37	6.64	7672	7640	43	29	67	71	107.7	107.7
26/11/98											102	100

DATE	Temperature		pH		Conductivity		Acidity (calc)		Alkalinity (mg/L)		Flow (L/minute)	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
10/12/98			6.55	6.79	7810	8165	39	19			85.7	82.3
17/12/98			6.58	6.91	7555	7495	47	16			71.2	67.7
23/12/98			6.83	6.98	10790	14400	49	29			51.8	53.1
11/01/99			7.00	7.16	12730	19410	25	17			175	210
18/01/99			6.76	7.23	7958	7745	29	17	73	73	145	191
26/01/99			6.48	6.95	7130	7174	43	20	54	65	76.3	91.3
02/02/99			6.24	6.80	7235	7340	52	20	46	48	61.7	64.6
09/02/99			5.74	6.20	11750	15260	64	43	20	39	42	40
17/02/99			5.89	6.52	6790	8184	53	21	24	36	40.7	40.7
10/03/99			6.69	6.84	4168	4104	18	12	81	79		
16/03/99			6.28	6.54	5073	5024	50	18	54	52		
23/03/99			6.09	6.62	7138	6998	54	18	27	25	89.3	107
30/03/99			5.72	6.30	8520	8558	67	48	8	8	54	140
09/04/99			5.29	5.36	8525	8475	67	45	9	8		
14/04/99			6.24	5.98	4184	8097			46	57	161.5	161.5
23/04/99			6.14	6.50	8010	7875	28	17	58	64	110.5	139.9
29/04/99			6.12	6.70	8360	8386	74	13	57	57	53.8	65.6
07/05/99			6.07		5566		26		80		85	0
14/05/99			7.10	7.45	4787	4507	23	18	107	107	168	240
19/05/99											72	60.5
03/06/99			6.45	6.73	6880	4753	35	15	70	80	76.4	85.7
08/06/99											233.3	233.3
18/06/99											153	40.8
25/06/99											105	
02/07/99			5.45	5.91	11090	10390	62	24	30	46	131.2	
09/07/99			5.43	6.21	11840	10880	65	24	15	56		
16/07/99			4.89	6.28	12340	12690	73	8	5	47	25	
23/07/99			5.22	6.18	10140	9780	75	50	5	24	20.5	
30/07/99			4.20	5.90	8760	9910	89	20	0	25		
06/08/99											17.9	

DATE	Temperature		pH		Conductivity		Acidity (calc)		Alkalinity (mg/L)		Flow (L/minute)	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
13/08/99											18.4	
20/08/99											68.3	
27/08/99											55.6	
03/09/99											25.3	
10/09/99											23.6	
16/09/99			6.20	6.71	5970	8607	71	21	31	44	23.8	
08/10/99			5.73	8.31	12190	11540	33	10	5	46	28.6	
14/10/99			4.90	6.73	12660	12510	41	21	5	39	27.3	
21/10/99			5.48	6.64	11500	10370	54	23	5	35	22.2	
29/10/99			6.62	7.10	11050	10470	27	16	61	92	40.9	
04/11/99			5.77	6.87	12880	11620	47	15	48	86	13.9	
11/11/99			6.10	6.52	11860	11460	36	18	62	82	59.1	
19/11/99			6.77	6.98	1826	2729	12	7	98	100	80.6	
25/11/99			6.31	6.28	10990	10990	36	24	72	86	74.8	
02/12/99			5.86	6.54	14030	12350	57	15	50	54	47.6	
08/12/99												
15/12/99											157.2	
20/01/00			6.88	6.42	11770	10760	49	24	60	74	110.3	
28/01/00											66.8	
04/02/00			5.96	6.47	8230	7840	51	15	52	62	48.4	
11/02/00			5.80	6.37	7110	7040	66	17	50	56	39.6	
Mean	11.8	14.1	6.06	6.60	7438	7750	47.4	20.3	49.6	66.1	98.6	127.6
Median	12.4	16.3	6.15	6.62	7100	7270	47.0	18.0	52.0	62.5	67.6	79.2
S.D.	1.68	4.56	0.61	0.50	2975	3142	19.79	9.20	27.63	34.16	86.99	105.81
Max.	13.8	19.0	7.10	8.31	14030	19410	107.0	50.0	107.0	189.0	420.0	420.0
Min.	8.0	3.7	4.20	5.16	660	1548	12.0	3.0	0.0	8.0	13.9	0.0
n	21	21	84	83	67	66	81	80	71	70	80	61

DATE	Fe (mg/L)		Mn (mg/L)		Al (mg/L)		Zn (mg/L)		SO_4 (mg/L)	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
14/11/97	20.50	5.00	5.50	2.80	10.90	1.10				
28/11/97	6.83	3.43	0.95	0.81	4.16	1.65			431	490
02/12/97	3.34	2.54	0.76	0.67	4.60	2.62			408	407
09/12/97	5.84	2.92	2.08	1.71	6.32	1.40			642	600
17/12/97	3.44	0.31	2.29	1.17	10.21	0.00			606	591
07/01/98	1.64	1.23	2.62	2.42	5.37	2.51			282	263
14/01/98	2.09	1.10	1.36	1.16	3.93	2.29			328	200
20/02/98									1296	1315
26/02/98	5.26	3.93	6.18	5.76	10.56	2.13			1495	1482
05/03/98	1.69	1.05	1.63	1.65	4.35	1.76			457	436
12/03/98	3.14	1.79	1.20	0.94	3.53	1.95			223	235
19/03/98	3.75	2.10	3.63	3.21	6.32	1.02			969	965
26/03/98	10.12	0.82	4.07	3.46		0.48			950	954
09/04/98	0.65	0.52	1.13	1.09	2.88	2.21			347	335
21/04/98	1.36	0.79	3.43	3.33	6.65	2.53			710	840
24/04/98	0.54	0.39	1.10	0.96	2.61	1.49			343	311
08/05/98	1.73	0.95	5.26	4.86	8.19	1.61			1431	1508
14/05/98	3.16	1.69	5.71	5.28	9.51	3.71			1480	1384
20/05/98	5.01	3.68	6.59	6.30	8.30	2.03			1541	1437
28/05/98	6.60	3.21	5.98	4.62	10.96	1.89			1377	1126
02/06/98	1.51	1.27	2.12	2.04	3.45	1.97			567	530
08/06/98	1.27	1.20	0.67	2.31	8.92	0.00				
09/06/98	0.92	0.47	2.23	1.97	4.10	1.45			653	573
16/06/98	0.75	0.42	1.55	1.42	2.10	1.44			552	502
17/06/98	1.20	0.40	1.40	1.33	1.90	1.13			628	642
18/06/98	2.74	0.40	2.60	2.35	6.21	2.24			812	792
19/06/98	0.75	0.40	3.08	2.11	3.10	1.78			878	833
20/06/98	1.10	0.45	3.43	3.15	3.92	1.77			962	947
21/06/98	0.96	0.52	3.64	3.27	3.72	1.81			1030	949
22/06/98	3.90	3.69	3.90	3.68	4.18	1.53			1074	1119

DATE	Fe (mg/L)		Mn (mg/L)		Al (mg/L)		Zn (mg/L)		SO_4 (mg/L)	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
24/06/98	0.99	0.75	4.22	4.12	5.41	2.38			1341	1317
25/06/98	2.00	1.41	4.31	4.17	4.62	3.29	3.46	3.5	1207	1305
30/06/98	2.53	1.30	5.32	5.23	7.23	3.23			1474	1462
02/07/98	1.76	1.35	5.87	2.92	6.02	3.51	3.34	2.92	1209	1421
06/07/98	5.22	3.90	6.57	6.42	8.14	4.20			1449	1396
07/07/98	4.29	2.85	6.24	6.00	9.86	5.33	3.47	7.19	1532	1460
08/07/98	6.37	3.50	6.94	6.58	5.00	0.00			1419	1427
09/07/98	9.81	3.17	5.91	5.10	7.20	2.10	2.49	1.64	1386	1327
10/07/98	5.74	3.84	6.29	6.25	7.15	0.36			1492	1389
11/07/98	5.77	2.53	5.93	4.96	7.57	2.30			1424	1134
12/07/98	4.74	1.53	4.71	2.24	4.21	0.65			975	522
16/07/98	5.49	3.30	6.31	6.15			2.21	2.11	1459	1411
23/07/98	5.64	2.20	5.22	3.49	6.76	2.13	2.15	1.12		
30/07/98	3.12	2.17	2.01	1.12	3.19	2.12	0.75	0.44		
06/08/98										
13/08/98	6.06	1.47	4.80	5.07			1.49	1.08	925	1003
20/08/98	10.29	4.75	6.44	6.38			1.9	1.05	1220	1178
11/09/98	7.99	3.05	4.34	3.56	4.28	0.59	1.36	0.31		
14/09/98	7.77	4.49	4.13	3.64	5.09	1.41	1.27	0.58		
17/09/98										
24/09/98	17.19	4.90	5.48	5.51	8.91	0.83	2.7	1.03		
02/10/98	4.29	1.96	1.82	1.26	3.58	2.32	0.66	0.34		
08/10/98										
15/10/98	6.61	3.01	3.16	2.25	3.23	0.52	0.84	0.4	565	502
22/10/98	6.33	2.84	2.37	1.99	3.26	1.10	0.74	0.44	502	530
29/10/98	3.38	1.88	1.50	1.31	2.37	1.12	0.72	0.44	304	355
04/11/98	1.71	1.50	1.09	1.08	2.13	1.78	0.81	0.79	301	314
12/11/98	3.41	2.23	3.51	3.47	4.93	2.09	1.64	1.41	570	604
19/11/98	3.73	2.65	3.56	3.32	5.36	3.30	1.6	1.44	552	604
26/11/98	4.11	2.48	3.44	3.07	5.39	1.27	1.55	1.03	588	597

DATE	Fe (mg/L)		Mn (mg/L)		Al (mg/L)		Zn (mg/L)		SO_4 (mg/L)	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
10/12/98	3.88	2.28	3.32	3.30	4.60	1.66	0.96	0.83	547	526
17/12/98	5.24	1.69	3.72	3.59	5.48	1.18	1.14	0.82		
23/12/98	5.66	3.80	4.48	4.14	5.61	2.68	1.39	1.13	742	687
11/01/99	3.36	2.83	1.69	1.61	2.87	1.60	0.85	0.87	407	490
18/01/99	3.50	2.66	2.05	1.96	3.49	1.60	1.16	1.03	429	407
26/01/99	4.92	2.33	3.18	3.09	5.13	1.85	1.53	1.26	544	532
02/02/99	6.80	2.93	4.16	4.08	5.80	1.25			717	695
09/02/99	10.18	6.24	2.58	2.63	7.46	4.92	1.21	1.24	1047	972
17/02/99	1.47	0.05	2.22	2.34	8.32	3.07	1.1	0.85	877	900
10/03/99	1.11	0.74	0.66	0.60	2.66	1.81	0.66	0.6	293	278
16/03/99	2.00	1.13	1.64	1.55	7.88	2.36	1.22	1.08	587	487
23/03/99	2.49	1.45	3.79	3.57	7.73	1.61	2.41	1.86	706	811
30/03/99	3.50	3.31	4.86	4.82	9.34	6.00	2.66	2.32	957	1039
09/04/99	5.18	4.23	5.04	4.97	8.71	5.11	2.3	2.16	1280	1186
14/04/99									343	453
23/04/99	2.85	2.29	0.95	2.04	3.85	1.70	0.95	0.81	404	446
29/04/99	16.06	1.59	3.58	2.94	6.95	0.85	1.49	0.8	670	653
07/05/99	2.95		2.28		3.00		0.91		506	
14/05/99	2.71	2.09	1.30	1.13	2.85	2.22	0.58	0.39	242	319
19/05/99	4.94	1.38	3.15	0.92	5.79	0.98	1.21	0.23	672	635
03/06/99	4.39	2.05	2.55	1.89	4.09	1.44	1.01	0.56	512	413
08/06/99	2.39	1.78	1.40	0.89	2.20	0.77	0.64	0.42	194	262
18/06/99	7.04	1.88	4.09	3.43	5.98	0.85	1.39	0.86	859	976
25/06/99	7.00		4.30		8.32		1.45		908	
02/07/99	7.50	3.52	4.13	3.26	7.33	2.14	1.39	0.95	873	763
09/07/99	7.33	3.29	4.11	2.60	7.89	2.32	1.67	0.91	901	743
16/07/99	8.17	1.19	5.12	1.64	8.69	0.55			699	1137
23/07/99	9.41	5.77	5.60	4.81	8.50	5.54			1227	949
30/07/99	9.89	3.26	6.18	5.55	10.18	0.72			1257	1204
06/08/99	20.03	1.96	7.90	0.33	6.52	5.03			1221	877

DATE	Fe (mg/L)		Mn (mg/L)		Al (mg/L)		Zn (mg/L)		SO_4 (mg/L)	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
13/08/99	14.32	1.26	6.26	0.30	5.66	2.84			1056	576
20/08/99	4.73	1.62	2.73	0.49	2.34	1.85			535	409
27/08/99	5.07	1.63	3.67	0.58	2.68	2.08			629	589
03/09/99	13.85	2.02	7.13	0.62	5.29	4.46			708	812
10/09/99	8.29	1.70	5.47	0.37	6.39	3.94			969	604
16/09/99	16.95	3.92	4.95	4.10	5.79	1.23			881	857
08/10/99	7.14	2.23	2.24	0.00	4.15	3.10	0.91	0.27	910	844
14/10/99	8.93	7.32	2.87	0.00	4.75	4.49	1.1	1.32	1006	964
21/10/99	11.37	5.33	4.32	0.77	5.51	4.97			1047	871
29/10/99	4.84	3.30	2.51	1.19	2.41	2.19			495	447
04/11/99	7.24	4.50	4.99	1.24	3.38	0.29			706	643
11/11/99	5.22	3.08	3.92	1.52	2.54	2.38			586	529
19/11/99	1.01	1.25	1.77	0.74	0.08	0.27			120	111
25/11/99	4.74	4.56	4.18	2.12	2.44	2.19			534	470
02/12/99	6.84	2.66	6.76	0.76	3.72	3.18			752	516
08/12/99	2.07	1.31	1.22	1.39	0.71	0.51			165	217
15/12/99	2.33	2.00	2.34	1.32	1.36	0.26	0.32	0.12	411	390
20/01/00	7.96	4.35	5.21	1.94	3.02	2.85	0.54	0.5	615	583
28/01/00	3.66	1.59	5.69	0.91	3.24	3.21	0.56	0.47	680	680
04/02/00	4.73	2.56	6.44	0.56	3.84	3.95	0.66	0.43	769	820
11/02/00	6.07	2.73	8.60	0.96	4.26	3.71	0.68	0.56	774	691

Mean	5.35	2.37	3.78	2.67	5.32	2.11	1.40	1.12	801	768
Median	4.74	2.14	3.70	2.28	5.05	1.89	1.21	0.86	710	680
S.D.	4.08	1.43	1.87	1.77	2.47	1.33	0.78	1.12	380	369
Max.	20.50	7.32	8.60	6.58	10.96	6.00	3.47	7.19	1541	1508
Min.	0.54	0.05	0.66	0.00	0.08	0.00	0.32	0.12	120	111
n	106	104	106	104	102	101	51	49	99	97

DATE	Ca (mg/L)		Mg (mg/L)		Na (mg/L)		K (mg/L)		Cl (mg/L)		SS (mg/L)	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
14/11/97	310	312	106	92	2037	1421	243	407				
28/11/97	336	232	45	38	1019	864	148	128	1575	1632		
02/12/97	158	128	50	48	1832	1506	211	229	2470	2175		
09/12/97	277	229	63	54	1390	1450	152	138	2313	2379		
17/12/97	277	192	60	57	1639	1666	219	221	2437	2545		
07/01/98												
14/01/98									801	754		
20/02/98	288	284	124	125	935	962	151	173	1163	1198	46	40
26/02/98	289	289	132	130	967	952	171	164	1542	1547	65	49
05/03/98									1195	1137	46	25
12/03/98	101	112	21	21	986	1241	95	82	1791	2688	341	180
19/03/98	214	219	80	83	1065	1068	198	206	1228	1249	420	
26/03/98									1662	1850	473	23
09/04/98									1386	1369	31	29
21/04/98									1237	1395	47	43
24/04/98									975	763	31	28
08/05/98									1208	1297	53	34
14/05/98									1267	1230	59	41
20/05/98												
28/05/98												
02/06/98												
08/06/98												
09/06/98									856	1101	29	24
16/06/98												
17/06/98												
18/06/98									1054	1072		
19/06/98												
20/06/98												
21/06/98												
22/06/98												

DATE	Ca (mg/L)		Mg (mg/L)		Na (mg/L)		K (mg/L)		Cl (mg/L)		SS (mg/L)	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
24/06/98									1105	1099	31	76
25/06/98									1133	1193		
30/06/98												
02/07/98									1029	1421		
06/07/98												
07/07/98									1248	1196		
08/07/98												
09/07/98									1376	1232		
10/07/98												
11/07/98												
12/07/98												
16/07/98									1459	1411		
23/07/98	232	207	101	73	380	355	77	75			56	42
30/07/98												
06/08/98												
13/08/98									963	1169		
20/08/98									1358	1352		
11/09/98												
14/09/98												
17/09/98												
24/09/98											67	24
02/10/98												
08/10/98												
15/10/98	193	190	52	49	840	791	100	85				
22/10/98	199	196	48	43	1003	957	92	92				
29/10/98	106	127	27	32	755	864	111	131	2629	2809		
04/11/98	133	134	31	29	991	1152	124	120	3083	3633		
12/11/98	169	168	62	53	1078	1097	142	136	2269	2484		
19/11/98	171	163	54	55	1074	1093	141	140	2236	2439		
26/11/98	205	237	61	67	1743	2418	140	156	3523	2925		

DATE	Ca (mg/L)		Mg (mg/L)		Na (mg/L)		K (mg/L)		Cl (mg/L)		SS (mg/L)	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
10/12/98	326	335	103	107	2552	2668	231	241	3374	3314		
17/12/98	362	408	126	128	2493	2586	294	300			55	35
23/12/98	408	451	141	156	2937	3418	505	370	3731	4224		
11/01/99	320	359	89	85	3246	3929	348	346	4224	4184	71	81
18/01/99	299	400	84	87	2697	2725	271	290	3401	3378		
26/01/99	382	362	121	114	2572	2589	297	283	3132	3109	38	39
02/02/99	243	281	68	63	954	958	97	89	2035	2085		
09/02/99	216	303	67	93	1344	1984	90	127	2907	3441	83	73
17/02/99	246	287	81	90	1052	1136	89	105	1889	2228		
10/03/99	150	131	32	24	600	390	57	42	1201	1209	51	29
16/03/99	188	251	55	56	706	820	72	74	1397	1185		
23/03/99	264	208	82		1148	851	107	96	1691	1809	55	43
30/03/99	348	297	113	107	1235	1188	173	180	2191	2246		
09/04/99	279	279	112	110	1222	1124	166	163	2075	2031		
14/04/99	123	170	35	49	571	1436	56	136	1056	2100		
23/04/99	168	171	52	51	1263	1073	164	155	2062	2194		
29/04/99	202	232	68	77	1224	1391	183	212	2239	2167		
07/05/99	182		56		901		140		1487			
14/05/99	145	155	39	37	792	749	130	121	440	1025		
19/05/99	228	238	80	79	1629	1661	268	277	3436	2861		
03/06/99	197	163	65	47	1149	825	188	154	1851	1691		
08/06/99	154	134	40	36	971	806	162	131	974	1389		
18/06/99									3309	3287		
25/06/99									2886			
02/07/99	257	264	101	95	1922	1842	327	325	3047	2852		
09/07/99									3043	2529		
16/07/99									2746	2993		
23/07/99									2621	2365		
30/07/99									2446	2620		
06/08/99									1860	1527		

DATE	Ca (mg/L)		Mg (mg/L)		Na (mg/L)		K (mg/L)		Cl (mg/L)		SS (mg/L)	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
13/08/99									705	940		
20/08/99									1018	749		
27/08/99									2437	2324		
03/09/99									2470	2864		
10/09/99									2589	1895		
16/09/99									1581	2415		
08/10/99	314	291	98	91	2163	2062	36.5	34.1	3939	3463		
14/10/99	354	345	110	110	2119	2114	35.7	36.2	3431	3537		
21/10/99									3563	3534		
29/10/99	182	188	65.2	62	1963	1874	328	310	4197	3296		
04/11/99									3674	3520		
11/11/99	225	189	79.5	75	2126	1979	380	353	3588	4163		
19/11/99												
25/11/99	186	186	80.9	71.9	2070	1978	314	276	3290	3379		
02/12/99												
08/12/99	122	115	26.3	24.2	508	363		55.2	940	749		
15/12/99	172	192	40.8	37.7	3251	3651	229	222	4535	5039		
20/01/00	232	220	81.2	77.3	2221	1902	319	316	3425	3043	84	49
28/01/00	225	223	74.8	76.9	1613	1448	234	245	2820	2819		
04/02/00	224	229	77.7	83.2	1291	1220	199	218	3503	2416	49	33
11/02/00	250		87.7	75.8	1108	1081	188	169	1978	1952		

Mean	232.0	234.2	73.5	71.9	1477	1514	183.9	182.7	2177	2206	99.2	47.3
Median	225	223	68	73	1224	1231	165	160	2062	2175	55	40
S.D.	75.06	81.36	30.07	31.29	719	813	98.57	95.54	1015	989	126.13	33.95
Max.	408	451	141	156	3251	3929	505	407	4535	5039	473	180
Min.	101	112	21	21	380	355	36	34	440	749	29	23
n	51	49	51	49	51	50	50	50	79	77	23	22

APPENDIX 3

Quaking Houses wetland data: Fe and acidity treatment efficiency; Fe and acidity loads; Fe and acidity area-adjusted removal rates

DATE			Acid load (g/d)				Fe load (g/d)			
	% acid removal	% Fe removal	Influent	Effluent	% acid load removal	Acid (g/m^2/d)	Influent	Effluent	% Fe removal	Fe (g/m^2/d)
14/11/97	81.3	75.6								
28/11/97	54.1	49.8								
02/12/97	39.4	24.0								
09/12/97	67.3	50.0								
17/12/97	95.5	91.0								
07/01/98	44.7	25.0								
14/01/98	39.3	47.4	12096	7344	39.3	10.8	903	475	47.4	0.97
20/02/98										
26/02/98	63.8	25.3								
05/03/98	50.0	37.9								
12/03/98	40.7	43.0								
19/03/98	68.8	44.0								
26/03/98		91.9								
09/04/98		20.0					108	86	20.0	0.05
21/04/98		41.9								
24/04/98		27.8								
08/05/98		45.1								
14/05/98	52.2	46.5	4571	2186	52.2	5.4	209	112	46.5	0.22
20/05/98	56.7	26.5								
28/05/98	70.2	51.4	4596	1368	70.2	7.3	361	176	51.4	0.42
02/06/98	34.6	15.9	6739	4406	34.6	5.3	391	329	15.9	0.14
08/06/98	88.7	5.5	22896	2592	88.7	46.1	549	518	5.5	0.07
09/06/98		48.9								
16/06/98	31.3	44.0	8294	5702	31.3	5.9	389	218	44.0	0.39
17/06/98	40.0	66.7	9072	5443	40.0	8.2	726	242	66.7	1.10
18/06/98	61.4	85.4								
19/06/98	41.7	46.7	5184	3024	41.7	4.9	162	86	46.7	0.17
20/06/98	46.7	59.1	7776	4147	46.7	8.2	285	117	59.1	0.38
21/06/98	41.4	45.8	6264	3672	41.4	5.9	207	112	45.8	0.22
22/06/98	42.1	5.4	7387	4277	42.1	7.1	758	717	5.4	0.09

DATE			Acid load (g/d)				Fe load (g/d)			
	% acid removal	% Fe removal	Influent	Effluent	% acid load removal	Acid (g/m^2/d)	Influent	Effluent	% Fe removal	Fe (g/m^2/d)
24/06/98	45.0	24.2								
25/06/98		29.5								
30/06/98	44.4	48.6	5599	3110	44.4	5.7	262	135	48.6	0.29
02/07/98		23.3					201	154	23.3	0.11
06/07/98	37.3	25.3	6368	3992	37.3	5.4	496	371	25.3	0.29
07/07/98	37.8	33.6								
08/07/98	65.4	45.1	4942	1711	65.4	7.3	605	333	45.1	0.62
09/07/98	60.3	67.7	5875	2333	60.3	8.1	848	274	67.7	1.30
10/07/98	67.7	33.1	5892	1901	67.7	9.1	546	365	33.1	0.41
11/07/98	58.7	56.2	5988	2471	58.7	8.0	548	240	56.2	0.70
12/07/98	75.6	67.7	3897	950	75.6	6.7	450	145	67.7	0.69
16/07/98		39.9					338	203	39.9	0.31
23/07/98	61.4	61.0	4416	1704	61.4	6.2	437	170	61.0	0.61
30/07/98	33.3	30.4	10886	7258	33.3	8.2	1258	875	30.4	0.87
06/08/98										
13/08/98		75.7					325	79	75.7	0.56
20/08/98		53.8					403	186	53.8	0.49
11/09/98	67.4	61.8	2928	955	67.4	4.5	509	194	61.8	0.71
14/09/98	56.0	42.2								
17/09/98										
24/09/98	74.4	71.5								
02/10/98	38.7	54.3								
08/10/98										
15/10/98	66.7	54.5	2862	954	66.7	4.3	525	239	54.5	0.65
22/10/98	55.9	55.1								
29/10/98	45.5	44.4	5322	2903	45.5	5.5	818	455	44.4	0.82
04/11/98	11.8	12.3	10282	9072	11.8	2.7	1034	907	12.3	0.29
12/11/98	45.0	34.6	6365	3501	45.0	6.5	543	355	34.6	0.43
19/11/98	32.6	29.0	6669	4498	32.6	4.9	578	411	29.0	0.38
26/11/98		39.7					604	364	39.7	0.54

DATE			Acid load (g/d)				Fe load (g/d)			
	% acid removal	% Fe removal	Influent	Effluent	% acid load removal	Acid (g/m^2/d)	Influent	Effluent	% Fe removal	Fe (g/m^2/d)
10/12/98	51.3	41.2	4813	2345	51.3	5.6	479	281	41.2	0.45
17/12/98	66.0	67.7	4819	1640	66.0	7.2	537	173	67.7	0.83
23/12/98	40.8	32.9	3655	2163	40.8	3.4	422	283	32.9	0.32
11/01/99	32.0	15.8	6300	4284	32.0	4.6	847	713	15.8	0.30
18/01/99	41.4	24.0	6055	3550	41.4	5.7	731	555	24.0	0.40
26/01/99	53.5	52.6	4724	2197	53.5	5.7	541	256	52.6	0.65
02/02/99	61.5	56.9	4620	1777	61.5	6.5	604	260	56.9	0.78
09/02/99	32.8	38.7	3871	2601	32.8	2.9	616	377	38.7	0.54
17/02/99	60.4	96.6	3106	1231	60.4	4.3	86	3	96.6	0.19
10/03/99	33.3	33.3								
16/03/99	64.0	43.5								
23/03/99	66.7	41.8	6944	2315	66.7	10.5	320	186	41.8	0.30
30/03/99	28.4	5.4	5210	3732	28.4	3.4	272	257	5.4	0.03
09/04/99	32.8	18.3								
14/04/99										
23/04/99	39.3	19.6	4455	2705	39.3	4.0	453	364	19.6	0.20
29/04/99	82.4	90.1	5733	1007	82.4	10.7	1244	123	90.1	2.55
07/05/99			3182		100.0	7.2	361			0.82
14/05/99	21.7	22.9	5564	4355	21.7	2.7	656	506	22.9	0.34
19/05/99		72.1					512	143	72.1	0.84
03/06/99	57.1	53.3	3851	1650	57.1	5.0	483	226	53.3	0.59
08/06/99		25.5					803	598	25.5	0.47
18/06/99		73.3					1551	414	73.3	2.58
25/06/99							1058			2.41
02/07/99	61.3	53.1	11714	4534	61.3	16.3	1417	665	53.1	1.71
09/07/99	63.1	55.1								
16/07/99	89.0	85.4	2628	288	89.0	5.3	294	43	85.4	0.57
23/07/99	33.3	38.7	2214	1476	33.3	1.7	278	170	38.7	0.24
30/07/99	77.5	67.0								
06/08/99		90.2					516	51	90.2	1.06

DATE			Acid load (g/d)				Fe load (g/d)			
	% acid removal	% Fe removal	Influent	Effluent	% acid load removal	Acid (g/m^2/d)	Influent	Effluent	% Fe removal	Fe (g/m^2/d)
13/08/99		91.2					379	33	91.2	0.79
20/08/99		65.8					465	159	65.8	0.70
27/08/99		67.9					406	131	67.9	0.63
03/09/99		85.4					505	74	85.4	0.98
10/09/99		79.5					282	58	79.5	0.51
16/09/99	70.4	76.9	2433	720	70.4	3.9	581	134	76.9	1.01
08/10/99	69.7	68.8	1359	412	69.7	2.2	294	92	68.8	0.46
14/10/99	48.8	18.0	1612	826	48.8	1.8	351	288	18.0	0.14
21/10/99	57.4	53.1	1726	735	57.4	2.3	363	170	53.1	0.44
29/10/99	40.7	31.8	1590	942	40.7	1.5	285	194	31.8	0.21
04/11/99	68.1	37.8	941	300	68.1	1.5	145	90	37.8	0.12
11/11/99	50.0	41.0	3064	1532	50.0	3.5	444	262	41.0	0.41
19/11/99	41.7	-23.8	1393	812	41.7	1.3	117	145	-23.8	
25/11/99	33.3	3.8	3878	2585	33.3	2.9	511	491	3.8	0.04
02/12/99	73.7	61.1	3907	1028	73.7	6.5	469	182	61.1	0.65
08/12/99		36.7								
15/12/99		14.2					527	453	14.2	0.17
20/01/00	51.2	45.4	7728	3772	51.2	9.0	1264	691	45.4	1.30
28/01/00		56.6					352	153	56.6	0.45
04/02/00	71.0	45.9	3573	1037	71.0	5.8	330	178	45.9	0.34
11/02/00	74.5	55.0	3789	968	74.5	6.4	346	156	55.0	0.43

Mean	53.4	46.4	5407	2649	52.9	6.4	525	276	46.4	0.59
Median	52.8	45.2	4816	2315	51.2	5.6	474	211	46.2	0.45
S.D.	16.90	23.00	3422	1863	18.02	5.98	300	199	24.13	0.51
Max.	95.5	96.6	22896	9072	100.0	46.1	1551	907	96.6	2.58
Min.	11.8	-23.8	941	288	11.8	1.3	86.2	2.9	-23.8	0.03
n	80	104	58	57	58	58	76	74	74	75

APPENDIX 4

Quaking Houses wetland data:

Mn, Al, Zn treatment efficiency and area-adjusted removal rates

DATE									
	% Mn removal	% Al removal	% Zn removal	% Mn load rem.	% Al load rem.	% Zn load rem.	Mn ($g/m^2/d$)	Al ($g/m^2/d$)	Zn ($g/m^2/d$)
14/11/97	49.1	89.9							
28/11/97	14.7	60.3							
02/12/97	11.8	43.0							
09/12/97	17.8	77.8							
17/12/97	48.9	100.0							
07/01/98	7.6	53.3							
14/01/98	14.7	41.7		14.7	41.7		0.20	1.61	
20/02/98									
26/02/98	6.8	79.8							
05/03/98	-1.2	59.5							
12/03/98	21.7	44.8							
19/03/98	11.6	83.9							
26/03/98	15.0								
09/04/98	3.5	23.3		3.5	23.3		0.02	0.25	
21/04/98	2.9	62.0							
24/04/98	12.7	42.9							
08/05/98	7.6	80.3							
14/05/98	7.5	61.0		7.5	61.0		0.06	0.87	
20/05/98	4.4	75.5							
28/05/98	22.7	82.8		22.7	82.8		0.17	1.13	
02/06/98	3.8	42.9		3.8	42.9		0.05	0.87	
08/06/98		100.0		-244.8	100.0			8.76	
09/06/98	11.7	64.6							
16/06/98	8.4	31.4		8.4	31.4		0.15	0.78	
17/06/98	5.0	40.5		5.0	40.5		0.10	1.06	
18/06/98	9.6	63.9							
19/06/98	31.5	42.6		31.5	42.6		0.48	0.65	
20/06/98	8.2	54.8		8.2	54.8		0.16	1.27	
21/06/98	10.2	51.3		10.2	51.3		0.18	0.94	
22/06/98	5.6	63.4		5.6	63.4		0.10	1.17	

DATE									
	% Mn removal	% Al removal	% Zn removal	% Mn load rem.	% Al load rem.	% Zn load rem.	Mn (g/m^2/d)	Al (g/m^2/d)	Zn (g/m^2/d)
24/06/98	2.4	56.0							
25/06/98	3.2	28.8	-1.2						
30/06/98	1.7	55.3		1.7	55.3		0.02	0.94	
02/07/98	50.3	41.7	12.6	50.3	41.7	12.6	0.76	0.65	0.11
06/07/98	2.3	48.4		2.3	48.4		0.03	0.85	
07/07/98	3.8	45.9	-107.2						
08/07/98	5.2	100.0		5.2	100.0		0.08	1.08	
09/07/98	13.7	70.8	34.1	13.7	70.8	34.1	0.16	1.00	0.17
10/07/98	0.6	95.0		0.6	95.0		0.01	1.47	
11/07/98	16.4	69.6		16.4	69.6		0.21	1.14	
12/07/98	52.4	84.6		52.4	84.6		0.53	0.77	
16/07/98	2.5		4.5	2.5		4.5	0.02		0.01
23/07/98	33.1	68.5	47.9	33.1	68.5	47.9	0.30	0.82	0.18
30/07/98	44.3	33.5	41.3	44.3	33.5	41.3	0.82	0.98	0.28
06/08/98									
13/08/98	-5.6		27.5	-5.6		27.5	-0.03		0.05
20/08/98	0.9		44.7	0.9		44.7	0.01		0.08
11/09/98	18.0	86.2	77.2	18.0	86.2	77.2	0.11	0.53	0.15
14/09/98	11.9	72.3	54.3						
17/09/98									
24/09/98	-0.5	90.7	61.9						
02/10/98	30.8	35.2	48.5						
08/10/98									
15/10/98	28.8	83.9	52.4	28.8	83.9	52.4	0.16	0.49	0.08
22/10/98	16.0	66.3	40.5						
29/10/98	12.7	52.7	38.9	12.7	52.7	38.9	0.10	0.69	0.15
04/11/98	0.9	16.4	2.5	0.9	16.4	2.5	0.01	0.48	0.03
12/11/98	1.1	57.6	14.0	1.1	57.6	14.0	0.01	1.03	0.08
19/11/98	6.7	38.4	10.0	6.7	38.4	10.0	0.08	0.73	0.06
26/11/98	10.8	76.4	33.5	10.8	76.4	33.5	0.12	1.38	0.17

DATE									
	% Mn removal	% Al removal	% Zn removal	% Mn load rem.	% Al load rem.	% Zn load rem.	Mn ($g/m^2/d$)	Al ($g/m^2/d$)	Zn ($g/m^2/d$)
10/12/98	0.6	63.9	13.5	0.6	63.9	13.5	0.01	0.82	0.04
17/12/98	3.5	78.5	28.1	3.5	78.5	28.1	0.03	1.00	0.07
23/12/98	7.6	52.2	18.7	7.6	52.2	18.7	0.06	0.50	0.04
11/01/99	4.7	44.3	-2.4	4.7	44.3	-2.4	0.05	0.73	-0.01
18/01/99	4.4	54.2	11.2	4.4	54.2	11.2	0.04	0.90	0.06
26/01/99	2.8	63.9	17.6	2.8	63.9	17.6	0.02	0.82	0.07
02/02/99	1.9	78.4		1.9	78.4		0.02	0.92	
09/02/99	-1.9	34.0	-2.5	-1.9	34.0	-2.5	-0.01	0.35	0.00
17/02/99	-5.4	63.1	22.7	-5.4	63.1	22.7	-0.02	0.70	0.03
10/03/99	9.1	32.0	9.1						
16/03/99	5.5	70.1	11.5						
23/03/99	5.8	79.2	22.8	5.8	79.2	22.8	0.06	1.79	0.16
30/03/99	0.8	35.8	12.8	0.8	35.8	12.8	0.01	0.59	0.06
09/04/99	1.4	41.3	6.1						
14/04/99									
23/04/99		55.8	14.7	-114.7	55.8	14.7		0.78	0.05
29/04/99	17.9	87.8	46.3	17.9	87.8	46.3	0.11	1.07	0.12
07/05/99									
14/05/99	13.1	22.1	32.8	13.1	22.1	32.8	0.09	0.35	0.10
19/05/99	70.8	83.1	81.0	70.8	83.1	81.0	0.53	1.13	0.23
03/06/99	25.9	64.8	44.6	25.9	64.8	44.6	0.17	0.66	0.11
08/06/99	36.4	65.0	34.4	36.4	65.0	34.4	0.39	1.09	0.17
18/06/99	16.1	85.8	38.1	16.1	85.8	38.1	0.33	2.57	0.27
25/06/99									
02/07/99	21.1	70.8	31.7	21.1	70.8	31.7	0.37	2.23	0.19
09/07/99	36.7	70.6	45.5						
16/07/99	68.0	93.7		68.0	93.7		0.28	0.67	
23/07/99	14.1	34.8		14.1	34.8		0.05	0.20	
30/07/99	10.2	92.9							
06/08/99	95.8	22.9		95.8	22.9		0.44	0.09	

DATE									
	% Mn removal	% Al removal	% Zn removal	% Mn load rem.	% Al load rem.	% Zn load rem.	Mn (g/m^2/d)	Al (g/m^2/d)	Zn (g/m^2/d)
13/08/99	95.2	49.8		95.2	49.8		0.36	0.17	
20/08/99	82.1	20.9		82.1	20.9		0.50	0.11	
27/08/99	84.2	22.4		84.2	22.4		0.56	0.11	
03/09/99	91.3	15.7		91.3	15.7		0.54	0.07	
10/09/99	93.2	38.3		93.2	38.3		0.39	0.19	
16/09/99	17.2	78.8		17.2	78.8		0.07	0.36	
08/10/99	100.0	25.3	70.3	100.0	25.3	70.3	0.21	0.10	0.06
14/10/99	100.0	5.5	-20.0	100.0	5.5	-20.0	0.26	0.02	-0.02
21/10/99	82.2	9.8		82.2	9.8		0.26	0.04	
29/10/99	52.6	9.1		52.6	9.1		0.18	0.03	
04/11/99	75.2	91.4		75.2	91.4		0.17	0.14	
11/11/99	61.2	6.3		61.2	6.3		0.46	0.03	
19/11/99	58.2			58.2			0.27		
25/11/99	49.3	10.2		49.3	10.2		0.50	0.06	
02/12/99	88.8	14.5		88.8	14.5		0.93	0.08	
08/12/99	-13.9	28.2							
15/12/99	43.6	80.9	62.5	43.6	80.9	62.5	0.52	0.57	0.10
20/01/00	62.8	5.6	7.4	62.8	5.6	7.4	1.18	0.06	0.01
28/01/00	84.0	0.9	16.1	84.0	0.9	16.1	1.04	0.01	0.02
04/02/00	91.3	-2.9	34.8	91.3	-2.9	34.8	0.93	-0.02	0.04
11/02/00	88.8	12.9	17.6	88.8	12.9	17.6	0.99	0.07	0.02

Mean	26.4	54.1	25.8	26.5	50.6	28.1	0.26	0.81	0.09
Median	12.7	55.8	27.5	15.4	52.5	27.5	0.16	0.71	0.07
S.D.	30.79	26.50	29.35	49.35	28.09	22.13	0.29	1.10	0.08
Max.	100.0	100.0	81.0	100.0	100.0	81.0	1.18	8.76	0.28
Min.	-13.9	-2.9	-107.2	-244.8	-2.9	-20.0	-0.03	-0.02	-0.02
n	102	99	49	74	70	39	72	70	39

APPENDIX 5

Quaking Houses wetland data: Fe, acidity, Mn, Al, Zn area-adjusted removal rates (dilution-adjusted) and values for first-order removal constants

DATE		DA	DA	DA	DA	DA					
	Mg DF	Acid (g/m^2/d)	Fe (g/m^2/d)	Mn (g/m^2/d)	Al (g/m^2/d)	Zn (g/m^2/d)	k_1 Fe (m/d)	k_1 acid (m/d)	k_1 Mn (m/d)	k_1 Al (m/d)	k_1 Mn (m/d)
14/11/97	0.87										
28/11/97	0.84										
02/12/97	0.96										
09/12/97	0.86										
17/12/97	0.95										
07/01/98											
14/01/98											
20/02/98	1.01										
26/02/98	0.98										
05/03/98											
12/03/98	1.00										
19/03/98	1.04										
26/03/98											
09/04/98											
21/04/98											
24/04/98											
08/05/98											
14/05/98											
20/05/98											
28/05/98											
02/06/98											
08/06/98											
09/06/98											
16/06/98											
17/06/98											
18/06/98											
19/06/98											
20/06/98											
21/06/98											
22/06/98											

DATE		DA	DA	DA	DA	DA					
	Mg DF	Acid ($g/m^2/d$)	Fe ($g/m^2/d$)	Mn ($g/m^2/d$)	Al ($g/m^2/d$)	Zn ($g/m^2/d$)	k_1 Fe (m/d)	k_1 acid (m/d)	k_1 Mn (m/d)	k_1 Al (m/d)	k_1 Mn (m/d)
24/06/98											
25/06/98											
30/06/98											
02/07/98											
06/07/98											
07/07/98											
08/07/98											
09/07/98											
10/07/98											
11/07/98											
12/07/98											
16/07/98											
23/07/98	0.72	4.68	0.46	0.07	0.67	0.11	0.075	0.077	0.010	0.102	0.040
30/07/98											
06/08/98											
13/08/98											
20/08/98											
11/09/98											
14/09/98											
17/09/98											
24/09/98											
02/10/98											
08/10/98											
15/10/98	0.94	4.20	0.62	0.14	0.48	0.08	0.091	0.130	0.035	0.222	0.086
22/10/98	0.90										
29/10/98	1.19	6.53	0.99	0.22	0.78		0.289	0.296	0.117	0.351	
04/11/98	0.94	1.33	0.15	-0.09	0.31	-0.05	0.061	0.056	-0.055	0.108	-0.040
12/11/98	0.85	5.16	0.29	-0.20	0.90	0.00	0.067	0.111	-0.037	0.176	-0.001
19/11/98	1.02	5.12	0.40	0.11	0.75	0.07	0.088	0.101	0.022	0.123	0.030
26/11/98	1.10		0.62	0.22	1.41	0.20	0.139		0.048	0.357	0.116

DATE		DA	DA	DA	DA	DA					
	Mg DF	Acid (g/m^2/d)	Fe (g/m^2/d)	Mn (g/m^2/d)	Al (g/m^2/d)	Zn (g/m^2/d)	k_1 Fe (m/d)	k_1 acid (m/d)	k_1 Mn (m/d)	k_1 Al (m/d)	k_1 Mn (m/d)
10/12/98	1.04	5.81	0.47	0.04	0.84	0.05	0.111	0.147	0.009	0.206	0.036
17/12/98	1.02	7.28	0.83	0.04	1.01	0.08	0.186	0.177	0.008	0.251	0.056
23/12/98	1.11	3.86	0.38	0.13	0.54	0.06	0.059	0.074	0.021	0.099	0.036
11/01/99	0.96	4.12	0.23	0.00	0.68	-0.03	0.050	0.135	0.001	0.214	-0.028
18/01/99	1.04	5.97	0.44	0.07	0.92	0.08	0.102	0.188	0.026	0.269	0.051
26/01/99	0.94	5.44	0.61	-0.02	0.79	0.05	0.119	0.122	-0.005	0.167	0.023
02/02/99	0.93	6.14	0.73	-0.05	0.90		0.107	0.123	-0.008	0.204	
09/02/99	1.39	4.54	0.78	0.09	0.54	0.04	0.078	0.069	0.029	0.071	0.029
17/02/99	1.11	4.54	0.19	0.02	0.74	0.04	0.322	0.095	0.005	0.102	0.034
10/03/99	0.75										
16/03/99	1.02										
23/03/99											
30/03/99	0.95	2.88	0.00	-0.04	0.53	0.04	0.000	0.034	-0.006	0.048	0.010
09/04/99	0.98										
14/04/99	1.40										
23/04/99	0.98	3.86	0.19	-0.41	0.77	0.04	0.050	0.120	-0.197	0.200	0.035
29/04/99	1.13	11.01	2.58	0.17	1.09	0.14	0.298	0.228	0.039	0.272	0.091
07/05/99											
14/05/99	0.95	2.21	0.28	0.06	0.28	0.09	0.079	0.073	0.033	0.075	0.131
19/05/99	0.99		0.83	0.52	1.13	0.23	0.207		0.199	0.289	0.270
03/06/99	0.72	3.56	0.39	-0.02	0.52	0.06	0.076	0.091	-0.004	0.125	0.046
08/06/99	0.90		0.31	0.31	1.03	0.13	0.100		0.184	0.501	0.167
18/06/99											
25/06/99											
02/07/99	0.94	15.67	1.61	0.29	2.17	0.16	0.207	0.265	0.052	0.349	0.095
09/07/99											
16/07/99											
23/07/99											
30/07/99											
06/08/99											

DATE		DA	DA	DA	DA	DA					
	Mg DF	Acid (g/m^2/d)	Fe (g/m^2/d)	Mn (g/m^2/d)	Al (g/m^2/d)	Zn (g/m^2/d)	k_1 Fe (m/d)	k_1 acid (m/d)	k_1 Mn (m/d)	k_1 Al (m/d)	k_1 Mn (m/d)
13/08/99											
20/08/99											
27/08/99											
03/09/99											
10/09/99											
16/09/99											
08/10/99	0.93	2.08	0.44	0.21	0.08	0.06	0.071	0.073	0.052	0.014	0.074
14/10/99	1.00	1.79	0.14	0.26	0.02	-0.02	0.012	0.042	0.065	0.003	-0.011
21/10/99											
29/10/99	0.95	1.36	0.18	0.17	0.01		0.031	0.044	0.065	0.004	
04/11/99											
11/11/99	0.94	3.27	0.38	0.45	0.00		0.063	0.085	0.119	0.001	
19/11/99											
25/11/99	0.89	2.20	-0.10	0.44	-0.01		-0.013	0.049	0.095	-0.002	
02/12/99											
08/12/99	0.92										
15/12/99	0.92		0.09	0.47	0.55	0.10	0.026		0.176	0.563	0.322
20/01/00	0.95	8.56	1.22	1.15	0.01	0.01	0.139	0.167	0.235	0.002	0.007
28/01/00	1.03		0.46	1.05	0.03	0.02	0.131		0.282	0.006	0.031
04/02/00	1.07	5.92	0.37	0.94	0.02	0.04	0.075	0.144	0.276	0.004	0.055
11/02/00	0.86	6.07	0.38	0.97	0.00	0.00	0.059	0.110	0.184	-0.001	0.004

Mean	0.98	5.01	0.53	0.23	0.60	0.06	0.105	0.118	0.061	0.161	0.062
Median	0.95	4.54	0.39	0.13	0.61	0.06	0.079	0.110	0.034	0.124	0.036
S.D.	0.13	2.99	0.50	0.35	0.48	0.06	0.081	0.065	0.099	0.147	0.080
Max.	1.40	15.67	2.58	1.15	2.17	0.23	0.322	0.296	0.282	0.563	0.322
Min.	0.72	1.33	-0.10	-0.41	-0.01	-0.05	-0.013	0.034	-0.197	-0.002	-0.040
n	49	29	34	34	34	29	34	29	34	34	29

APPENDIX 6

Quaking Houses wetland surface and sediment water quality

SURFACE WATER AND SEDIMENT WATER CHEMICAL ANALYSES AT QUAKING HOUSES (28th October 1999)

Sample ID	Sample description	Temperature (deg C)	pH	Eh (mV)	Conductivity (uS/cm)	Alkalinity (mg/L as $CaCO_3$)	Fe (mg/L)	Mn (mg/L)	Zn (mg/L)	Al (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO_4 (mg/L)	Cl (mg/L)	Total Organic Carbon (mg/L)	Inorganic Carbon (mg/L)
#1 W	Open water surface, first pond	10.8	6.77	84	10650	86	5.3	1.63	0.59	3.67	175.5	62.9	181	30.5	453	2983	<7.0	22
#1 W (D)							6.3	2.02	1.3	6.04								
#1 S	20 cm below sediment surface (water 6 cm deep)	10.6	6.73	-109	10150		601	28.35	5.85	0.5	161	35.4	1651	41	661	2953	22	130
#1 S (D)							3368	42.52	125.3	4054	2227	989.8	1966	635.8				
#2 W	Influent water	12.9	6.55	-38	10230	82	6.77	1.64	0.59	3.67	166	55.2	1564	26.6	446	2958	<7.0	23
#3 W	Amongst reeds, first pond	12.6	7.2	-74	9104	244	1.9	1.31	0.14	0.89	205.8	71	1459	23.1	381	2005	9.1	66
#3 W (D)							2.54	1.81	0.94	3.77								
#3 S	17 cm below sediment surface (water < 1 cm deep)	11.6	6.52	-186	10290		89	6.08	2.62	0.86	148.7	44.1	596.7	88.6	462	2826	15	150
#3 S (D)							323.4	6.32	31.15	425.4	427.6	171.2	1817.8	328.6				
#4 W	Open water surface, second pond	11.2	7.11	-58	9885	88	2.73	1.42	0.35	1.26	191	61.4	1735	29.7	382	2743	<7.0	25
#4 W (D)							3.05	1.81	1.78	4.23								
#4 S	20 cm below sediment surface (water 15 cm deep)	10.6	6.62	-275	11290		105.2	7.28	8.77	8.87	397.6	120.2	2045	366.7	529	3017	8.2	130
#4 S (D)							192.2	7.46	14.88	241	409.8	130.2	2035	329.6				
#5 W	Amongst reeds, second pond	9.7	6.99	-61	9163	92	1.41	1.05	0.27	0.72	166.7	56.4	1617	26.9	413	2732	7.2	27
#5 W (D)							1.62	1.39	0.91	3.28								
#5 S	15 cm below sediment surface (water 30 cm deep)	10.1	7.39	-79	6900		15.46	21.81	1.98	0.69	674.6	123.8	1252	231.2	523	2121	9.7	54
#5 S (D)							945.4	37.46	17.89	959.4	687.8	239.6	1269.6	345.4				
#6 W	Effluent water	10.1	6.97	-65	9635	92	1.95	1.33	0.32	0.98	176.8	61.6	1662	28.1	411	2882	<7.0	26

Notes:	
	W indicates surface water sample
	S indicates sediment water sample
	(D) indicates acid-digested sample
	All sediment samples are filtered (0.45um) (after digestion where applicable)
	All samples are filtered (0.20 um) for analysis of Ca, Mg, Na, K, SO_4 and Cl

SURFACE WATER AND SEDIMENT WATER CHEMICAL ANALYSES AT QUAKING HOUSES (17th December 1999)

Sample ID	Sample description	Temperature (deg C)	pH	Eh (mV)	Conductivity (uS/cm)	Alkalinity (mg/L as $CaCO_3$)	Fe (mg/L)	Mn (mg/L)	Zn (mg/L)	Al (mg/L)	SO_4 (mg/L)	Cl (mg/L)	Total Organic Carbon (mg/L)	Inorganic Carbon (mg/L)
#1 W	Influent water	7.2	6.78		5988	94	2.47	1.4	0.48	2.47	315	1676	< 7.0	16
#1 W (D)							7.7	1.38	0.79	2.27				
#2 W	Open water surface, first pond	5.5	6.77	502	6099	100	6.85	1.5	0.57	7.41	319	1900	< 7.0	14
#2 W (D)							13.75	1.48	0.41	8.88				
#3 S	First pond sediment (7 cm below surface)	5.3	6.67				769.5	16.9	39.94	567	447	2365	18	18
#3 S (D)							2174	21.06	71.24	2279				
#4 W	Open water surface, second pond	4.7	6.74			88	5.87	1.42	0.71	7.13	289	1876	< 7.0	15
#4 W (D)							6.14	1.29	0.21	3.46				
#5 S	second pond sediment	6	6.83				134.16	8.45	3.83	121.6	260	1684	8	23
#5 S (D)							260.8	9.12	3.62	168.3				
#6 W	Upstream tributary		6.9			180	82.94	0.74	0.97	15.78	386	527	8	38
#6 W (D)							144.9	0.88	0.78	51.87				
#7 W	Stream, downstream of wetland		6.73			108	8.86	2.82	0.55	5.12	314	1787	10	25
#7 W (D)							17.88	2.87	0.28	5.75				
#8 W	Effluent from wetland		6.62				2.41	1.38	0.5	2.73	333	2008	8	21
#8 W (D)							5.99	1.37	0.29	2.69				

Notes:
W indicates surface water sample
S indicates sediment water sample
(D) indicates digested sample
All sediment samples are filtered (0.45um) (after digestion where applicable)
Exact sample locations indicated on attached map
All samples are filtered (0.20 um) for analysis of SO_4 and Cl

SURFACE WATER AND SEDIMENT WATER CHEMICAL ANALYSES AT QUAKING HOUSES (29th March 2000)

		Temperature (deg C)	pH	Eh (mV)	Conductivity (uS/cm)	Fe (mg/L)	Mn (mg/L)	Zn (mg/L)	Al (mg/L)	SO_4 (mg/L)	Cl (mg/L)
#1 W	Surface water sample	13.6	7.25	-80	7010	4.06	3.17	0.99	4.35	692	1850
#1 S (D)	sediment water sample	11.8	7.04	-166	8648	3288	43.6	295.1	5086	368	2866
#2 W	Surface water sample	12	7.16	0	6980	3.91	3.31	0.99	3.1	685	1829
#2 S (D)	sediment water sample	8.8	6.8	-134	9540	3493	45.32	268.7	4528	266	2582
#3 W	Surface water sample					4.11	3.08	0.99	3.49	687	1838
#3 S (D)	sediment water sample	8.7	6.73	-93	7355	1810	24.54	147.1	3222	430	3477
B	digested blank					4.1	0.41	0	5.17		

Notes: All digested samples filtered (0.45 um) for metal analysis
All samples filtered (0.20 um) for anion analysis
All samples replicates (taken within 1 metre of each other in first pond)
W indicates surface water sample
S indicates sediment water sample
(D) indicates acid-digested sample

APPENDIX 7

Kimblesworth pilot-scale reactor raw water quality and quantity

DATE	Temperature (Deg C)			pH			Conductivity (uS/cm)			Dissolved Oxygen (mg/L)			Flow (L/hour)	
	Inf	Eff A	Eff B	Inf	Eff A	Eff B	Inf	Eff A	Eff B	Inf	Eff A	Eff B	Eff A	Eff B
12/04/99	13.6	10.3	8.8	7.08	8.15	8.15	2253	2227	2153				84	14.2
21/04/99	12.6	10.5	10.2	7.09	8.08	8.14	2280	2277	2256	1.08	9.78	9.76	72	57.6
28/04/99	15.5	13.3	12.6	7.03	8.11	8.33	2275	2208	2186	2.00	9.40	9.76	81.6	55.2
07/05/99	17.9	18.1	16.7	7.30	8.21	8.26	2292	2180	2156	1.48	9.40	8.96	19.5	54.6
12/05/99	13.8	13.6	13.1	7.10	8.18	8.23	2236	2199	2180	2.40	9.20	9.54	106.8	50.4
19/05/99	14.8	14.7	13.6	7.55	8.13	8.25	2268	2207	2182	2.36	9.40	9.64	92.4	66
02/06/99	14.5	14.9	14.4	6.97	7.96	8.08	2280	2217	2178	2.92	9.44	9.28	92.4	45.6
09/06/99	14.3	12.7	12	7.18	8.21	8.39	2303	2202	2204	2.68	8.68	10.08	37.2	31.2
10/06/99	14.1	13.8	13.8	7.70	8.40	8.50	2276	2280	2259	1.80	9.40	9.52	720	720
11/06/99	13.8	13.4	13.5	7.74	9.20	9.21	2333	2262	2254	2.32	9.52	10.08	587	495
12/06/99	14.2	13.9	13.7				2308	2264	2245	2.00	9.60	9.88	284	223
13/06/99				6.77	8.29	8.43							89	48
18/06/99	16.4	16.7	16	7.30	8.47	8.67	2277	2248	2233	1.16	8.96	9.44	771	636
01/07/99	15	15.6	14.9	7.35	8.40	8.70	2292	2275	2271	1.44	9.88	9.96	348	324
08/07/99	19.8	21.1	20.4	7.08	7.66	7.81	2073	2055	2049	2.52	9.32	9.60	250	242
14/07/99										2.60	9.76	9.76	227	199
21/07/99										1.32	9.60	9.68	216	190
05/08/99	15.5	16.4	16	7.24	8.13	8.26	2336	2262	2246	1.64	9.36	9.40	152	114

Mean	15.1	14.6	14.0	7.23	8.24	8.36	2272.1	2224.2	2203.5	1.98	9.42	9.65	235.0	198.1
Median	14.5	13.9	13.7	7.18	8.18	8.26	2280	2227	2204	2	9.4	9.66	129.4	90
S.D.	1.83	2.77	2.75	0.27	0.33	0.33	61.14	57.21	58.55	0.58	0.30	0.30	230.86	214.93
Max.	19.8	21.1	20.4	7.74	9.2	9.21	2336	2280	2271	2.92	9.88	10.08	771	720
Min.	12.6	10.3	8.8	6.77	7.66	7.81	2073	2055	2049	1.08	8.68	8.96	19.5	14.2
n	15	15	15	15	15	15	15	15	15	16	16	16	18	18

DATE	Alkalinity (mg/L as $CaCO_3$)			Acidity$_{calc}$ (mg/L as $CaCO_3$)			SO_4 (mg/L)			Cl (mg/L)		
	Inf	Eff A	Eff B	Inf	Eff A	Eff B	Inf	Eff A	Eff B	Inf	Eff A	Eff B
12/04/99	695	708	650	3.3	1.7	1	353	343	350	120	119	124
21/04/99	699	688	662	3.6	1.5	1.2	362	355	350	126	124	122
28/04/99	724	733	665	3.7	1.6	1.5	336	359	349	127	131	117
07/05/99	735	659	657	3.7	1.2	1.2	365	369	355	141	129	123
12/05/99	713	695	673	3.4	1.3	0.9	368	400	373	120	126	117
19/05/99	730	683	666	3.3	1.3	1	381	383	386	136	136	120
02/06/99	714	711	648	3.5	1.4	0.9	336	382	389	120	238	142
09/06/99	712	688	630	3.6	1.4	0.9	381	384	378	120	119	122
10/06/99	716	698	698	4.7	3.1	3	381	383	406	121	122	121
11/06/99	734	698	722	4.5	8	2.6	390	379	378	120	120	119
12/06/99	730	716	672				381	382	374	187	125	123
13/06/99				4.7	1.8	2.9	388	385	384	133	122	122
18/06/99	708	691	683	0	0	0						
01/07/99				4.1	1.6	1.6	398	391	381	127	124	127
08/07/99	716	684	652	0	0	0	399	404	403	157	123	117
14/07/99	748	720	720				355	382	387	124	395	249
21/07/99	732	698	724				387	395	393	369	236	403
05/08/99	738	698	688	3.8	1.8	1.3	412	415	419	129	128	129
Mean	721.5	698	675.6	3.3	1.8	1.3	374.9	381.8	379.7	145.7	153.9	146.9
Median	720	698	669	3.6	1.5	1.2	381	383	381	127	125	122
S.D.	14.7	17.3	28.3	1.4	1.9	0.9	21.5	17.9	20.2	60.1	72.5	72.9
Max.	748	733	724	4.7	8	3	412	415	419	369	395	403
Min.	695	659	630	0	0	0	336	343	349	120	119	117
n	16	16	16	15	15	15	17	17	17	17	17	17

DATE	Fe (total) (mg/L)			Mn (mg/L)			Ca (mg/L)			Mg (mg/L)			Na (mg/L)			K (mg/L)		
	Inf	Eff A	Eff B	Inf	Eff A	Eff B	Inf	Eff A	Eff B	Inf	Eff A	Eff B	Inf	Eff A	Eff B	Inf	Eff A	Eff B
12/04/99	1.18	0.38	0.30	0.66	0.55	0.23	93	83	72	37	36	37	336	338	372	17	18	18
21/04/99	1.38	0.32	0.28	0.59	0.49	0.37	101	76	68	40	39	39	343	365	326	19	18	17
28/04/99	1.50	0.49	0.55	0.57	0.41	0.26	88	78	65	37	36	34	349	353	346	15	30	25
07/05/99	1.49	0.40	0.47	0.57	0.25	0.22	106	78	79	40	38	38	402	380	384	19	18	22
12/05/99	1.24	0.21	0.11	0.64	0.50	0.38	101	95	93	39	39	41	408	388	406	21	20	22
19/05/99	1.24	0.30	0.24	0.59	0.42	0.29	123	93	85	48	39	39	477	387	405	26	20	20
02/06/99	1.36	0.34	0.22	0.59	0.41	0.27	104	96	54	40	40	27	408	407	252	20	19	13
09/06/99	1.30	0.24	0.16	0.71	0.56	0.34												
10/06/99	1.83	1.04	0.93	0.81	0.71	0.75												
11/06/99	1.70	3.68	0.70	0.79	0.77	0.75												
12/06/99	1.84	0.66	0.55	0.77	0.68	0.57												
13/06/99	1.81	0.44	0.50	0.80	0.58	1.10												
18/06/99																		
01/07/99	1.50	0.20	0.24	0.80	0.67	0.62												
08/07/99							102	89	73	41	41	40	389	393	397	18	17	17
14/07/99	1.08	0.50	0.31	0.55	0.45	0.41												
21/07/99	1.16	0.29	0.35	0.54	0.39	0.39												
05/08/99	1.31	0.40	0.19	0.80	0.58	0.51												
Mean	1.43	0.62	0.38	0.67	0.53	0.47	102.3	86.0	73.6	40.3	38.5	36.9	389.0	376.4	361.0	19.4	20.0	19.3
Median	1.37	0.39	0.305	0.65	0.525	0.385	101.5	86	72.5	40	39	38.5	395.5	383.5	378	19	18.5	19
S.D.	0.25	0.84	0.22	0.11	0.14	0.24	10.28	8.25	12.12	3.45	1.77	4.52	46.54	22.75	52.42	3.25	4.17	3.77
Max.	1.84	3.68	0.93	0.81	0.77	1.1	123	96	93	48	41	41	477	407	406	26	30	25
Min.	1.08	0.2	0.11	0.54	0.25	0.22	88	76	54	37	36	27	336	338	252	15	17	13
n	16	16	16	16	16	16	8	8	8	8	8	8	8	8	8	8	8	8

APPENDIX 8

Statistical analysis techniques

STATISTICAL ANALYSIS TECHNIQUES

Descriptive statistics used in this work have predominantly been limited to reporting the mean value and the range where appropriate. The mean has been used partly because it is easily calculable, but also because it is widely used, and therefore allows comparison of the data here with other works. One of the risks of reporting the mean is that outliers in the time series may strongly influence its value. However, in this work outliers have generally been removed from the data set before calculating the mean. The range of values within a time series is also reported, to indicate the overall variability of water quality, at Quaking Houses in particular.

A number of statistical techniques have been employed in analysing the Quaking Houses data. Where possible parametric tests have been used, as these are more powerful tools than the alternative non-parametric tests (Hammond and McCullagh, 1980). However, a key assumption of parametric tests is that the data under investigation are approximately normally distributed (see below) (Hammond and McCullagh, 1980). Correlation coefficients and partial correlation coefficients have been calculated in this work using a parametric test (the product moment correlation). Statistical correlation is a method by which to test the degree of association between two sets of variables (Hammond and McCullagh, 1980). The product moment correlation coefficient (*r*) is calculated as follows (Hammond and McCullagh, 1980):

$$r = \frac{1/n \, \Sigma \, (a-a')(b-b')}{\sigma_a \, . \, \sigma_b} \qquad \text{(A.1)}$$

where,

r = correlation coefficient

n = number of pairs

a, b = variables a and b

a', b' = means of variable sets a and b

σ_a, σ_b = standard deviations of a and b

The correlation coefficient (*r*) is equivalent to the square root of the coefficient of determination (commonly written R^2). Partial correlation enables the relationship between two factors to be tested whilst removing the influence of a third variable. It is calculated as follows (Hammond and McCullagh, 1980):

$$r_{xy,z} = \frac{r_{xy} - (r_{xz} \cdot r_{yz})}{\sqrt{\{(1-r_{xz}^2)(1-r_{yz}^2)\}}} \qquad \text{(A.2)}$$

where, x, y and z = variables

$r_{xy,z}$ = partial correlation coefficient (i.e. correlation between x and y while z is controlled)

The significance of the correlation coefficient is indicated by the probability level (p). For example, if a correlation coefficient is significant at a probability level of 0.05 this means that there is a 5% probability that the observed relationship between the two pairs of variables is actually a chance occurrence. If the correlation coefficient is significant at a probability level of 0.001 this means that there is a 0.1% probability that the relationship is a chance occurrence. In this work the significance of a correlation coefficient is indicated by probability levels of 0.05, 0.01 and 0.001 (0.001 indicating the strongest relationship). The probability level for a given correlation coefficient is calculated from the t statistic (Hammond and McCullagh, 1980):

$$t = r\sqrt{\left[\frac{n-2}{1-r^2}\right]} \qquad \text{(A.3)}$$

The appropriate probability level (p) can then be read from tables of the t-distribution common in many statistics text books (e.g. Hammond and McCullagh, 1980).

Because these correlation tests are parametric it has been necessary to mathematically transform some variables in order that they approximate a normal distribution. Normal scores plots have been used to assess the most appropriate mathematical transformations of the data. A normal scores plot is a transformation of the cumulative probability curve, which shows the probability of occurrence of a particular value in a set of variables. Specifically, when plotted on probability paper

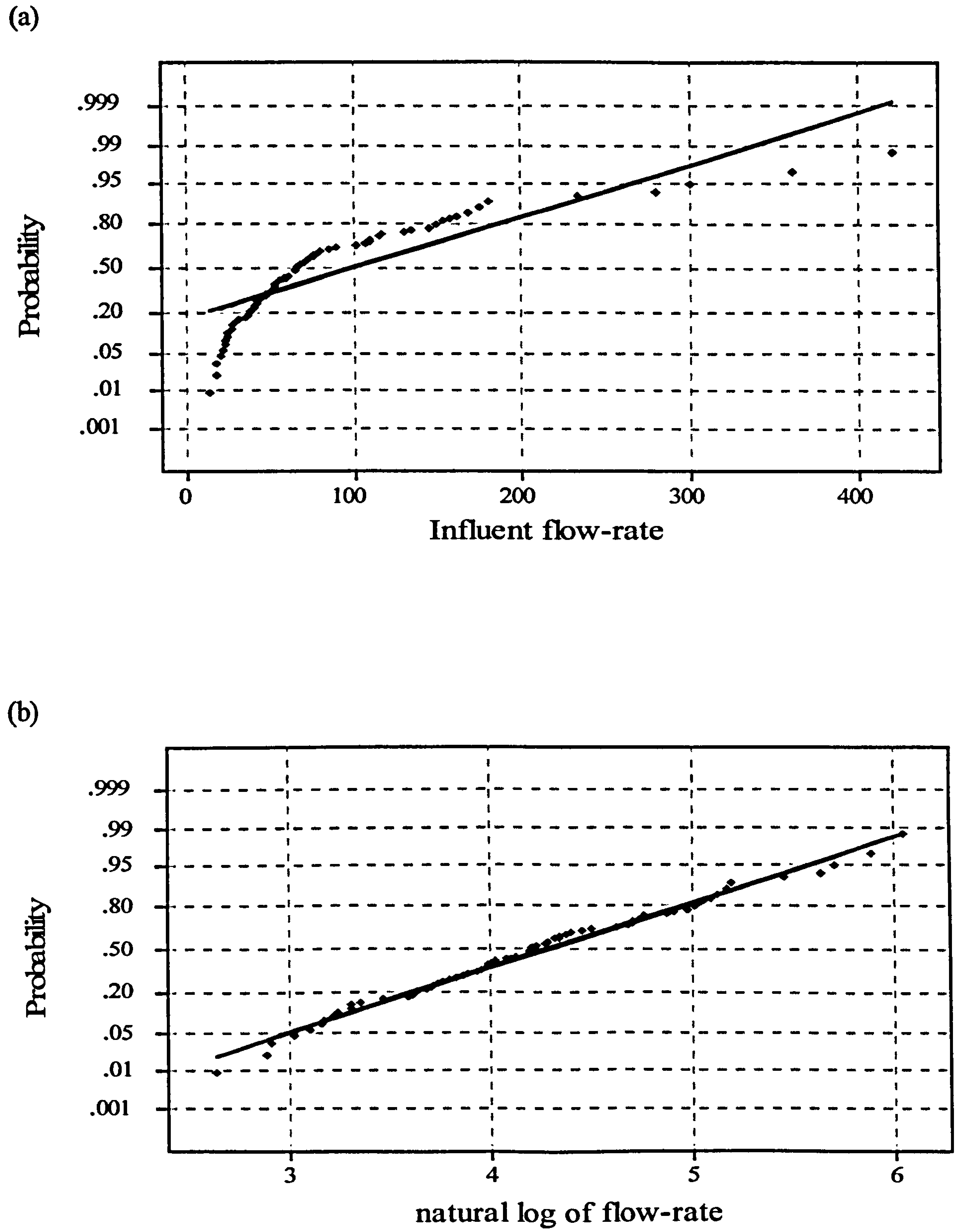

Figure A1 **Normal scores plots for influent flow-rate.** The raw data produces a non-linear plot (a), which indicates that the data are not normally distributed. Therefore the data are transformed in (b), by calculating the natural logarithm ($\log_e$) of the flow-rate. In this way a normal distribution is generated, and the data are amenable to parametric statistical analysis.

the cumulative probability curve is known as a normal scores plot. A normally distributed set of data will plot as a straight line in a normal scores plot, and this is therefore a good visual means of assessing whether a set of variables are normally distributed.

In this work where data are not normally distributed the natural logarithms ($\log_e$) or the square roots of the variables have been taken to yield a normal distribution (i.e. a straight line on the normal scores plot). For instance, Figure A1 illustrates the normal scores plots for influent flow-rate, using the raw data (Figure A1(a)) and the transformed data (Figure A1(b)). Clearly the transformed data (natural logarithm) approximate a normal distribution far better than the original data.

It is clearly not possible to perform tests for significant differences using variables that have been transformed in different ways (or not at all). Therefore a non-parametric test has been adopted for quantifying significant differences between variables (particularly influent and effluent concentrations of metals). The Mann-Whitney U test has been used for this purpose, as it is one of the most powerful non-parametric techniques available (Hammond and McCullagh, 1980). In this technique all variables are put in rank order, although the identity of two sets of variables is retained. The statistic is then calculated by inspecting each value of variable x and noting how many values of variable y precede it (Hammond and McCullagh, 1980). The statistic is most conveniently manually calculated as follows (Hammond and McCullagh, 1980):

$$U = n_1 n_2 + \tfrac{1}{2} n_1 (n_1 + 1) - R_1 \qquad \text{(A.4)}$$

where, U = Mann-Whitney coefficient

n_1 and n_2 = number of values in variable sets 1 and 2

R_1 = sum of the ranks given to values in n_1

Autocorrelation has been used as a method of time series analysis, with the primary aim of ascertaining whether there are any seasonal trends in the data. Autocorrelation coefficients measure the correlation between observations from a single variable set at different distances apart (Chatfield, 1989). The distance apart is the lag period, k. For example, for k =3, the autocorrelation for variable x, with n number of observations would be:

$$(x_1, x_4), (x_2, x_5), (x_3, x_6), \ldots\ldots\ldots\ldots (x_{n-3}, x_n)$$

Again, because the technique is parametric, the transformed data are used for these analyses.

Although the water quality data for the wetland at Quaking Houses, and the pilot-scale reactors at Kimblesworth, have been recorded in an Excel spreadsheet, the majority of the statistical analysis in this work has been calculated using Minitab for Windows. The latter software is more versatile in terms of the number of statistical tools available. In addition, McCullough and Wilson (1999) have recently shown that some of the statistical tools in Excel are in fact unreliable. Unless explicitly stated all of the statistical analysis in the following work has been calculated using the well-known Minitab software.