COUPLED HYDRAULIC AND GEOCHEMICAL PERFORMANCE ASSESSMENT OF PASSIVE MINE WATER TREATMENT SYSTEMS IN THE UK

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ABSTRACT

Current design practice for aerobic wetlands treating net-alkaline mine water in UK applications of passive treatment is based on zero-order kinetics for pollutant removal; the commonly used area-adjusted removal formula. Lagoons are designed to allow 48 hours of estimated retention time. However, there is significant variation in performance between systems. Neither of these approaches takes account of the hydraulic factors that may influence treatment performance. Therefore, this study aimed to improve understanding of both hydraulic and geochemical factors that govern contaminant behaviour, such that future design of treatment systems is able to optimise treatment efficiency and make performance more predictable, and improve performance over the long-term. Assessment of the hydraulic behaviour (flow pattern) of the treatment systems was accomplished by means of tracer tests. The tracer tests and simultaneous sampling of mine water were undertaken at eight UK Coal Authority mine water treatment systems (lagoons and wetlands) within Northern England (main study areas) and part of southern Scotland. Analyses of mine water samples were also undertaken in the laboratory alongside the field tests for assessment of geochemical processes controlling iron removal in the lagoons and wetlands studied.

Analyses of the tracer test results were performed using a residence time distribution (RTD) analysis to account for the different shapes of tracer breakthrough curves observed. There appear to be multiple influences that possibly affect the RTDs in lagoons and wetlands e.g. vegetation and seasonal variation (growing or non-growing season), system age, flow and geometry (length-to-width ratio and depth). The RTD analysis shows that lagoons generally have a more dispersed flow pattern, associated with a more pronounced short-circuiting effects and a long tail compared to wetlands. A modelling approach using a tanks-in-series (TIS) model was adopted to precisely analyse and characterise the RTDs, in an effort to account for the different flow patterns across the treatment systems. Generally, lagoon RTDs are characterised by a greater flow dispersion compared to wetlands (i.e. higher dispersion number, D and lower number of TIS, n). Consequently, the hydraulic efficiency, $e\lambda$ for lagoons is much lower than wetlands (mean of 0.20 for lagoons compared to 0.66 for wetlands). This is attributed primarily to a much lower volumetric efficiency, e_v in lagoons, meaning that a greater proportion of the total volume of the lagoon system is not being involved in the flow of water through them, with implications for design to optimise performance. In contrast, in wetlands a greater volumetric efficiency is evident, and there is therefore a longer relative mean residence time for retention and attenuation of iron.

On the evidence of field data, in lagoon systems the iron removal processes are primarily controlled by ferrous iron oxidation, whilst in wetlands the removal is controlled by iron settlement. The time- and concentration-dependence of iron removal (oxidation and / or settlement rate) has also been investigated in the laboratory alongside the field data. The rates are faster in lagoons compared to wetlands due to higher concentration of iron available for the processes. General trends showed that efficient treatment performance for iron removal corresponds with greater system hydraulic efficiency in wetlands compared to lagoon systems. The greater hydraulic efficiency in wetlands was mainly attributed to a greater volumetric efficiency in the wetland systems. In contrast, shorter relative mean residence time was found in lagoons, thus a lower retention time for iron attenuation and lower removal efficiency as a consequence.

For lagoon systems, performance can be optimised by ensuring greater volumetric efficiency (hence residence time), which can be achieved with a large length-to-width ratio system (up to a ratio of 4.7), but also a greater depth (up to 3.0 m), though only if systems are regularly maintained (dredged). For wetlands, the use of the area-adjusted removal rate formula appears to work well for the design of aerobic wetlands, despite the observed concentration-dependence of iron removal processes. However, use of first-order removal formula (TIS basis) would be a more appropriate approach to the design of mine water treatment systems since it takes account of the flow pattern effect on pollutant removal processes, in addition to the first-order kinetics (concentration-dependence) for iron removal. Regular sludge removal (yearly) is recommended in lagoons to provide longer residence time because lagoon depth and volume tends to rapidly decrease over time due to build up of ochre and debris (7-49% depth reduction per year). Thinning of reeds is recommended whenever apparent channelisation would otherwise dominate the flow pattern, and therefore limit the capacity for adsorption and settlement of precipitated iron hydroxide.

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A	Area
AMD	Acid mine drainage
α	Shape parameter
β	Scaling parameter
CA	Coal authority
C_b	Benchmark concentration
C_i	Influent concentration
C_o	Effluent concentration
C_p	Expected peak tracer concentration
cm	Centimetre
CSTR	Completely-stirred tank reactor
D	Dispersion number
$\mathcal{D}$	Dispersion coefficient
d	Day
DO	Dissolved oxygen
$E(\mathrm{t})$	RTD distribution function
$E(\theta)$	Normalised RTD
EC	Electrical conductivity
Eh	Redox potential
EQS	Environmental quality standards
e_v	Volumetric efficiency
e_{RTD}	RTD efficiency
e_λ	Hydraulic efficiency
$g(t)$	Gamma distribution function
g	Gram
HDPE	High density polyethylene
h	Water depth
IMPS	Inorganic media passive system
ICP-OES	Inductively coupled plasma - optical emission spectrometer
k_o	Zero-order removal constant
k_1	First-order removal constant
k_{TIS}	TIS first-order removal rate

k_v	Volumetric removal rate constant
kg	Kilogram
L	Length
LSQ	Least squares error
L	Litre
LOD	Limit of detection
L/W	Length-to-width ratio
M	Mass of tracer
M_0	Zeroth moment
M_1	First moment
M_2	Second moment
m	Metre
mg	Miligram
min	Minute
mS	Millisiemen
mL	Millilitre
µm	Micrometre
µg	Microgram
M	Mol
NaBr	Sodium bromide
Na-fluorescein	Sodium fluorescein
NaCl	Sodium chloride
n	Number of tanks-in-series
nm	Nanometre
NTU	Nephelometric turbidity unit
PF	Plug-flow
PFD	Plug-flow with dispersion
Pe	Peclet number
PRB	Permeable reactive barrier
Q_{avg}	Average flow rate
Q_i	Inlet flow rate
Q_o	Outlet flow rate
Q_d	Design flow

RAPS	Reducing and alkalinity producing system
RMS	Root mean squares error
RTD	Residence time distribution
SFBS	Subsurface flow bacterial sulphate reduction system
σ_θ^2	Normalised (dimensionless) variance
σ^2	Variance
s	Second
τ_θ	Normalised time
τ_n	Tracer nominal residence time
τ_{an}	Actual nominal residence time
τ_p	Tracer peak time
τ_m	Tracer mean residence time
T_ρ	Tracer density
t_p	Expected time to peak
t	Time
TIS	Tanks-in-series
τ_i	Mean residence time in one tank
t_D	Delay time
u	Water velocity
V_i	Volume in each tank
V_{eff}	Effective volume
v_p	Expected peak tracer velocity
V	Nominal volume
W	Width

CHAPTER 1

INTRODUCTION

1.0 INTRODUCTION

1.1 INTRODUCTION TO MINE WATER ISSUES

1.1.1 Mine water –related issues in the UK

Drainage from abandoned coal and non-coal mines are two mining related issues in the UK. Coal mining can result in drainage that is contaminated with high concentrations of dissolved iron, manganese, aluminium and sulphate (Hedin et al., 1994, Younger et al., 2002). Non-coal (principally metal) mining on the other hand can release drainage containing ecotoxic contaminants into surface and groundwaters such as arsenic, cadmium, copper, iron, nickel, manganese, lead and zinc (Wolkersdorfer, 2008; Mayes et al., 2009; Mayes et al., 2010). However, most of the coal and ore-fields are now abandoned. Widespread mine closures in the UK between late 1980s and early 1990s led to extensive surface water pollution (Younger, 1998). Iron is commonly reported the primary contaminant in relation to abandoned coal mines (e.g. Jarvis and Younger, 1999; Younger, 2000a; Younger et al., 2002; Johnston et al., 2007; Kruse et al., 2009) while zinc is the most common contaminant reported from abandoned metal mines (e.g. Gozzard, 2008; Mayes et al., 2009; Mayes et al., 2010).

The UK has a long and distinguished history of both coal and metal mining but only since 1994, when the UK Government's Coal Authority was established, has there been a strategic approach for managing the pollution impacts arising from those activities, at least for coal mines (Jarvis and Rees, 2005; CL:AIRE, 2006; Johnston et al., 2007). Thus the majority of mine water remediation approaches in the UK are related to discharges from the abandoned coal mines (Jarvis and Rees, 2005). Issues such as the absence of legal liabilities i.e. national system or government authority have hindered parallel development of a strategic approach for remediation of pollution from the abandoned non-coal mines (Johnston et al., 2007; Mayes et al., 2009). However, the more recent research attention has emphasis on initiative to such remediation approach for abandoned non-coal mine sites on a national scale (e.g. Jarvis et al., 2007; Jarvis et al., 2008; Mayes et al., 2009; Mayes et al., 2010) aiming at systematic identification and prioritisation of polluting mine sites for remediation planning.

Certainly, the pollution from abandoned mines in the UK is a barrier to achieving good chemical and ecological status in the water bodies as required by the European Union-Water Framework Directive (2000/60/EC) (Johnston et al., 2007). This directive is the operational tool in setting objectives for water protection and management with regard to existing and future discharges into aquatic environment. In line with the objectives of Water Framework Directive (2000/60/EC), directive on priority substances (Directive 2008/105/EC) has been set out which provides environmental quality standards (EQS) for priority substances and certain other pollutants with the aim to achieve long-term improvements in the chemical and ecological quality of both surface and groundwaters.

Problems associated with mine water issues generally include rising mine waters and surface water pollution arising from discharges of acidic and/or metalliferous mine waters from abandoned mine and spoil heaps (Jarvis and Rees, 2005). Flooded coal mine are often associated with adits and shafts that provide ready conduits for mine water discharge into the rivers. Since cessation of pumping, groundwater is rebounding and potentially threatens the surface waters. Spoil heaps continue to leach metals and sulphate into ground and surface waters, which poses potential health and safety risks (Younger et al., 2002; Johnston et al., 2007). Furthermore, mine water pollution is currently one of the most severe and most widespread forms of aquatic pollution in the UK (Younger, 2001). Drainage containing metals (i.e. iron, manganese, aluminium and sulphates) can acidify the local watercourses and so either kills or limits the growth of the river ecology (CL:AIRE, 2006). Issues in relation to non-coal mining are not the focus of this study, though it may have pertinence to metal mines in future years. Following sections provide some insights to the fundamentals of related issues with regard to abandoned coal mining generally, and specifically toward the coverage of this thesis work.

1.1.2 The role of the UK Coal Authority

Before 1994, there was no strategic approach to dealing with mining pollution in the UK. The Coal Authority was established in that year by the central Government. This government-funded body is responsible for addressing the coal mine related issues previously vested in British Coal Corporation. The UK Coal Authority has initiated the implementation of mine water treatment schemes to remediate potential areas impacted with acidic and/or metalliferous mine drainage. Currently, the Coal Authority operates more than 40 full scale treatment schemes for abandoned coal mines over the UK (Johnston et al., 2007; Coal Authority). These treatment schemes have greatly improved the quality of over 100 km of rivers and have prevented a similar length from becoming contaminated (Johnston et al., 2007). These are in line with the requirements of the Water Framework Directive, pressing on the initiative for remediation of existing mine discharges and to prevent new discharges from coal mine workings. Although initially there was no statutory obligation on the Coal Authority with regard to such mine pollution works, due to the scale of the mine closure the Authority was granted statutory powers in 2003. This enables the Authority to take appropriate actions upon preventing and mitigating the effect of coal mines discharges. Following this, the Coal Authority and both the Environment Agency (for England and Wales) and the Scottish Environment Protection Agency have developed a priority list of mine water discharges emphasising their environmental impacts on water quality and prioritisation for treatment planning and also aesthetics to local communities (Jarvis and Rees, 2005; Johnston et al., 2007).

1.1.3 Mine water remediation: active and passive treatment

Because mine water pollution is a significant environmental issue, polluted mine water must be treated prior to discharging into receiving stream. Particular solutions which operate with minimal maintenance and use only naturally available energy source have often been favoured for remediation of mine discharges (Younger, 2000a). The cost effective treatment is associated with manipulation of the local environment conditions in the treatment system so that particular contaminant removal processes are optimised (PIRAMID Consortium, 2003). There is nevertheless still a requirement for active, chemical treatment of some discharges wherever the remediation required is beyond the capabilities of passive treatment. The active treatment is particularly suited when land availability is restricted, or if contaminant load (i.e. concentration multiplied by flow) is very high. One of the advantages of active over passive treatment is the precise process control that is possible e.g. the dose of reagents required can be adjusted in response to influent loading or the receiving watercourse condition (Younger et al., 2002). The UK is currently well advanced in the development of passive treatment systems for mine waters, with more full scale systems in place than in any other European country (CL:AIRE, 2006).

1.2 OVERVIEW OF PASSIVE TREATMENT TECHNOLOGIES IN THE UK

The concept of passive treatment has been applied in the UK since the early 1990s to cope with the problems associated with mine water pollution. Adoption of so-called passive treatment system for amelioration of mine-impacted waters has been recognised for the long term remediation of such discharges wherever land availability is not limiting (Younger et al., 2002). Since 1994, there have been advances in passive treatment systems for the long term remediation of polluted mine drainage, spoil heap leachates and waters emerging from flooded underground mine workings (CL:AIRE, 2006). In general, the treatment technologies introduced for remediation and amelioration of mine-impacted waters include three main types of system (Younger et al., 2002):

- Inorganic media passive systems (IMPS)
- Wetland-type passive systems
- Subsurface flow bacterial sulphate reduction systems (SFBS)

Note that this categorisation of passive treatment technology is only to facilitate the understanding of widening range of such treatment technologies; there may be inter-related use of one type in conjunction to another from different category above e.g. IMPS may be incorporated with some wetland-type passive systems (Younger et al., 2002).

The passive mine water treatment adopted is primarily dependent on the type of mine water (whether the mine water is net-alkaline or net-acidic) or specific hydraulic circumstances. These are detailed in section 2.2 of Chapter 2. In the UK, the majority of these treatment systems remediate net-alkaline, ferruginous mine waters from abandoned coal mine sites (Jarvis and Rees, 2005; Johnston et al., 2007) and are the main focus of this study. Six types of passive systems are generally in use for mine water treatment, with examples from the UK including (Younger, 2000a):

- Aerobic, surface flow wetlands, which are often termed reed beds (applied to treatment of net-alkaline mine waters) e.g. Kruse et al. (2007); Kruse et al. (2009)
- Anaerobic, compost wetlands with significant surface flow (treatment of net-acidic mine waters) e.g. Jarvis and Younger (1999)

- Mixed compost / limestone systems, with predominantly subsurface flow (referred to as Reducing and Alkalinity Producing Systems (RAPS) for remediation of acidic mine waters) e.g. Younger et al. (2004); Wolkersdorfer et al. (2005)
- Permeable Reactive Barriers (PRBs) (to treat acidic, metalliferous ground waters) e.g. Amos and Younger (2003)
- Closed-system limestone dissolution systems (for zinc removal from alkaline waters) e.g. Nuttall and Younger (2000)
- Roughing filters (for aerobic treatment of net-alkaline ferruginous mine waters) where land availability is limited e.g. Jarvis and Younger (2001)

In practice, depending upon the types of mine water (i.e. net-acidic or net-alkaline) the treatment option may require deployment of more than one of the systems in series (e.g. aerobic wetland(s) following settlement lagoon(s) in most UK applications for net-alkaline, iron-rich mine water, such as those investigated in this study). Although passive treatment systems have operated with a high rate of success, the fact remains that the design of such units is empirically-based rather than process based (CL:AIRE, 2006). There has been variability in treatment performance in terms of contaminant removal (e.g. iron) in these passive treatment systems which require a clear understanding of this removal processes. Therefore, a more precise understanding of the process mechanisms in passive systems will give greater confidence in treatment performance and allow for optimisation of system design. The link between hydraulics and geochemical factors may be important for better understanding the processes by which contaminants are treated. This is what this study intends to investigate i.e. whether these hydraulic and geochemical factors may govern the overall treatment system performance for such systems.

1.3 OVERVIEW OF THE IMPORTANCE OF HYDRAULIC RESIDENCE TIME IN PASSIVE TREATMENT SYSTEMS

Hydraulic performance in passive treatment systems is often associated with the hydraulic residence time within the system (e.g. Martinez and Wise, 2003b; Lin et al., 2003; Kjellin et al., 2007). The time a fraction of water spends within a system may reflect the patterns of water movement across the system and the extent of treatment of polluted waters (Thackston et al., 1987). The relative importance of residence time as a measure of hydraulic performance of passive treatment systems, in particular within wetland-type treatment systems, has been discussed in many studies (e.g. Thackston et al., 1987; Werner and Kadlec, 1996; Martinez and Wise, 2003b; Persson et al., 1999; Goulet et al., 2001). However, within the Coal Authority's passive treatment sites, investigation of the actual residence time to reflect the hydraulic performance of the treatment systems has not been widely explored.

Such an investigation is particularly of interest to better understand the impacts the residence time (hence the flow pattern) has on the hydraulic performance of the system, which potentially have an effect on pollutant removal. This is compounded by first-order removal kinetics of some contaminants e.g. iron; removal is not only dependent on the chemical factors i.e. concentration, pH, dissolved oxygen but also the time it takes to attenuate the pollutant (e.g. Jarvis and Younger, 2001; Goulet et al., 2001). Understanding the actual flow patterns rather than assuming plug-flow, which is rarely the case in actual systems is a key objective of this investigation. Determining sufficient residence time and understanding flow characteristics of systems is vitally important in the design of passive treatment system for they dictate the sizing for optimal use of the system (Jarvis and Younger, 1999).

1.3.1 Overview of previous studies on hydraulic residence time in passive treatment systems

Detailed investigations of system residence time have not been widely explored in the passive treatment of mine water within the UK. Internationally, a summary hydraulic performance of various free water surface (FWS) and horizontal subsurface flow (HSSF) wetlands in the United States, Australia, Spain and France has been presented in Kadlec and Wallace (2009). The tracer test results of these treatment systems indicated that the actual residence times are often less than the nominal residence times. Irrespective of mine water or other wastewater treatment system, review of several passive treatment systems with respect to system residence time are summarised in Table 1.1.

Table 1.1 Hydraulic residence times in several passive treatment systems

Treatment system	**Nominal residence time**	**Actual residence time**	**Comments**	**Reference**
▪ RAPS ▪ Wetland (mine water)	▪ 2.7-3.6 days ▪ 7.9 days	▪ 4-8 days ▪ 2-3 days	▪ RAPS II with higher flow rates (90-110 L/min) indicated a longer residence time compared to RAPS I with lower flow rates (30-50 L/min) ▪ Interpretation of the mean residence time was also affected by the density of the tracer used i.e sodium chloride	Wolkersdorfer et al. (2005)
▪ Full-scale RAPS ▪ Pilot-scale RAPS (mine water)	▪ Not reported ▪ Not reported ▪	▪ 57 hours ▪ 7.5 hours	▪ Breakthrough curves modelled to distinguish the dispersive characteristics between the systems ▪ Despite the faster time to peak at the pilot-scale system, the importance of matrix diffusion in that system was not diminished	Goebes and Younger (2004)
▪ Pilot-scale wetland ▪ Full-scale (wastewater and agricultural runoff)	▪ 75 hours ▪ 69 hours	▪ 53-55 hours ▪ 60 hours	▪ Tracer test conducted to observe the performance of different types of tracers	Lin et al. (2003)
▪ Constructed wetland, cell-by-cell ▪ System scale (domestic wastewater)	▪ 5-33 hours ▪ 2.57-60.5 hours	▪ 13.09-21.65 hours ▪ 18.1-54.6 hours	▪ The short-circuiting experienced in the study was attributed to the non-uniform vegetation distribution, suboptimal cell shapes and variable microtopography of the wetland cells	Martinez and Wise (2003b)
▪ Constructed wetland (wastewater)	▪ 2.91-3.62 days	▪ 2.7-4.17 days	▪ Simulation of solute transport in the wetland systems indicated 8-47% hydraulic residence time difference from the nominal retention time	Keefe et al. (2004)
▪ Higher-loaded wetland ▪ Lower-loaded wetland (dairy wastewater)	▪ 54.5 hours	▪ 27 hours ▪ 55 hours	▪ Impact of organic matter accumulation on wastewater residence time was investigated ▪ There was no direct relationship found	Tanner et al. (1998)
▪ Permeable reactive barrier (PRB) (colliery spoil leachate)	▪ 2-60 days	▪ 4-24 hours	▪ Substrate characterisation to achieve maximum addition of alkalinity and removal of acidity and metals for treatment of colliery spoil leachate	Amos and Younger (2003)

As shown in the table, the actual residence time is often less than the nominal residence time. Preferential flow paths (i.e. short-circuiting with dead zones), internal obstructions such as plants and litter, and incomplete mixing within a system are amongst the common factors to result in low contact time on a limited area (Kadlec and Knight, 1996). This in turn, reflects the hydraulic efficiency of the system. It is therefore, the intention of this study to investigate whether such factors may have influence on hydraulic performance of mine water treatment systems studied. Although review of various passive treatment systems is presented here (Table 1.1), only settlement lagoons and wetlands are investigated in this study.

1.4 OVERVIEW OF TREATMENT PERFORMANCE IN PASSIVE TREATMENT SYSTEMS IN THE UK

The primary objective for effective remediation in passive mine water treatment are pH correction and/or metals removal (PIRAMID Consortium, 2003). Certainly, the primary pollutant of concern in UK coal mine water discharges is iron. Aluminium, manganese and sulphates are additional pollutants in many cases (e.g. Younger et al., 2002; Jarvis and Younger, 2005). Additionally, iron is the most commonly studied pollutant with respect to mine water treatment (e.g. Henrot and Wieder, 1990; Tarutis et al., 1992; Wieder, 1994; Hedin, 1994). Treatment performance of a system is measured by assessing the extent to which the system removes the particular pollutant of concern; this is often measured as the pollutant or load removal efficiency. Treatment efficiency is simply the percentage of removal from the change in concentration of pollutant in the influent and effluent of treatment system. Load removal efficiency is the measure given as the percentage of pollutant removal by the change in pollutant loadings (i.e. concentration multiplied by flow rate) in the influent and effluent of treatment system (Tarutis et al., 1999; Younger et al., 2002).

The iron removal in aerobic mine water treatment systems such as those investigated in this study is principally due to oxidation of ferrous iron to ferric iron and the subsequent hydrolysis and precipitation of ferric iron to form ferric hydroxide (Younger et al., 2002). These are given in the following equations (Hedin et al., 1994) and are further detailed in section 2.9 of Chapter 2.

$$\text{Oxidation:} \quad Fe^{2+} + \tfrac{1}{4} O_2 + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2} H_2O \qquad [1.1]$$

Hydrolysis: $Fe^{3+} + 2H_2O \rightarrow FeOOH_{(suspended)} + 3H^+$ [1.2]

Settling: $FeOOH_{(suspended)} \rightarrow FeOOH_{(settled)}$ [1.3]

Studies on iron removal within UK's Coal Authority mine water treatment systems have been reported by many authors (e.g. Jarvis and Younger, 1999; Younger, 2000a; Jarvis and Younger, 2001; Younger et al., 2004; Younger and Moustafa, 2004; Kruse et al, 2007; Johnston et al., 2007). A summary of the treatment performance for iron in several mine water treatment systems in the UK is presented in Table 1.2. As seen in the table, irrespective of the treatment system types, iron removal efficiency varies greatly from as low as 24% to as high as 99%. The lowest iron removal was found in a settlement lagoon while the highest removal was found in an aerobic wetland. It is therefore interesting to recognise what factors contribute to such variations. Again, settlement lagoons and wetlands are the two types of passive treatment system being investigated in this study.

Younger et al., (2002) have presented a summary of constructed wetland systems performance in the United States, given in the metric of a commonly used treatment system performance measure, the area-adjusted removal rate. This treatment performance metric was derived from the zero-order kinetics for pollutant removal (Hedin et al., 1994). The removal rates (in unit $g/m^2/d$) varied greatly from one treatment site to another (e.g. iron removal ranged between 0.5 and 42.7 $g/m^2/d$. This variation in iron removal rates can be associated with different chemical characteristics of the different sites and may also be attributable to the hydraulic factors in the systems, and hence assumption of the zero-order kinetics may not be appropriate in such situations. This highly variable treatment performance may reflect the first-order kinetics (concentration-dependence) for iron removal that provides one of the bases for the recommended design formula by Tarutis et al. (1999). Hedin (2008) has also shown the concentration-dependence nature for iron removal (both iron oxidation and settlement) in a passive treatment scheme consisting of a series of ponds and aerobic wetland in Pennsylvania, United States. On the other hand, the influence of hydraulics on treatment performance cannot be ruled out (Kadlec, 2000; Goulet et al. 2001; Younger et al., 2002). Therefore, geochemical factors governing iron removal in net-alkaline mine water is again an interest of this study; specifically to identify whether there is a link between these geochemically determined processes and system hydraulic performance (i.e. hydraulic residence time). Such an assessment will improve the understanding of those processes with respect to current design practice and for optimisation of the system design.

Table 1.2 Treatment performance of the UK mine water treatment system

Type of treatment system	**Location**	**Average Influent Fe**	**Average Effluent Fe**	**Removal efficiency (%)**	**References**
Treatment of net-alkaline waters					
Aerobic wetland	Lambley, Northumberland	3.8	1.6	58	Kruse et al., 2007
	Whittle, Northumberland	20.8	1.7	92	Kruse et al., 2007
	St Helen Auckland, County Durham	3	0.3	90	Younger, 2000a
	Edmondsley, County Durham	27	0.1	99	Younger, 2000a
Settlement lagoon	Acomb, Nothumberland	34.1	5.05	85	Kruse et al., 2007
	Whittle, Northumberland	28.6	21.6	24	Kruse et al., 2007
Surface catalysed oxidation of ferrous iron (SCOOFI)	Kimbersworth, County Durham	1.43	0.41	85	Jarvis and Younger, 2001
Treatment of net-acidic waters					
Reducing and alkalinity producing system (RAPS)	Bowden Close, County Durham	40	<10	>75	Younger et al., 2004
		20	3	85	Younger, 2000b
Compost wetland	Quaking Houses, County Durham	4.55	2.5	45.4	Jarvis and Younger, 1999
		10	1	90	Younger, 2000a
Permeable reactive barrier	Shillbottle, Northumberland	100	25	75	Younger, 2000a
		>800	~10	98	Younger and Moustafa, 2004
		>300	~10	95	Jarvis et al., 2006

1.5 RESEARCH AIMS AND OBJECTIVES

Settlement lagoons and aerobic wetlands are regarded as 'proven technology' for passive treatment of net-alkaline, ferruginous mine waters within the UK application of passive treatment. However, one of the limitations of the current design practice for these passive mine water treatment systems is that hydraulic factors are not being accounted for in the design of such systems. This has significantly led to limited understanding of the hydraulic characteristics of the treatment systems which, together with the knowledge of the geochemical processes governing pollutant removal, are central in the assessment of the overall treatment system performance. With regard to the variation in current treatment systems performance, this study aims to investigate the coupled hydraulic and geochemical factors influencing performance of passive mine water treatment systems, specifically in settlement lagoons and wetlands. The specific objectives of the study are:

i) To assess the most appropriate tracer and modelling approach to use in the hydraulic performance assessment of mine water treatment systems
    - Assessment of the most appropriate tracer for use in mine water treatment systems, specifically to determine the hydraulic residence time
    - Assessment of the most appropriate modelling technique for characterising the tracer flow patterns across the mine water treatment systems

ii) To assess the hydraulic factors that govern residence time distribution of a treatment system
    - Assessment of the impact of flow pattern on water residence time distribution within settlement lagoons and wetlands
    - Assessment of the physical influences on variation of flow pattern and residence time distribution e.g. effects of system geometry (i.e. length to width ratio and depth), age of system, vegetation and flow rate

iii) To assess geochemically related factors on the removal of the main pollutant (iron)
    - Assessment of the chemical characteristics of mine waters and the rates of iron removal in the field

  - Assessment of the controlling factors for iron removal in mine water in field and laboratory conditions (i.e. rates of iron oxidation and settlement)

iv) To evaluate of the links between hydraulic and geochemical factors in assessing the overall treatment system performance

v) To evaluate the implications for design and maintenance of mine water treatment systems based on the hydraulic performance and treatment efficiency

Thus, it is the intention of this study to investigate these hydraulic and geochemical factors that affect the overall treatment system performance. Such an assessment has not been widely investigated within the UK application of mine water passive treatment. Therefore, this study will provide an insight into a greater understanding on both hydraulic and geochemical factors that govern contaminant behaviour right from the design of such treatment systems to optimise treatment efficiency, through to improved performance over the long-term. These objectives will be achieved by:

i. Assessment of system hydraulic performance (through a series of tracer tests to measure the actual residence time across the systems and to assess the flow pattern effects on hydraulic performance)

ii. Assessment of geochemical factors relating to treatment performance (through simultaneous sampling of mine water during each tracer test to analyse the mine water characteristics and performance in terms of iron removal, and laboratory analysis of controlling mechanisms for iron removal)

1.6 STUDY SITE

1.6.1 Site descriptions

The study was undertaken at eight UK Coal Authority mine water treatment systems within Northern England (main study areas) and part of southern Scotland, which consist of mine water treatment wetlands and settlement lagoons (Figure 1.1). The systems were designed to treat net-alkaline (i.e. alkalinity > acidity), ferruginous mine water with design flow capacity ranging between 10-88 L/s and influent iron concentration from 6 mg/L to 60 mg/L. Irrespective of lagoon or wetland, these include a range of relatively small to very large systems, of between 600-11400 m^2 treatment area (see Table 1.3). Most wetlands are basically designed based on a constant area-adjusted removal rate of 10 $g/m^2/d$ of iron removal (Hedin et al., 1994), an approach which is based on a zero-order removal model for pollutant attenuation. In typical applications of passive treatment within the UK coal mine water treatment systems, settlement lagoons serve as a pre-treatment unit preceded by an aeration cascade, aimed at removing about 50% iron by means of hydrolysis and settlement of ferric hydroxides, prior to final polishing in the wetland systems (or a series of wetlands) (Younger et al., 2002). The typical design approach for settlement lagoons is to allow 48 hours estimated retention time.

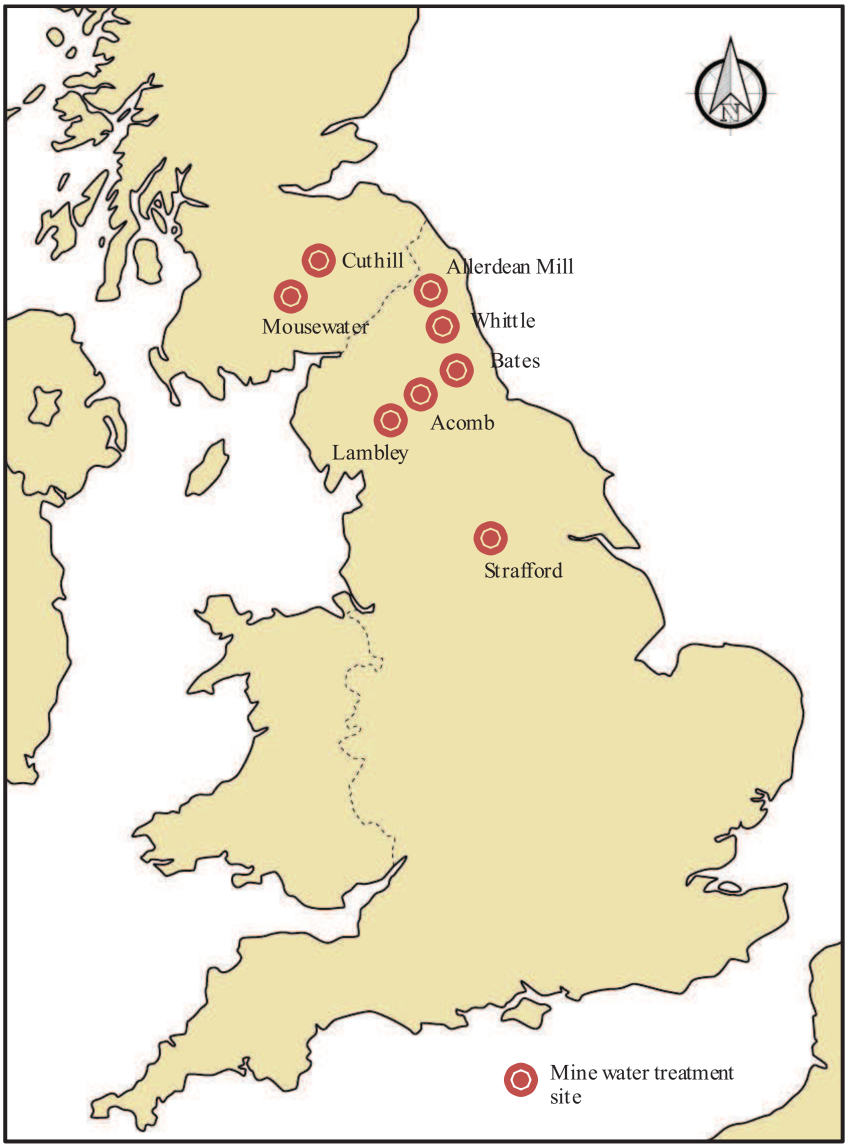


Figure 1.1 Locations of the coal mine water treatment systems investigated in this study

Table 1.3 Useful information of the investigated mine water treatment schemes operated by the UK Coal Authority

Site name	Location	Scheme type	Flow design capacity (L/s)	No. of settlement lagoon	Total treatment area (m^2)	No. of wetland (cell)	Total treatment area (m^2)	Completion date	Influent pH	Influent Fe (mg/L)
Lambley	Northumberland, England	Pumped/ Passive	88	-	-	4	4388	2006	6.65	6.58
Acomb	Northumberland, England	Pumped/ Active/Passive	15	2	750	2	600	2002	7.09	33.69
Whittle	County Durham, England	Pumped/ Passive	45	2	900	3	7124	2002	7.06	32.59
Allerdean Mill	Northumberland, England	Pumped/ Passive	10	3	1970	3	3171	2007	6.60	9.72
Bates	Northumberland England	Pumped/ Passive	76	4	11400	3	8000	2003	6.73	18.96
Strafford	South Yorkshire, England	Pumped/ Passive	20	1	850	1	1690	2007	6.88	6.60
Mousewater	Lanarkshire, Scotland	Gravity/ Passive	50	1	3036	2	8400	2004	5.81	14.58
Cuthill	West Lothian, Scotland	Pumped/ Passive	45	1	726	3	2744	2003	7.18	17.41

1.6.1.1 Lambley

The Lambley mine water treatment scheme comprises a pumping station located adjacent to the mine water pipeline followed by a wetland system (of four wetland cells in series). The mine water is pumped from a wet well at a mean rate of 88 L/s; flow in excess of the pump's capacity will overflow down the original pipe to the river. A pump switching on and off is used to maintain a near constant water level in the pumping shaft. The flow discharges into the River South Tyne approximately 150 m upstream of the mine water discharge. The wetland was designed using an area-adjusted iron removal of 10 g/m^2/d, with a design influent iron concentration of 6 mg/L for a total treatment area of approximately 4388 m^2. The layout of the treatment scheme is shown in Figure 1.2 below.

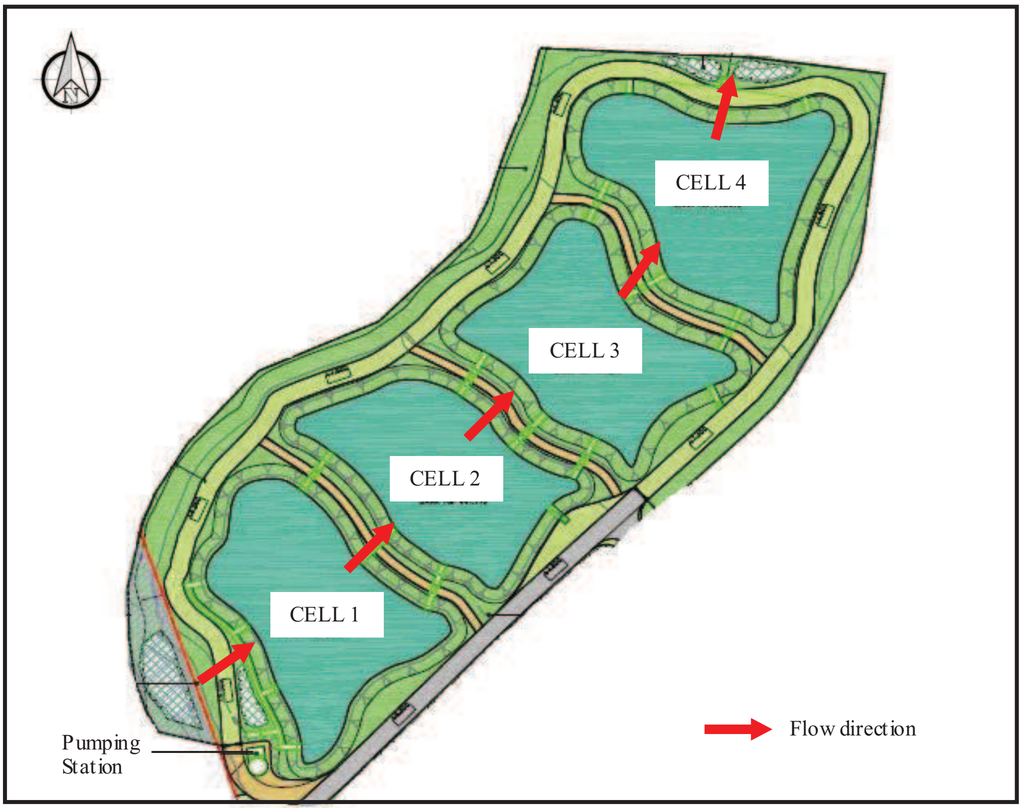


Figure 1.2 Layout of Lambley mine water treatment wetland (courtesy of UK Coal Authority)

1.6.1.2 Acomb

The Acomb mine water treatment schemes include two settlement lagoons that operate in parallel and two reedbeds in series (Figure 1.3). Mine water is pumped from the top of the drift into an aeration tower. The mine water is then passed into the lagoon systems which are identical in size and layout with a design depth of 3m and a total treatment area of 750 m^2. The mine water is dosed with hydrogen peroxide prior to discharge into the lagoons to aid rapid conversion of ferrous to ferric iron (due to poor lagoon performance during early operation). The lagoons are trapezoidal basins with a total volume of 2164 m^3 and have some peripheral planting around the units to improve the aesthetics of the scheme. The lagoon systems were originally designed based on the estimated 48 hours retention time for a design flow of 15 L/s. However, design areas were limited by the land availability hence the systems have approximately 40 hours retention time during early operation. The mine water then flows into two reedbeds in sequence with a total area of 1200 m^2 planted with *Typha latifolia* and *Phragmites australis*. The flow from the treatment systems discharges into the Red Burn, approximately 1000 m above its confluence with the River Tyne.

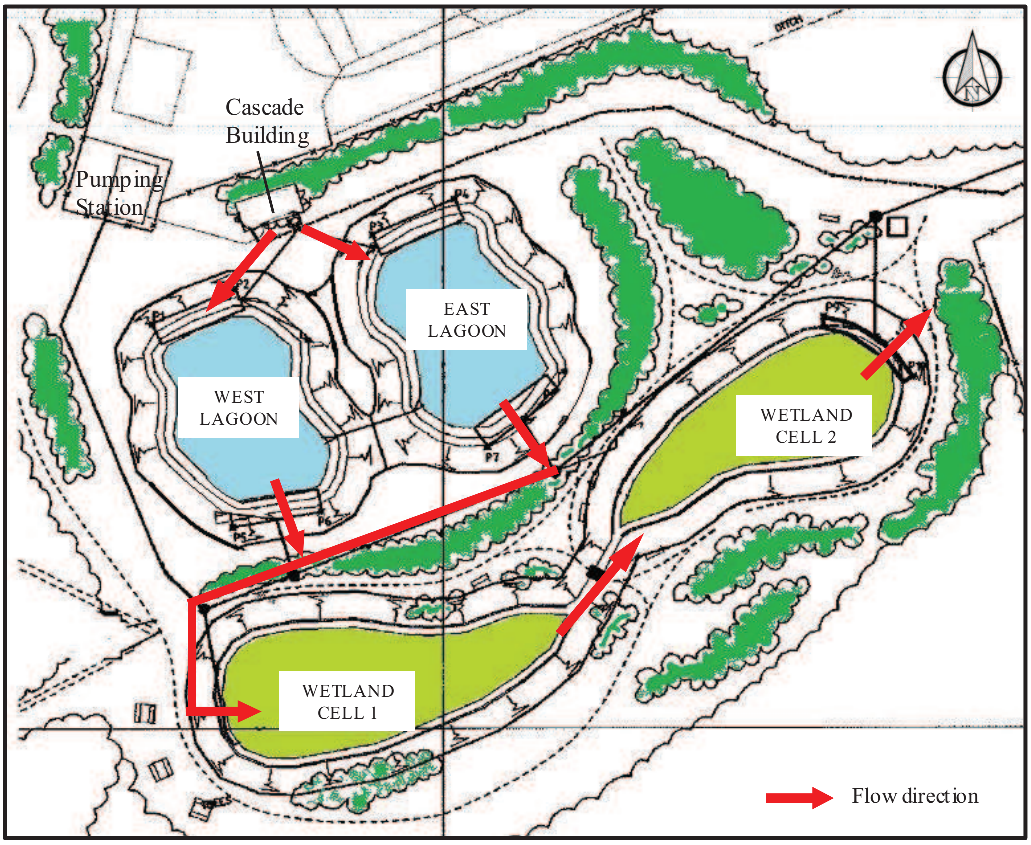


Figure 1.3 Layout of Acomb mine water treatment scheme (courtesy of UK Coal Authority)

1.6.1.3 Whittle

The scheme at Whittle comprises a mine water pumping pipeline, aeration cascade, two elongate settlement lagoons, three aerobic wetlands in series and sludge drying beds (Figure 1.4). The mine water is pumped via a drilled borehole 70 m into the Whittle Colliery drift and flows through an aeration cascade at the head of the treatment systems. The mine water then passes into two settlement lagoons (separated by a central bund) that operate in parallel. These lagoons have a design depth of 1.65 m and a total treatment area of 900 m^2. The lagoons were designed to remove 50 % iron for a design flow of 45 L/s and influent iron concentration of about 40 mg/L. Flow across the lagoons combined at the system outlet prior to enter the first of three wetlands. These wetlands operate in series, approximately identical in size, each of which has an area of 2400 m^2. They were designed using an area-adjusted iron removal of 10 $g/m^2/d$. Wetland 1 and 3 are planted with *Typha latifolia* while *Phragmites australis* planted in wetland 2. The final discharge flows into the Hazen Burn, a tributary of the River Coquet.

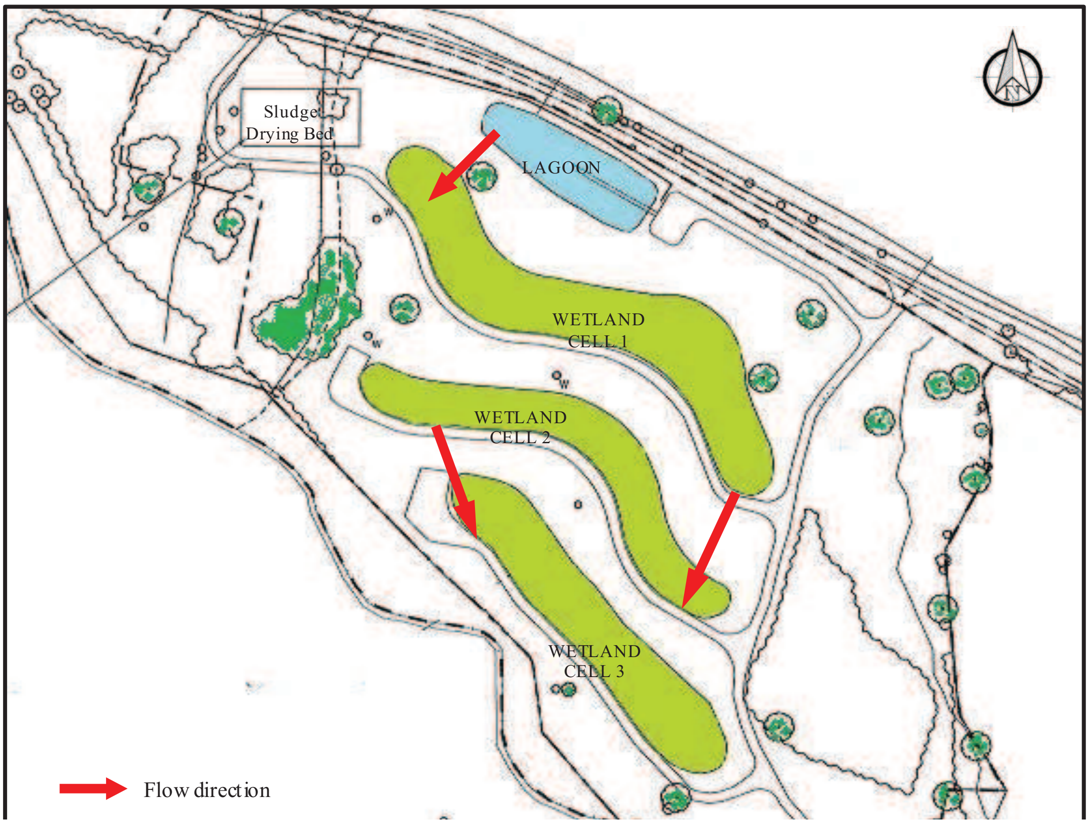


Figure 1.4 Layout of Whittle mine water treatment scheme (courtesy of UK Coal Authority)

1.6.1.4 Allerdean Mill

The scheme consists of mine water treatment lagoons (2 parallel settlement lagoons receive pumped mine water and a settlement pond that receives mine water via gravity flow) and 3 wetlands in series (Figure 1.5). The mine water is pumped from a pump chamber into a flow splitting structure to distribute the flow between the parallel lagoons. These lagoons, each has an area of 883 m^2 and has a depth of 1.6 m. The gravity pond has a treatment area of 426 m^2 and a depth of 2 m. The mine water from these lagoons and that from the gravity pond enter the first of three wetlands in sequence in three separate open flow channels. Each of these wetland cells has a treatment of 1066, 1111 and 994 m^2 prior to final polishing in an open water wetland. The final flow discharges into the Allerdean Mill Burn.

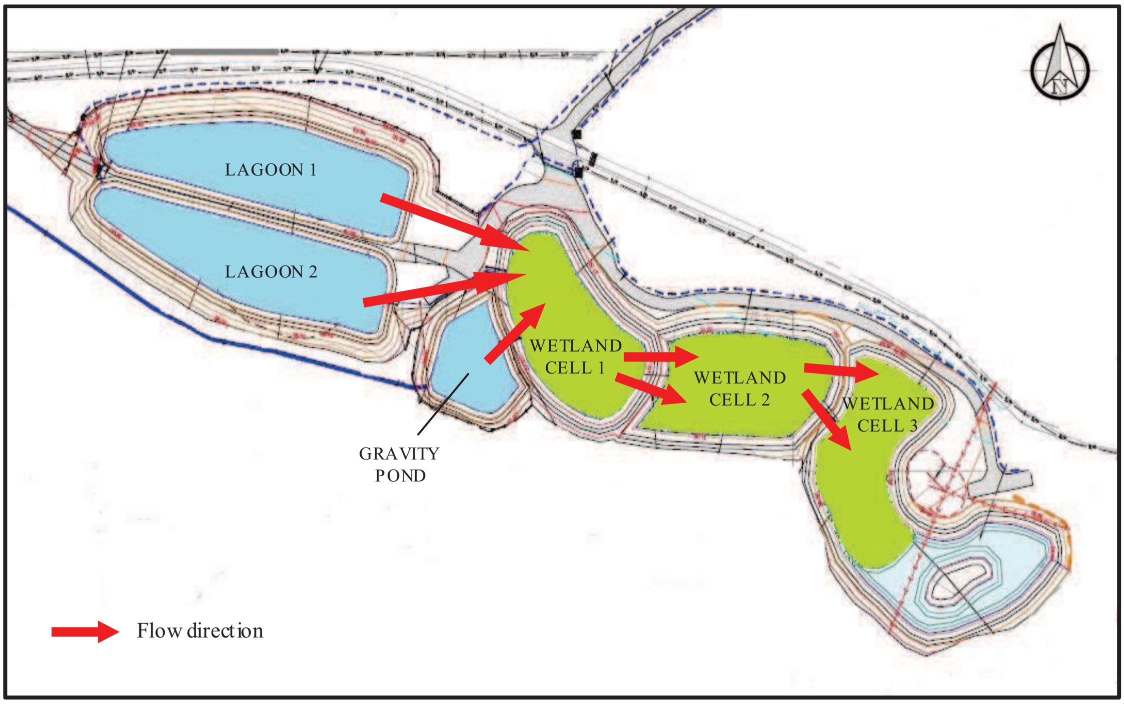


Figure 1.5 Layout of Allerdean Mill mine water treatment scheme (courtesy of UK Coal Authority)

1.6.1.5 Bates

The Bates treatment scheme comprises a series of four settlement lagoons and three wetlands in series. The mine water is pumped from a pumping shaft and splits into two separate channel into the lagoons (Figure 1.6). The scheme was designed on a flow of 100 L/s and influent iron concentration of 60 mg/L. The treatment lagoons have a total area of 11400 m^2 and each has a design depth of 3 m. Aeration cascades are provided between the lagoons (see Figure 1.5) to encourage further oxidation and settlement of ferrous iron within the lagoons. The flows from the lagoons combine prior to entering the wetlands. As the mine water is saline i.e. conductivity of 13,000 µS/cm, the series of wetlands become a living test area for various reeds such as *Typha latifolia, Phragmites australis, Plantago maritima, Triglochlin maritima, Spartina maritima, Juncus gerardii, Juncus maritimus, Scirpus maritimus* etc., to test the survival of those reeds in such a saline water. These wetlands are therefore operated with minimal mine water passing through the systems. The wetlands have a total treatment area of 6210 m^2. The flow from this treatment scheme discharges into the Wansbeck Estuary at Blyth.

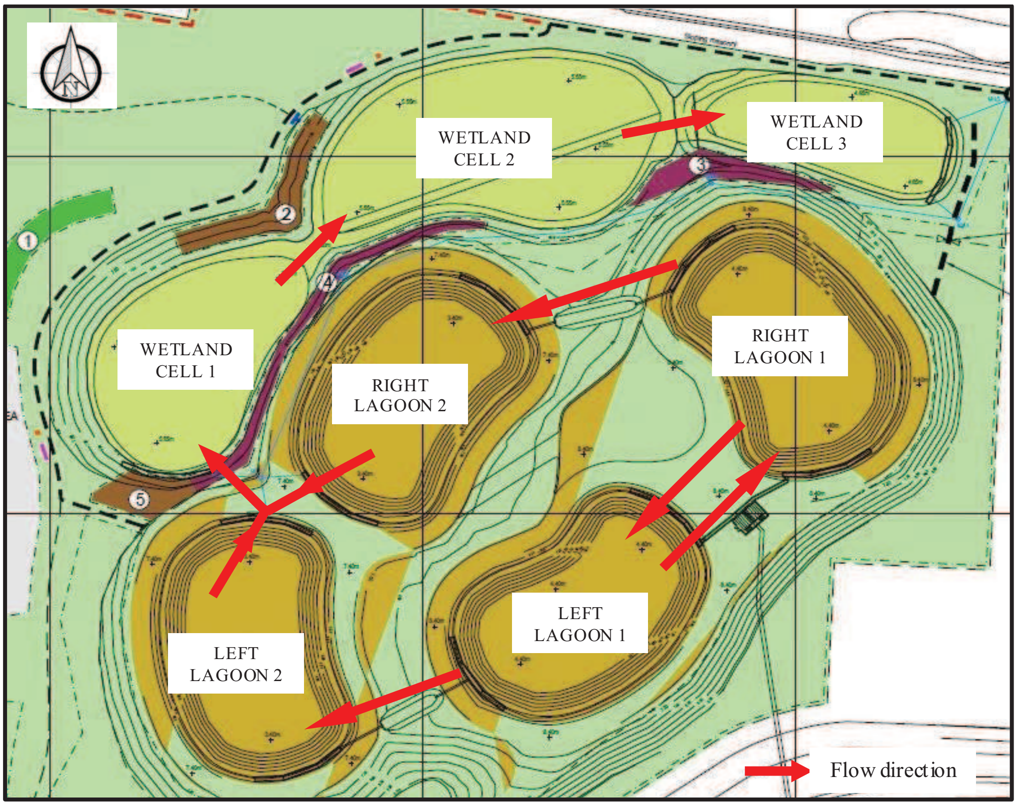


Figure 1.6 Layout of Bates mine water treatment scheme (courtesy of UK Coal Authority)

1.6.1.6 Strafford

The scheme at Strafford comprises an aeration cascade, a settlement lagoon and a wetland (Figure 1.7). The mine water is pumped from a shaft before discharging into an aeration cascade at the head of the treatment scheme. Mine water then flows through a settlement lagoon which was designed with a depth of 3 m and a treatment area of 850 m^2. The lagoon has two outlet channels that eventually combine before entering the wetland. the wetland has an area of 1690 m^2 and is planted mainly with *Phragmites australis* and some *Typha latifolia*. There are also planting blocks that are constructed as small islands in the wetland planted with *Viburnum opulus* and *Cornus sanguine*. Treated mine water then discharges into the Stainborough Dike.

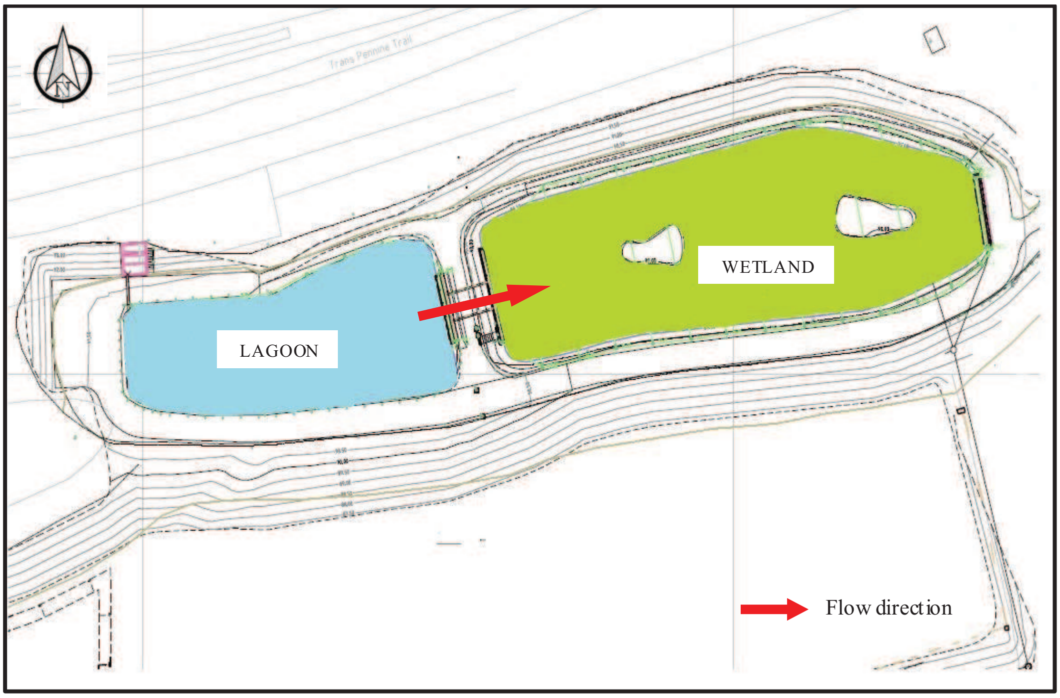


Figure 1.7 Layout of Strafford mine water treatment scheme (courtesy of UK Coal Authority)

1.6.1.7 Mousewater

The treatment scheme at Mousewater is entirely passive where the mine water flows via gravity around the treatment site. The scheme was designed to treat the ochreous mine water discharging from a mine adit across the site. The scheme comprises a settlement lagoon and two wetland cells in series (Figure 1.8) and was designed to treat 25 mg/L of influent iron. The mine water enters the system into a settlement lagoon with a unique layout and is divided by a precast concrete dividing wall into two halves. This enables either half to be drained down for maintenance while the other half continues to operate. The lagoon has a design depth of 2.8 m and a total treatment area of 3036 m^2. Mine water then flows through an open water channel into the first of two wetlands in series which have a total treatment area of 8400 m^2. The treated mine water then discharges into the Mouse Water.

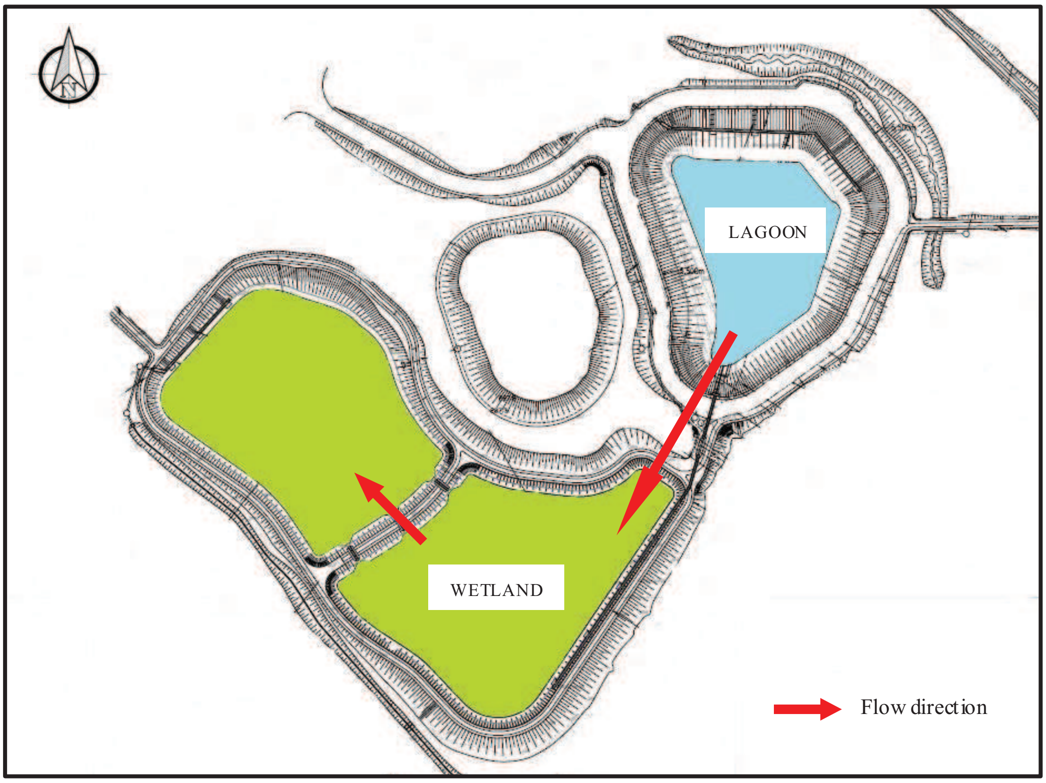


Figure 1.8 Layout of Mousewater mine water treatment scheme (courtesy of UK Coal Authority)

1.6.1.8 Cuthill

The Cuthill mine water treatment scheme consists of two settlement lagoons in parallel and three wetlands in series (Figure 1.9). The mine water is pumped from a mine adit to a chamber where the mine water is collected prior to flow into the systems. From the chamber, mine water is pumped 240 m via a rising main before discharging into a 65 m long aeration cascade in 150 mm steps. The mine water then passes through the settlement lagoons that operate in parallel which is divided by a precast concrete dividing wall to allow one to operate while the other is emptied for maintenance purposes. Each of the lagoons is 1.5 m deep and has a treatment area of 367 m^2 and 359 m^2 respectively. These lagoons allow at least 8 hour retention before the mine water enters the wetlands. The three wetlands operate in series, each of which has an area of 1098 m^2, 914 m^2 and 732 m^2. These wetlands serve for final polishing of the mine water before discharging into the Breich Water.

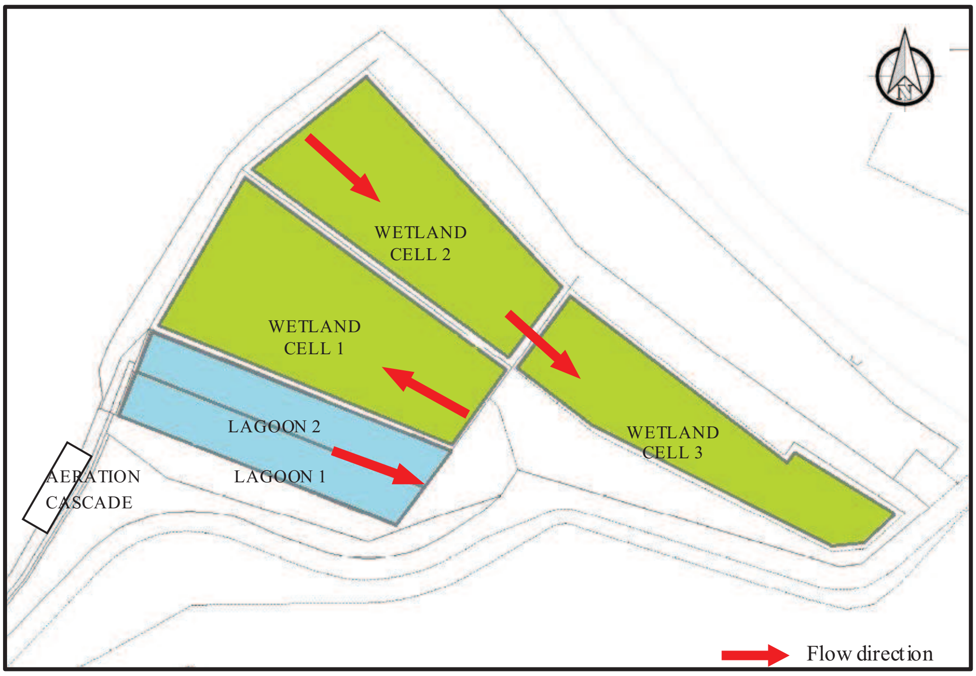


Figure 1.9 Layout of Cuthill mine water treatment scheme (courtesy of UK Coal Authority)

1.7 THESIS STRUCTURE

Following this chapter, the remaining chapters of the thesis are outlined below:

CHAPTER 2: LITERATURE REVIEW

Overview of the topics covered throughout the study; theoretical background and fundamentals of the hydraulic and geochemical factors governing the performance of passive mine water treatment systems.

CHAPTER 3: METHODOLOGY

Details of the methods undertaken during the field and laboratory work throughout the study; field work included mine water sampling and a series of tracer tests, and laboratory work included the analytical analysis of water quality and tracers and laboratory column experiments.

CHAPTER 4: RESULTS AND DISCUSSION I: HYDRAULIC PERFORMANCE OF MINE WATER TREATMENT SYSTEMS

Results and discussion on the hydraulic factors that govern the hydraulic performance of the mine water treatment systems investigated. These include the analysis and interpretation of tracer test results; evaluation of the different residence time distributions (RTDs) observed from the tracer tests, possible influences on the RTDs and evaluation of the modelling approach to precisely evaluate the RTDs.

CHAPTER 5: RESULTS AND DISCUSSION II: GEOCHEMICAL PERFORMANCE OF MINE WATER TREATMENT SYSTEMS, AND RELATIONSHIPS TO HYDRAULIC PERFORMANCE

Results and discussion on the geochemical factors related to treatment performance of mine water treatment systems investigated; mine water characteristics, iron removal rate and the controlling geochemical processes for iron removal. This is followed by discussion of the relationship between system hydraulic and geochemical factors affecting system performance. Implications for design and maintenance of such systems conclude the results and discussion of this thesis.

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

Summary of the major contributions and findings of this thesis and the summary of the work done in the fulfilment of the research aims and objectives. Recommendations for future research directions follow.

APPENDICES

Related information to support the thesis contents

CHAPTER 2

LITERATURE REVIEW

2.0 INTRODUCTION

This chapter provides an overview of the topics covered throughout the study. These include review of the origins of mine water pollution and the types of mine water treatment system, followed by the theoretical background and fundamentals of the hydraulic and geochemical factors governing the performance of passive mine water treatment systems.

2.1 ORIGINS OF MINE WATER POLLUTION

2.1.1 Mineral weathering

Minerals and coal are largely chemically stable under in situ geological conditions however upon interference from human activities (e.g. excavation), these solids become chemically unstable when exposed to the atmosphere (Younger et al., 2002; Wolkersdorfer, 2008). When in contact with water, the sulphide minerals associated with metal ores can produce potentially toxic solutes. Releases of metal ions, acidity and ochre from the mining activities are significant environmental hazards to freshwater resources. Acidity is caused by the weathering of pyrite ($FeS_2(s)$) while other sulphide minerals (e.g. sphalerite ($ZnS(s)$), galena ($PbS(s)$) and arsenopyrite ($FeAsS(s)$) weathering can release the metal ions into solutions containing dissolved oxygen (Younger et al., 2002). Ochre results when iron (which is usually the predominant pollutant cation in the water around a mine) precipitates under oxic conditions as iron oxyhroxide minerals. These can visibly be seen as yellow to red-brown deposits at the effluents at mine site (Wolkersdorfer, 2008).

Pyrite (FeS_2) is the most abundant sulphide mineral associated with coal deposits and some metallifrous ore bodies (Younger et al., 2002; Wolkersdorfer, 2008). Pyrite is exposed to the environment through excavation of mineral deposits below the natural groundwater level during mining activities (Younger et al., 2002). It is commonly accepted that disulphide weathering and particularly the oxidation and dissolution of pyrite and marcasite (which has the same composition as pyrite but with a different crystallographic structure) are the initial reactions in the formation of acidic and/or metalliferous mine drainage (Singer and Stumm, 1970; Banks et al., 1997; Wolkersdorfer, 2008). The generalised chemical reactions governing the oxidation of pyrite and subsequent acid generation were originally developed by Singer and Stumm (1970), as demonstrated in Eqn. 1.1 to Eqn. 1.4.

$$FeS_{2(s)} + 7/2\,O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4{}^{2-} + 2H^+ \qquad [2.1]$$

$$Fe^{2+} + 1/4\,O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O \qquad [2.2]$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \qquad [2.3]$$

$$FeS_{2(s)} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4{}^{2-} + 16H^+ \qquad [2.4]$$

Certainly, the overall reaction produces protons thus releases acid into the mine water leading to acidic nature of the mine drainage (Singer and Stumm, 1970). Pyrite weathering, besides releases proton acidity, also produce sulphate and releases soluble ferrous iron (Fe^{2+}) as shown in Eqn. 2.1. In the presence of sufficient oxygen or when exposed to the atmosphere, dissolved ferrous iron is oxidized to ferric iron (Fe^{3+}), consuming acidity (Eqn. 2.2). Reactions in Eqn. 2.1 and 2.2 are catalysed by bacterial activity. Most of the bacteria responsible for the development of acid mine drainage are chemotrophic bacteria, specifically the chemolithotrophs (e.g. *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*), which use inorganic electron-donating sources as their energy supply (Banks et al., 1997; Kelly and Wood, 2000). This energy is obtained from the oxidation of sulphide, primarily from pyrite and also from other sulphide minerals. Ferric iron further reacts to precipitate as iron oxyhydroxide (ochre), a process that also produces acidity (Eqn. 2.3). This reaction is abiotic and often does not occur until the water has left the mine (Wolkersdorfer, 2008).

Ochre is the most common precipitate associated with mine water and it can cause an ugly staining of the surface streams, which becomes the reason why they need to be 'treated' prior to entering watercourses (Banks et al., 1997; Wolkersdorfer, 2008). As in the passive treatment systems investigated in this study (i.e. settlement lagoons and wetlands), oxidation of ferrous to ferric iron, and precipitation of ferric iron as hydroxide are essentially the most important processes in the attenuation of iron-rich mine water before discharging to the receiving streams. The release of protons through reactions 2.1 -2.3 can cause the pH to rapidly decrease. As pH reaches about 4, ferric iron becomes the predominant oxidant (Singer and Stumm, 1970). Ferric iron reacts with pyrite to produce more acidity and ferrous iron (Eqn. 2.4). Ferrous iron produced in reaction 2.4 can then be further oxidised by the available dissolved oxygen, perpetuating the cycle as represented in Eqn. 2.1 – Eqn. 2.4. The cycle continues until the pyrite is exhausted which can take up to more than 100 years (Younger et al., 2002). There are always other sulphide minerals found alongside the pyrite, however weathering of these minerals may not necessarily produced acidity but will release soluble metal ions to solution (Banks et al., 1997; Younger et al., 2002; Wolkersdorfer, 2008). Some of the examples of sulphide mineral weathering other than pyrite and are commonly found in surface and underground mines are:

$$Sphalerite\text{: } ZnS_{(s)} + 2O_{2(aq)} \rightarrow Zn^{2+} + SO_4{}^{2-} \quad [2.5]$$

$$Galena\text{: } PbS_{(s)} + 2O_{2(aq)} \rightarrow Pb^{2+} + SO_4{}^{2-} \quad [2.6]$$

$$Millerite\text{: } NiS_{(s)} + 2O_{2(aq)} \rightarrow Ni^{2+} + SO_4{}^{2-} \quad [2.7]$$

$$Greenockite\text{: } CdS_{(s)} + 2O_{2(aq)} \rightarrow Cd^{2+} + SO_4{}^{2-} \quad [2.8]$$

$$Covellite\text{: } CuS_{(s)} + 2O_{2(aq)} \rightarrow Cu^{2+} + SO_4{}^{2-} \quad [2.9]$$

$$Chalcopyrite\text{: } CuFeS_{2(s)} + 4O_{2(aq)} \rightarrow Cu^{2+} + Fe^{2+} + 2SO_4{}^{2-} \quad [2.10]$$

The properties of final drainage waters ultimately depend on the quantity of metal sulphides exposed within the strata i.e. the higher metal sulphide content, the greater the concentration of the metal (Banks et al., 1997). However, this may be limited by the availability of oxygen and water (Singer and Stumm, 1970).

2.1.2 Source of natural attenuation of acidic mine water

The presence of mine drainages which are naturally alkaline with high concentrations of iron is often the case of influent waters to mine water treatment scheme within the UK Coal Authority sites (Younger et al., 2002). Natural attenuation of acidic water is provided by weathering of minerals that have the ability to consume the protons (e.g. calcite) as produced from Eqn. 2.1 – Eqn. 2.4, which are typically present in the host rock of the raw material deposit (Wolkersdorfer, 2008). On the other hand, where calcite is initially present (and without significant acidity input), rapid dissolution of this mineral will maintain a discharge in solubility equilibrium with the mineral and thus net-alkaline as long as it is appreciably present (Younger et al., 2002). This will determine whether mine water discharge is net-acidic or net-alkaline. In the UK, many coalfields contain a significant amount of carbonate minerals within their surroundings (e.g. ankerite being an important carbonate mineral) which can neutralise much of the acidity (Younger P L, Newcastle University, pers. comm.).

Carbonate minerals such as calcite, dolomite and ankerite are well known to buffer mine water pH, but oxi-hydrate and silicate minerals also buffer the pH when carbonates are not present or they have been consumed (Blowes et al., 2003). In passive systems, calcite dissolution is primarily the source of natural attenuation of acidic mine water and is given in the following reaction (Younger et al., 2002)

$$CaCO_{3(s)} + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad [2.11]$$

In addition to the reaction above, weathering of aluminosilicate minerals (e.g. K-feldspar, anorthite and biotite) consumes acidity but the dissolution rates are much slower than for calcite (Blowes et al., 2003).

2.2 REVIEW OF PASIVE MINE WATER TREATMENT SYSTEM TYPES

2.2.1 Treatment of net-alkaline/net-acidic mine waters

The types of passive treatment for polluted mine waters depends primarily on the nature of the mine water i.e. whether net-alkaline or net-acidic. Mine water is regarded as net-alkaline when the alkalinity in greater concentration than the acidity (alkalinity > acidity) (Younger et al., 2002). Treatment units as recommended by the PIRAMID Consortium (2003) for systems receiving net-alkaline or net-acidic ferruginous mine waters are summarised in Table 2.1 and Table 2.2, respectively, with examples of UK applications of passive treatment. Of these passive treatment options for polluted mine waters, the study only focused on the treatment of net-alkaline waters; where most treatment schemes investigated include aeration unit and/or settlement lagoon(s) serve as the pre-treatment unit(s) prior to final pollutant polishing in the subsequent aerobic wetland(s). These options are used when iron loads are relatively high and strict regulatory standards for effluent quality are to be met (i.e. total iron < 0.5 mg/L). On the other hand, where iron loads are comparatively low, wetland-only treatment system is used (PIRAMID Consortium, 2003). Within these investigated systems, treatment processes are typically not limited by the available dissolved oxygen (i.e. provision of some form of aeration cascade) and the pH level (i.e. net-alkaline pH), therefore time seems to be a likely variable to limit the removal processes given a range of influent iron concentrations (or loads).

Table 2.1 Treatment options for net-alkaline mine waters

Treatment type	Application	Example (Reference)
Aeration units	▪ To promote the oxidation of ferrous to ferric iron to facilitate the removal of iron ▪ Suspended ferric iron are subsequently removed by means of sedimentation in the following treatment i.e. settlement lagoons and / or wetland systems ▪ For strongly alkaline mine water aeration also serve to release CO_2 for pH increase thus enhancing the rate of ferrous iron oxidation	(Jarvis and Younger, 2005)
Settlement lagoons	▪ Amelioration of net-alkaline mine waters with high iron concentrations i.e. total iron content of mine water exceeds 5 mg/L by means of settlement of ferric hydroxides ▪ Settlement lagoon used in conjunction with treatment wetland for systems receiving high concentration of iron (i.e. > 50 mg/L) ▪ Aim at removing at least 50% iron, if properly sized and maintained, they could possibly remove > 60-70% of iron	Whittle (CL:AIRE, 2006) Acomb (Kruse et al., 2007) Shilbottle (Younger and Moustafa, 2004)
Aerobic wetlands	▪ Primarily efficient for treatment of net alkaline, ferruginous mine waters ▪ Water flows through the wetland under aerobic conditions with iron being precipitated as iron oxy(hydroxide) on the wetland substrate ▪ The mechanisms of wetland treatment for metal removals (primarily for iron) include sedimentation of suspended flocs, filtration of flocs by plant stems, adsorption of aqueous metal species, precipitation of hydroxides on plant stems and the wetland sediment surface, and direct plant uptake of iron and other metals ▪ Pre-treatment with settlement lagoons (probably with pre-aeration) are always preferred in a way to minimise rapid accumulation of ochre	(Batty and Younger, 2002) (Younger et al., 2002)
SCOOFI reactors	▪ Passive treatment option for ferruginious net-alkaline mine waters in areas of difficult terrain and with limited land availability ▪ To let the ferruginious oxygenated mine water pass over the high surface area media to develop a layer of ochre coating ▪ Ferric hydroxide layer then acts as a highly reactive surface for the adsorption and in situ oxidation of ferrous iron	(Jarvis and Younger, 2001) (Jarvis and Younger, 2005)

Table 2.2 Treatment options for net-acidic mine waters

Treatment type	**Application**	**Example (Reference)**
Compost wetlands	▪ Resemble aerobic wetlands for they receive surficial inflows of mine water ▪ Comprise of a layer of anoxic substrates (> 300 mm thick) containing various forms of organic matter ▪ Treatment mechanisms include the reduction of sulphate to hydrogen sulphide which consumes proton (reducing acidity), reduction of sulphate to form hydrogen sulphide with generation of bicarbonate alkalinity, and metal removal by means of metal reactions with hydrogen sulphide to form insoluble metal monosulphide. ▪ Provision of an aerobic wetland in the subsequent treatment is advised to encourage oxygenation of the treated water for further removal of metals as hydroxides ▪ Capable of generating greater alkalinity for acidity reduction and metal removals but may release metals at the same time they attenuate them	Quaking Houses, County Durham (Jarvis and Younger, 1999)
Reducing and alkalinity producing systems (RAPS)	▪ Improved passive treatment for acidic mine waters with high concentrations of dissolved oxygen, ferric iron and / or aluminium. ▪ To provide an alkaline condition for the acidic mine waters prior to be treated in subsequent aerobic passive units (e.g. settlement lagoons and / or aerobic wetlands) ▪ To remove dissolved oxygen from the mine water in the compost layer so that iron remain in ferrous form (to avoid oxidation of ferrous to ferric iron) ▪ Alkalinity is then generated as the water flows down through the underlying limestone bed.	Bowden Close, County Durham (Younger et al., 2004)
Anoxic limestone drains (ALDs)	▪ To promote dissolution of calcite (limestone) to sufficiently raise pH, generating bicarbonate alkalinity thus neutralising acidity ▪ Provides pre-conditioning circumstances for the metals to readily form precipitates in the subsequent treatment ▪ ALDs are normally buried trenches (filled with limestone), inundated with water that flows horizontally through the drain ▪ The greatest challenge when dealing with ALD treatment is the formation of ochre coating on the limestone surfaces which is called armouring ▪ For this reason, ALDs are not recommended at current practice of passive treatment for acidic mine water (RAPS applications may be considered as an improvement of the ALDs).	Younger et al., 2002
Permeable reactive barriers (PRBs)	▪ Based on the same geochemical processes as RAPS; incorporate carbonate dissolution of limestone in the absence of ferric iron and bacterial sulphate reduction for a passive treatment of acidic ground waters ▪ The rise in pH accelerates the precipitation of metals as hydroxides and hydrosulphates	Shilbottle (Younger and Moustafa, 2004)

2.2.2 Current design practice for passive treatment of net-alkaline mine waters

In the treatment of net-alkaline mine waters, sufficient dissolved oxygen must be present to oxidise ferrous iron to ferric iron in order to facilitate removal of iron as ferric (Fe^{3+}) precipitates. For mine waters that have low concentrations of dissolved oxygen, aeration is important to enable conversion of the ferrous to ferric iron because upon emergence to the surface environment iron is often present in the ferrous iron (Fe^{2+}) form (Younger et al., 2002). Direct precipitation of ferrous iron as a hydroxide requires a higher pH (approximately pH 8.5); however in a passive system reaching such a pH value is difficult. Conversely, precipitation of ferric iron as hydroxides requires a slightly lower pH (approximately pH 7.0) which is achievable in a passive system (PIRAMID Consortium, 2003). Therefore it is necessary to oxidise ferrous to ferric iron in the presence of sufficient dissolved oxygen and this can be achieved by means of aeration (i.e. some form of cascade). This is commonly followed by a treatment in settlement lagoon(s) with subsequent aerobic wetland(s) treatment (PIRAMID Consortium, 2003). Note that the use of aeration, settlement lagoons and aerobic wetlands for the treatment of a ferruginous mine waters is only recommended if the water is net-alkaline and iron is the only contaminant of interest (Younger et al, 2002). This is because the net result of the hydrolysis of ferric iron following the oxidation is a release of protons [H^+], which would lead to a reduced pH if alkalinity is not present. Thus, these treatment options are inadvisable for highly acidic mine waters and for waters containing significant concentrations of toxic metals (Younger et al, 2002). Details of the oxidative removal of iron are reserved for section 2.9. The bases for the design of such systems are provided below.

2.2.2.1 Aeration units

As stated above, oxidation of ferrous to ferric iron is required to facilitate removal of iron as hydroxides. The primary objective in designing an oxidation feature is to ensure sufficient dissolved oxygen is transferred to the water to oxidise the Fe^{2+} present in solution (Younger et al., 2002). It should also be noted that the oxidation of ferrous iron is not only dependent on the presence of dissolved oxygen but also depends on the concentration of ferrous iron available and on the pH whereby this chemical oxidation reaction at pH between 4 and 8 can be described by the model developed by Singer and Stumm (1970):

$$\frac{d\,Fe^{2+}}{dt} = \frac{k\,[Fe^{2+}][O_2]}{[H^+]^2} \qquad [2.12]$$

According to this model, the reaction is first-order with respect to ferrous iron and dissolved oxygen and second order with respect to pH. In the pH range 6 to 8 which is commonly encountered in passive treatment systems, the reaction rate in Eqn. 2.12 is fast enough to make passive treatment feasible (Younger et al., 2002).

The principle for the design of an aeration unit is to maximise the water surface area for oxygen transfer from the atmosphere to the water. In passive treatment, an aeration cascade is typically provided for the influent waters to be well-oxygenated. This is typically designed as a series of steps to break the flow into thin films so that greater water surface area is available for oxygen transfer (PIRAMID Consortium, 2003). Recommended design is to provide 100 mm of step width for every 1 L/s of flow, with a height of 500-800 mm (Younger et al., 2002).

2.2.2.2 Settlement lagoons

Having converted most of the ferrous iron to suspended iron hydroxide by means of dissolved ferrous iron oxidation and hydrolysis of dissolved ferric iron, the next step is to settle the (oxy)hydroxide iron from suspension in a settlement lagoon (Younger et al., 2002). Generally, a settlement lagoon should be considered to be used upstream of the first wetland in the sequence of passive treatment systems if the total iron content of mine water exceeds 5 mg/L (PIRAMID Consortium, 2003). As in the case of initial iron contents in the mine water exceeding 50 mg/L, a series of aeration cascades and settlement lagoons will be required, of which there needs to be one aeration cascade for every 50 mg/L of ferrous iron in water with an iron removal unit after each (Jarvis and Younger, 2005). Settlement lagoons can be very useful for removing high concentration of iron as it is far easier to routinely remove sediments from a settlement lagoon than from a vegetated wetland (Younger et al., 2002).

The aim of the design of settlement lagoon is to ensure that the retention time being sufficiently long for the solid particles to settle out. The sizing formulae previously used in the design of settlement lagoon include (PIRAMID Consortium, 2003):

- Stipulating a nominal hydraulic retention time of 48 hours
- Stipulating 100 m^2 of lagoon area per L/s of water to be treated
- Application of aerobic wetland sizing criteria (i.e. area-adjusted removal rate of 10 $g/m^2/d$)

The use of standard retention of 48 hours has been widely applied to the design of mine water treatment lagoon in the UK (PIRAMID Consortium, 2003). In the UK applications, settlement lagoons are typically deployed with the aim of removing at least 50% of incoming iron and if properly sized and maintained they could possibly remove > 70% of iron from the mine water discharges (PIRAMID Consortium, 2003; Jarvis and Younger, 2005).

2.2.2.3 Aerobic wetlands

Aerobic wetlands are amongst the most popular passive treatment unit processes as they are relatively simple to design and construct, and are primarily efficient for treatment of net alkaline, ferruginous waters (PIRAMID Consortium, 2003). The basic principle of aerobic wetlands is that water flows through the wetland under aerobic conditions with iron being precipitated as iron (oxy)hydroxide on the wetland substrate (Jarvis and Younger, 2005). The mechanisms of wetland treatment for metals removal (primarily for iron) include sedimentation of suspended flocs, filtration of flocs by plant stems, adsorption of aqueous metal species, precipitation of hydroxides on plant stems and the wetland sediment surface, and direct plant uptake of iron and other metals (Younger et al., 2002). Direct plant uptake can play a significant role during iron removal in such wetland system particularly for polishing the pre-treated mine water (Batty and Younger, 2002). Pre-treatment with settlement lagoon(s) (probably with aeration) are always preferred in the UK applications of aerobic wetlands, to minimise rapid accumulation of ochre and to maintain treatment efficiency thus sustaining the life of the aerobic wetland (CL:AIRE, 2006).

The design approach for aerobic wetlands treating mine waters is currently based on the zero-order removal model (area-adjusted removal formula) recommended by Hedin et al. (1994). Despite recommended first-order removal model (i.e. the concentration-dependence for iron removal) by Tarutis et al. (1999), the area-adjusted removal formula remains the most useful approach in most UK applications (Younger et al., 2002). The wetland area required can be calculated by substituting an areal iron removal rate (R_A) of 10 g/m^2/d (or 20 g/m^2/d if a reasonable improvement is to result rather than stringent regulatory standard (PIRAMID Consortium, 2003)) into Eqn. 2.13 below. This will also require the values of site-specific flow rate (Q_d), influent iron concentration (C_i) and the target effluent iron concentration (C_t). This sizing formula of an aerobic wetland is given by the following (Younger et al., 2002):

$$A = \frac{Q_d\,(C_i - C_t)}{R_A} \qquad [2.13]$$

Where;

A = required wetland area (m^2)

Q_d = mean daily flow rate (m^3/d)

C_i = mean daily influent contaminant concentration (mg/L)

C_t = concentration of contaminant in final discharge (mg/L)

R_A = area-adjusted contaminant removal rate ($g/m^2/d$)

The area-adjusted contaminant removal rate to be used in the above equation was derived by Hedin et al. (1994) by monitoring a wide range of existing wetland systems performance in the United States. A summary of the performance of such systems has been presented in Younger et al. (2002), in which the removal rates (given in metric of $g/m^2/d$) were very variable from one treatment site to another (e.g. iron removal ranged between 0.5 and 42.7 $g/m^2/d$). Therefore, assumption of the zero-order kinetics may not be appropriate in such situations given the different chemical characteristics (and possibly the hydraulics) of the different systems. This has also been criticised by e.g. Tarutis et al. (1999) who recommended the use of first-order kinetics as the basis for the design of wetland (and system similar to it). This design issue is further detailed in section 2.10. On the other hand, the influence of hydraulics on treatment performance may also be significant (Kadlec, 2000; Goulet et al., 2001; Younger et al., 2002). Therefore, it is interesting to account for these several issues to efficient use of current design formula and hence the aim of this study to assess these geochemically- and hydraulically-related factors on treatment system performance.

2.3 USE OF TRACER TESTS

2.3.1 Use of tracer tests in assessing hydraulic performance

As noted earlier, hydraulic assessment is important for the evaluation of treatment system performance alongside geochemical factors. Tracer tests can be a reliable means of accomplishing this assessment (e.g. Simi and Mitchelle, 1999; Kadlec, 2000; Martinez and Wise, 2003b; Lin et al., 2003; Mena et al., 2008; Sherman et al., 2009). A tracer study would indicate the travel time of water (measured by an inert tracer) and the possible deviation of the water flow-through from an ideal condition (discussion on tracer flow patterns are reserved for section 2.4). This in turn, would reflect the hydraulic efficiency of the treatment system and pollutant removal as a consequence (Schmid et al., 2004). Therefore, the use of a conservative tracer is important to represent the actual flow movement in a treatment system for understanding the processes by which polluted water is being treated (Cox et al., 2003). Properties to be considered in selecting a tracer include detectability, toxicity, solubility, cost and sorption characteristics (Kilpatrick and Wilson, 1989). Generally, the tracer used should preferably be (Wood and Dykes, 2002):

- highly soluble in water at stream temperatures
- stable in the presence of light, sediment or other substances in natural waters
- easily detected at low concentrations
- absent or present at low concentrations in the natural environment such that it does not influence measurement
- relatively inexpensive
- non-toxic to stream biota and without long term impacts on water quality or the environment

2.3.2 Types of tracer

Tracers can be used to determine the transport and fate of contaminants in water so that the dispersion of the contaminants as they travel through the system can be assessed. Tracer tests can be conducted either by use of artificial tracers (where suitable tracers are injected into the water system) or by natural tracers (naturally occurring constituents present in the water system). A classification of tracers is presented in Table 2.3.

Table 2.3 Classification of tracers (adapted from Käss, 1998 and Wolkersdorfer, 2008)

Tracer classification		Examples
i.	Artificial tracers	
▪	Water soluble tracers	▪ Dyes, salts, surfactants, aromas, and other chemical, radioactive and neutron activatable tracers
▪	Particulate tracers (water insoluble tracer)	▪ Club moss (*Lycopodium*) spores, fluorescent microspheres, bacteria, bacteriophages, geobombs, other particulate tracers
ii.	Natural tracers	▪ Stable isotopes, environmental chemicals, organisms

Of these tracers, salt and dye tracers are the most commonly applied types of tracers for use in surface water and in many instances in mine water applications. Examples of the tracers used with advantages and limitations of each type, are summarised in Table 2.4. Further details of some of these tracers are provided below.

2.3.2.1 Salt tracers

Generally, salts are the most commonly used tracer, because they are cheap, largely inert and typically not hazardous. Furthermore, salt tracer experiments are a convenient and widespread method for use in studies on constructed wetland or ponds (Schmid et al., 2004). Bromide and chloride solutions are commonly used for both groundwater and surface water tracing. These salts are very soluble, relatively inexpensive, conservative, easily detectable at low concentrations and non-toxic (Wright and Moore, 2003). Nevertheless, there are several factors that could possibly interfere with the conservative behaviour of salt tracers.

- ***Density stratification***

Relatively large amounts of salt injection solution may be required in order to raise the background levels of salts. Consequently, this will result in a higher solution density than the water being investigated. Because of the difference in density, it is possible that the injected tracer to sink to a much lower depth and need a long time to mix with the water (Käss, 1998). The processes governing the formation of density stratification due to salt tracer injections into wetland ponds with vegetation were studied by Schmid et al. (2004). The study indicated that there were distinct limits to the injected salt mass if the distortion of breakthrough curves by density effects was to be avoided. It is thus important that the concentration of tracer introduced should not be so high to avoid density stratification as 1% of density difference between the ambient wetland water and the tracer impulse could trigger this effect (Kadlec and Wallace, 2009).

- ***Electrical conductance***

Chloride solutions are commonly electrolytes or solutions of specific ions (Gordon et al., 1992). Therefore, addition of this salt could effectively be measured in terms of electrical conductivity. In order to obtain a clear chloride concentration over background, a comparably large amount of salt would need to be injected. This in turn results in a marked rise in the ion content which corresponds to an increase in the electrolytic conductivity (Käss, 1998). Schmid et al (2004) converted electrical conductivity values obtained from the addition of sodium chloride and potassium bromide to chloride and bromide concentrations by using calibration curves. It was found that the electrical conductivity of a dilute aqueous solution changed more rapidly with chloride than with bromide concentration, and it was thus concluded that conversion for chloride was more accurate in relation to conductivity.

- ***Emergent vegetation***

Emergent vegetation may have some effects on both flow pattern and salt mixing. Mixing affected by the presence of emergent stems was observed to be stronger than without vegetation (Schmid et al., 2004). The upper concentration limit to be observed is typically higher in the presence of emergent plants.

2.3.2.2 Dye tracer

Dyes are another commonly used tracer because they are still visible and measureable at low concentration (Käss, 1998). Despite this, there are several physical, chemical and biological influences on the use of the fluorescent dyes.

i. Physical influences on fluorescent dyes

- ***pH-dependency of the fluorescent dyes***

pH may have some effects upon the intensity of fluorescent dyes in the aqueous solution. Uranine for instance reaches about 80% of its maximal fluorescence intensity at pH 7 (Käss, 1998). This fluorescence intensity would change variably depending on the pH of the water. The reasons for the response of fluorescent dyes to pH changes are possibly due to ionisation and structural changes. For instance, fluorescein, structural changes may occur as pH decrease. Therefore, when using strong pH-dependant dyes such as uranine and pyranine, it is important to observe the pH value in the sample prior to analysis.

- ***Background fluorescence***

This can arise from the presence of suspended sediment and/or natural fluorescence within the water system. The presence of apparent background fluorescence in water can cause interference in tracer studies, for instance, very low tracer concentrations or significant recoveries to be in excess of 100% in quantitative work (Smart and Laidlaw, 1977). Suspended sediment in water could raise background fluorescence and reduces effective dye fluorescence because of light absorption and scattering by the sediment particles (Smart and Laidlaw, 1977). The other cause of fluorescence background has been reported to be attributed to the fluorescence of algae and other natural plant pigments (Rabinowitch, 1951). The majority of algae and phytoplankton contain the green pigment chlorophyll which has a strong red fluorescence in water.

ii. Chemical and biological behaviour of dye tracers

The behaviour of dye tracers can either be associated with adsorptive or non-adsorptive characteristics as they travel through a water system. These effects could be observed and quantified through the tracer losses (e.g. tracer mass recovery) at the end of a tracer study. Factors that predominantly contribute to tracer losses across a water system are photochemical decay, chemical decay, biodegradation and adsorption on mineral or organic materials.

- ***Photochemical decay***

Fluorescence is caused when the molecules revert to the lower energy state by the emission of light. As compounds fluoresce, they often decompose owing to oxidation and other chemical changes. The rate of decay is dependent on dye concentration, light intensity and wavelength (Smart and Laidlaw, 1977). The decay rates are very high for fluorescein, which rapidly loses its fluorescence under bright sunlight conditions.

- ***Chemical decay***

Feuerstein and Selleck (1963) reported that vigorous agitation of dye solution may cause reduction in fluorescence even under dark conditions. High photosensitivity of photine CU and fluorescein for instance, may result in significant decay over short periods when these samples are removed from dark conditions. On the other hand, Rhodamine B was found more susceptible to chemical decay (Smart and Laidlaw, 1977).

- ***Biodegradation***

Dyes are also known to be biodegradable in both aerobic and anaerobic systems (Hunter, 1973). In systems with large population of microorganisms, it is likely that biodegradation would be a significant cause of dye loss. However, in the majority of surface waters it will be unnecessary to consider biodegradation of the dye tracers because bacterial populations will be very much lower than those in the biologically hostile environments, i.e. activated sludge systems or sewage oxidation ponds (Smart and Laidlaw, 1977).

- ***Adsorptive dye loss***

Adsorption of dyes onto sediment surfaces is mainly irreversible, therefore a high resistance to adsorption is important for a dye tracer (Smart and Laidlaw, 1977). The type and concentration of sediments seem to have some effects on the adsorptive behaviour of a dye. There is a marked decrease in the percentage of dye loss with increasing initial dye concentration (Smart and Laidlaw, 1977). Scott et al. (1969) found that at high sediment concentrations the substrate is a less efficient adsorbent to dye than it is at low sediment concentrations. In environments containing abundant organic matter, losses of dyes due to adsorption will be much more of a problem than it will be in even the most turbid inorganic fluvial system (Smart and Laidlaw, 1977). Greater adsorption would also be expected at low pH values, for instance the increased dye losses at high humus concentrations (Grover, 1971). In addition, losses may also be associated with dye adsorption onto equipment used during experiment (Yotsukara et al., 1970).

2.3.3 Tracer amount

There are numerous mathematical equations provided in the literature for estimating optimal tracer amount, but they can be different (i.e. by up to 8 orders of magnitude) between the lowest and the highest estimates (Field, 2003). In fact, tracer amount depends largely on site-specific considerations (Wolkersdorfer, 2008). Potential equations for calculating the tracer amount are listed in Table 2.5. Generally, these equations have been found to be less exact than is commonly desired because of the relative obscurity, confusing nature and inconsistency surrounding the use of existing tracer mass estimation equations (Käss, 1998; Field, 2003). Käss (1998) concluded that expert knowledge is more important than a list of equations, and that the empirical values from field experiences are important for estimating applicable tracer amount (Wolkersdorfer, 2008). Field (2003) claimed that tracer mass estimation by conjecture (guess method) is a useful technique to constrain various uncertainties regarding the system investigated. Even though the use of, for instance, the Efficient Hydrologic Tracer Tracer Design (EHTD) computer code by Field (2003), may be useful in calculating tracer amount, the mine water scenario is not yet included in the code (Wolkersdorfer, 2008). Note that the tracer mass estimated from the equations as listed in Table 2.5 should be regarded as a starting point for site-specific considerations rather than ultimate values. Again, these equations were based on original practitioners' experience at particular field sites, and not necessarily on measured hydraulic parameters or solute transport theory (Field, 2003). Review of the the amount of tracer and assumptions used in previous tracer experiments were also carried out for comparing the calculated tracer amount (Table 2.6).

Table 2.4 Types of tracers typically employed in mine water applications with advantages and limitations of each

Types of tracer	Advantages	Limitations	References
Water soluble tracer			
➢ Salts			
▪ *Bromide*	▪ Non-reactive (conservative) ▪ Found at low background concentrations ▪ Easily detected at low concentrations ▪ Easy to analyse ▪ Has low toxicity ▪ Does not undergo sorption or chemical and biological transformations ▪ Easy to handle ▪ Inexpensive ▪ Preferred as a tracer in transport studies		▪ Bowman, 1984; Davis et al., 1980; Lin et al., 2003; Keefe et al., 2004 ▪ Flury and Papritz, 1993 ▪ Martinez and Wise, 2003b ▪ Edwardson et al., 2003
		▪ Bromide loss due to being readily taken up by plants ▪ On-site analysis is difficult ▪ Requires large bromide addition where high background concentration ▪ Potential source of potentially toxic disinfection by-products in drinking water supplies	▪ Whitmer et al., 2000 ▪ Lin et al., 2003
▪ *Chloride*	▪ Behaves conservatively ▪ Highly soluble in water ▪ Often present at low concentrations in surface waters environment ▪ Relatively inexpensive ▪ Non-toxic to stream biota and no long term impacts to water quality ▪ Does not adsorb to negatively charged soil minerals	▪ Chloride contents in soils may be higher as it comes from fertilisers, manures and defrosting agents ▪ Density effect would lead tracer to sink to a much lower depth and need a long time to mix with the water	▪ Bencala et al., 1983 ▪ Wood and Dykes, 2002 ▪ Flury and Papritz, 1993 ▪ Käss, 1998; Schmid et al., 2004

Table 2.4 Types of tracers typically employed in mine water applications with advantages and limitations of each (cont')

Types of tracer	Advantages	Limitations	References
➢ *Dyes*			
▪ *Rhodamine WT*	▪ Easily detected at low concentrations ▪ Not affected by background fluorescence concentration	▪ Behave non-conservatively due to sorption onto sediments and photochemical degradation	▪ Lin et al., 2003; Keefe et al., 2004; Bencala et al., 1983
		▪ Conservancy for long duration experiment with large organic proportion	▪ Martinez and Wise, 2003b
		▪ Uptake by living organisms	▪ Bencala et al., 1983
▪ *Sodium fluorescein*	▪ Adding alkaline salt increases the fluorescence and the solubility of fluorescein		▪ Käss, 1998
	▪ Easily detectable in low concentrations	▪ Sensitive to light and sorption properties in acidic media	▪ Smart and Laidlaw, 1977; Wolkersdorfer et al., 2002
➢ *Radioactive isotopes*		▪ Isotopes already present in mine water could interfere with the tracer injected	▪ Wolkerdorfer et al., 2002
		▪ Restrictive permit from responsible authorities for conducting a radioactive tracer test	▪ Schmid et al., 2004
		▪ Detection is expensive	▪ Wolkersdorfer, 2002
Water insoluble tracers			
➢ *Club moss spores*	▪ Suitable tracer in most underground mine water tracing ▪ Outer layer of spores is resistant to chemical and microbiological influences ▪ Easily detected ▪ Relatively cheap		▪ Wolkersdorfer et al., 1997; Wolkersdorfer and Hasche, 2001; Wolkersdorfer, 2002
	▪ Small quantities may contain billions of tracer particles ▪ They can travel for a relatively long distance and could still be detected at 30 km away	▪ Difficulties for quantitative measurement (i.e. first appearance, maximum concentration) ▪ Due to density effect, they could possibly sink in slowly flowing underground water	▪ Käss, 1998

Table 2.4 Types of tracers typically employed in mine water applications with advantages and limitations of each (cont')

Types of tracer	Advantages	Limitations	References
➢ Microsphere	▪ Suitable for rough conditions in karst groundwaters and mine waters ▪ Chemically stable even in mine water environments ▪ Multiple coloured spores can be used at the same time ▪ Non-toxic	▪ Microsphere surface should be neutrally charged to avoid sorption effects	▪ Wolkersdorfer et al., 2002; Wolkersdorfer, 2002
Natural tracers			
➢ Environmental chemicals	▪ Sulphate and manganese have the greatest utility as natural tracers in stream systems and potentially in other acidic stream systems ▪ Naturally present in water without any addition or tracer injection	▪ Generally conservative behaviour of solutes in aerated systems; however does not necessarily ensure that the substances are suitable natural tracers ▪ The differences in concentrations between the different water systems studied must be substantially large for the solutes to be used as natural tracers ▪ Conservative tracer behaviour may be different in different systems	▪ Bencala et al., 1987 ▪ Schemel et al., 2006
➢ Environmental isotopes	▪ Stable isotopes such as the isotopes of O and S in SO_4^{2-} can be used as tracers of natural and anthropogenic influences on groundwater		▪ Bottrell et al., 2008

Table 2.5 Equations for estimating tracer mass

Equation	**Comments**	**Reference**
$M = C_b \ x \, V_n$ where: M Tracer amount (g) C_b Benchmark concentration (g/m^3) V_n Nominal water volume (m^3)	▪ Target peak concentration should be at least 20-50 times the background concentration and at least 50 times the detection limit ▪ Completely mixed tracer mass should achieve a benchmark concentration at least 10-20 times the background concentration ▪ benchmark concentration will be 30-70% of the peak concentration ▪ at the time of 95% tracer mass, the tracer would still be detectable above the background concentration	Kadlec and Wallace (2009); Lin et al. (2003)
$M = L \ x \ k \ x \ B$	Suitable for Na-fluorescein	Wolkersdorfer (2008)
$M = 0.56\left(\frac{QC_p t_p}{1000}\right)^{0.91}$	Suitable for dye tracer injection	Field (2003)
$M = 0.56\left(\frac{QC_p L}{1000 v_p}\right)^{0.91}$		Field (2003)
$M = 17\left(\frac{QC_p L}{3.6 \ x \ 10^6}\right)^{0.91}$		Field (2003)
$M = \frac{QL}{3600}$	Suitable for Na-fluorescein detection	Milanovic (1981); Gaspar (1987)
$M = L\left[\left(1 + \frac{Q}{1.8 \ x \ 10^4}\right) + \frac{Q}{3600}\right]$	Valid only when Q ≤ 5 m3/s and L ≥ 12 km	Milanovic (1981); Gaspar (1987)
$M = \frac{Q^2 L}{3600 q}$	Expected to overestimate tracer mass for large systems > 1km	Gaspar (1987)
$M = \frac{C_p T_\rho QL}{2500 v}$	Applicable for surface water and was intended for travel time studies using Rhodamine WT	Aley (1999)
$M = \frac{QC_p T_p T_\rho \tau}{747.23}$	Represent the impulse release in surface water stream	Kilpatrick and Cobb (1985)
where: M Tracer amount (g) C_p Expected peak tracer concentration (mg/m^3) T_p Tracer purity (%) T_ρ Tracer density (g/cm^3) L Expected tracer transport distance (m) Q Flow rate (m^3/h) t_p Expected time to peak (h) τ Mean tracer travel time (h) q Inflow rate (m^3/h) k Tracer coefficient (0.1-20000)* B Factor for general set up of tracer test (0.1-10)* v Mean water velocity (m/h) v_p Expected peak tracer velocity (m/s) * Refer Wolkersdorfer (2008) for details		

Table 2.6 Amount of tracer employed in various tracer tests with different types of tracer and reported volume of system

Tracer type/ Water system	**Volume of system (m^3)**	**Amount of tracer (g)**	**Assumption**	**Reference**
Na-fluorescein				
Underground mine	180	15	~100 µg/L tracer peak	Wolkersdorfer et al., 2007
	293	20	~100 µg/L tracer peak	
	338	150		
	2,500,000	250	~0.1 µg/L tracer peak	
Reducing and alkalinity producing system (RAPS)	363 270	69.96 50.41		Wolkersdorfer et al., 2005
NaBr				
Reducing and alkalinity producing system (RAPS)	363 270	2,860 2,130		Wolkersdorfer et al., 2005
Wetland	22,000-28,000	27,000	Detection above baseline (200 µg/L) 95% tracer recovery	Lin et al., 2003
KBr				
Wetland	2246	24,000-30,000		Wachniew et al., 2000
	6240	20,000-25,000		
LiBr				
Reducing and alkalinity producing system (RAPS)	363 270	1,710 1,270		Wolkersdorfer et al., 2005
NaCl				
Wetland	792	25,800		Wolkersdorfer et al., 2005
Rhodamine WT				
Wetland	22,000-28,000 ~988,000	10,400 57,200	Detection above baseline 95% tracer recovery	Lin et al., 2003

2.4 TRACER FLOW PATTERNS

2.4.1 Basics of ideal and non-ideal flow patterns

On the basis of chemical reactor principles, there are two ideal steady-state flow reactors; plug-flow (PF) and completely-stirred tank reactor (CSTR) reactors (Fogler, 1992). The PF reactor is characterised by the fact that there must be no mixing or diffusion along the flow path i.e. no element of fluid overtaking or mixing with any other elements ahead or behind, hence the residence time is the same for all elements of fluid (Levenspiel, 1972). In the CSTR, the fluid contents are well-stirred and uniform throughout, and thus the exit fluid has the same composition of the fluid with the reactor (Levenspiel, 1972). However, for wetlands and ponds, these two ideals are rarely the case in real applications of such systems (reactors) (Kadlec and Wallace, 2009). Deviation from these ideals are typically associated with the channelling of the flowing fluid, recirculation of fluid or by creation of stagnant region within the reactor, and are termed “non-ideal” flow patterns (Levenspiel and Turner, 1970). Levenspiel (1999) identified factors accounting for non-ideal flow patterns as:

i) the residence time distribution of material flowing through the reactor
ii) the aggregation state of the flowing material and
iii) the earliness or lateness of mixing of material in the reactor.

Investigation of such factors is why tracer tests are typically undertaken, to examine the extent of non-ideal flow patterns particularly in the real reactors such as the wetlands and lagoons investigated in this study. In the following sections (section 2.5 – section 2.8), the bases for the interpretation of tracer test results are presented to account for the non-ideal flow patterns observed during the tracer tests in passive mine water treatment systems conducted throughout the study.

2.5 INTERPRETATION OF TRACER TEST RESULTS

2.5.1 Tracer breakthrough curves

Plots of concentration versus time are the simplest illustrations of tracer test results, without taking into account other factors such as water flows and tracer mass exiting the treatment system which may possibly have impacts during tracer test. A plot of tracer concentration as a function of time is known as a tracer breakthrough curve.

This illustration of results enables comparison of different tracer concentrations detected over a period of time but it yields the drawback that for different treatment systems with different characteristics (i.e. flow rates, volumes), reliable comparison of the pattern and spread of tracer flow-through is difficult. Because the movement of tracer is an important factor in determining performance of a treatment system, reliance on the tracer breakthrough alone is insufficient to provide essential information on how the system is performing.

2.5.2 Residence time distribution (RTD)

Residence time distribution (RTD) versus time is another way of presenting the tracer test results. On the basis of chemical reactor principles, flowing fluid (e.g. water) taking different routes through a reactor may take different lengths of time to pass through the reactor (Levenspiel and Turner, 1970; Levenspiel, 1972). This is evident in those reactors (i.e. treatment systems) investigated in this study (see tracer test results in section 4.2 of Chapter 4). The distribution of these times for the water leaving the reactor is called the exit age distribution or the residence time distribution of water (Levenspiel and Turner, 1970; Levenspiel, 1972). Note that the term age is referred to the time spent by the water in the reactor.

Therefore, RTD is a measure of relative time tracer spends as it flows through and the distribution of flow across the system. RTD is also regarded as a reliable tool for interpreting tracer test results in non-steady and/or non-ideal flow systems thus illustrating the change of flow movement from ideal flow patterns (Levenspiel, 1972; Kadlec, 1994; Werner and Kadlec, 1996). Because RTD is the product of tracer concentration and flow rate divided by the amount of tracer exiting the system (Kadlec, 1994; Kadlec and Wallace, 2009), this illustration of results also in some way indicates the change of tracer breakthrough curves due to these factors. Additionally, the RTD is also a useful measure for characterising hydraulic performance of a system (e.g. Kadlec, 1994; Martinez and Wise, 2003b). RTD is typically represented by an E curve as a function of time, $E(t)$ (Levenspiel, 1972; Kadlec, 1994; Martinez and Wise, 2003b; Kadlec and Wallace, 2009). Note that mathematical solution to this is readily available in the literature (i.e. Levenspiel, 1972). In a broader context, RTD is the probability density function for residence time (in the treatment systems) which, under steady flow conditions, is given as (Levenspiel, 1972; Kadlec and Wallace, 2009):

$$RTD, E(t) = \frac{Q(t)C(t)}{\int_0^\infty Q(t)C(t)dt} \qquad [2.14]$$

where $E(t)$ = residence time distribution (d^{-1}); $Q(t)$ = flow rate at system outlet (m^3/d); $C(t\ \ )$ = outlet tracer concentration (g/m^3). The denominator is the total of tracer mass recovered at system outlet and is equivalent to the zeroth moment, M_0 from moment analysis (Kadlec and Wallace, 2009).

$$M_0 = \int_0^\infty Q(t)C(t)\,dt \cong \sum_{i=1}^{n} Q_i\,(t)C_i\,(t)\Delta t \qquad [2.15]$$

where M_0 = total mass of tracer recovered at system outlet (g); n = number of samples. In this study, the RTD is used to illustrate the actual tracer responses during the experiment (i.e. changes in tracer concentrations and flow rates) to observe the variations in flow movement across the systems. If it is assumed that the flow rate is constant throughout the tracer test, then the RTD is simply the change of concentration over time (Kadlec and Wallace, 2009).

$$RTD, E(t) = \frac{Q(t)C(t)}{\int_0^\infty Q(t)C(t)dt} = \frac{C(t)}{\int_0^\infty C(t)dt} \qquad [2.16]$$

This assumption is, however, only applicable for steadily flowing systems, which is rarely the case in actual treatment wetland or pond due to event driven factors such as rainfall, evaporation and flow pumping (Werner and Kadlec, 1996; Kadlec, 1994). Therefore, RTD curves are preferable and are more representative of the tracer test results considering all factors influencing experimental conditions.

If plug-flow conditions apply, where all the water fractions (i.e. tracer spike) exit the system at time, t_n, the RTD is given by (Levenspiel, 1972):

$$RTD(t) = \delta_D(t - \tau_n) \qquad [2.17]$$

where δ_D = Dirac delta function; t = elapsed time (d); τ_n = nominal residence time. As in the case of completely-mixed flow conditions, where the tracer impulse is uniformly distributed within the system, RTD can be represented by a continuously-stirred tank reactor (CSTR) and the RTD takes the form of (Levenspiel, 1972):

$$RTD(t) = \frac{1}{\tau_n} exp\left(\frac{t}{\tau_n}\right) \qquad [2.18]$$

However, neither plug-flow nor completely-mixed conditions occur in real tracer movement within treatment wetlands and/or ponds, due to inevitably uneven flow distribution resulting from flow short-circuiting and the presence of dead zones, for example. RTD is therefore often assumed as a series of equally sized, perfectly mixed tanks-in-series (TIS), and the RTD is represented as (Levenspiel, 1972):

$$RTD(t) = \frac{n^n}{\tau^n \Gamma(n)} t^{n-1} exp\left(-\frac{nt}{\tau}\right) \quad [2.19]$$

where n = number of tanks-in-series (unitless); t = time (d); τ = mean tracer residence time (d); $\Gamma(n)$ = gamma function of n,= $\int_0^\infty t^{N-1}\, exp(-\mathrm{t})\, dt$, to allow n being accounted as non-integer variables, or (n-1)!, if n is an integer (d^{-1});

2.5.3 Normalisation of tracer RTD

Normalisation of the experimental data is performed as a means for comparing different treatment systems under different experimental conditions (i.e. different tracer concentrations, flow rates and amount of tracer added) during the tracer tests. A simple illustration of tracer test results from a concentration curve can be normalised by dividing the tracer concentration by the estimated outlet concentration during the test, *Co* (Werner and Kadlec, 1996).

$$Normalised\ concentration, C(\Theta) = \frac{C(t)}{C_o} \quad [2.20]$$

where $C_o = \frac{M\ (mass\ of\ tracer\ added\ ,g)}{V\ (system\ volume\ ,m^3)}$

Taking into account the effects of several important parameters involved in the changes of the tracer response curve (i.e. system volume and flow rate) during a tracer test, RTD curves are preferable to concentration curves. Normalisation of RTD curves is performed by multiplying the tracer RTD by the tracer estimated (nominal) residence time, τ_{an} (Werner and Kadlec, 1996).

$$Normalised\ RTD, E(\Theta) = E(t)\tau_{an} = \frac{Q(t)C(t)}{M_o}\tau_{an} \quad [2.21]$$

where τ_{an} is the actual nominal residence time as calculated by Eqn. 2.33 below. The time the tracer test takes, t can also be normalised by dividing by the tracer nominal residence time, τ_{an}.

$$Normalised\ time, \tau_\Theta = \frac{t}{\tau_{an}} \quad [2.22]$$

2.5.4 Moment analysis of residence time distribution

Moment analysis of the tracer RTD determines several key characteristics of tracer movement in a particular treatment system e.g. recovered tracer at the outlet of a treatment system, the mean residence time tracer takes for passing through the system and the spread of the tracer movement from mean residence time. These characteristics of tracer movement in a treatment system are given by three analyses of moments i) zeroth moment (yields the tracer amount recovered from tracer test), ii) first moment (yields the mean of residence time distribution) and iii) second moment (yields the spread of tracer from the mean RTD).

The zeroth moment, M_0 which corresponds to the total of tracer mass recovered at system outlet is given by the following (Kadlec, 1994; Martinez and Wise, 2003b; Kadlec and Wallace, 2009):

$$M_0 = \int_0^\infty Q(t)C(t)\, dt \cong \sum_{i=1}^{n} Q_i\,(t)C_i\,(t)\Delta t \qquad [2.23]$$

where $Q(t)$ = flow exiting the system (m^3/d); $C(t)$ = tracer concentration exiting the system (g/m^3); n = number of samples. M_0 has unit of g of mass recovered. This is simply the same as M_0 used for determining the tracer RTD (Eqn. 2.15). The first absolute moment, M_1 gives the centroid of the distribution of residence time and equals the mean time, corresponding to actual tracer residence time (Kadlec, 1994; Martinez and Wise, 2003b; Kadlec and Wallace, 2009).

$$M_1 = \tau_m = \int_0^\infty tE(t)\, dt \cong \sum_{i=1}^{n} tE_i\,(t)\Delta t \qquad [2.24]$$

where M_1 = τ_m = tracer mean residence time (d); $E(t)$ = residence time distribution (RTD) (d^{-1}). Details of Eqn. 2.24 above are given as (Kadlec, 1994):

$$\tau_m = \int_0^\infty tE(t)\, dt = \frac{\int_0^\infty tQ\,(t)C(t)dt}{\int_0^\infty Q\,(t)C(t)dt} \cong \frac{\sum_{i=1}^{n} tQ_i\,(t)C_i\,(t)\Delta t}{\sum_{i=1}^{n} Q_i\,(t)C_i\,(t)\Delta t} \qquad [2.25]$$

The ratio of tracer mean to nominal residence time will give an approximation of the active volume during passage of water through the system, which is termed the system volumetric efficiency. The system nominal residence time is typically written as:

$$\tau_n = \frac{V}{Q} \qquad [2.26]$$

where τ_n = tracer nominal residence time (d); V = system volume (m^3); Q = flow rate (m^3/d). Note that appropriate use of flow (i.e. inflow, Q_i, outflow, Q_o or average Q_i and Q_o) is essential to yield accurate nominal residence time, and hence system volumetric efficiency. It will be shown later that the actual nominal residence time, τ_{an} is used in this study, and is calculated using Eqn. 2.33 below rather than using Eqn. 2.26 above.

The second absolute moment, *M₂* produces the deviation of tracer flow movement from the centroid of residence time, or the variance, corresponding to the spread of tracer as it flows through a system (Kadlec, 1994; Martinez and Wise, 2003b; Kadlec and Wallace, 2009).

$$M_2 = \sigma^2 = \int_0^\infty (t-\tau_m)^2 E(t)\,dt \cong \sum_{i=1}^{n}(t-\tau_m)^2 E_i(t)\Delta t \qquad [2.27]$$

where σ^2 is the variance of the residence time distribution (d^2). Details of Eqn. 2.27 above are given as (Kadlec, 1994).

$$\sigma^2 = \int_0^\infty (t-\tau_m)^2 E(t)\,dt = \frac{\int_0^\infty (t-\tau_m)^2 Q(t)\,C(t)dt}{\int_0^\infty Q(t)C(t)dt} \cong \frac{\sum_{i=1}^{n}(t-\tau_m)^2 Q_i(t)C_i(t)\Delta t}{\sum_{i=1}^{n} Q_i(t)C_i(t)\Delta t} \qquad [2.28]$$

This variance of the RTD is characterised by the dispersive behaviour of the flow created by the distribution of velocities of flow-through (i.e. lateral, longitudinal or vertical mixing) within a system, and can be written in the dimensionless form of:

$$\sigma_\theta^2 = \frac{\sigma^2}{{\tau_m}^2} \qquad [2.29]$$

The dimensionless variance is a measure of flow deviation from mean residence time (the greater the deviation, the more it disperses from an ideal flow pattern, the poorer hydraulic performance) of a system. It is also known as the coefficient of variation of pollutant for hydraulic residence time (Persson et al., 1999). Taking into account the RTD analysis in accordance with TIS model, the dimensionless variance is given by the following expressions (Kadlec and Wallace, 2009).

$$\sigma_\theta^2 = \frac{\tau_m - \tau_p}{\tau_m} = \frac{1}{n} \qquad [2.30]$$

where τ_p = tracer peak time (d); n = number of tanks in series (unitless). Thus, it can be seen that this dimensionless variance is inversely related to the number of tanks-in-series, n TIS.

Clearly, computation of M_0, M_1 *and* M_2 are largely dependent on the tracer concentrations and flow measurements, which Kadlec (1994) reported can be different between i) dynamic tracer and flow and ii) dynamic tracer and average flow. Therefore, in the first instance, computation of M_0, M_1 *and* M_2 are compared using dynamic and average flow measured during the tracer tests. This is presented in section 4.2 of Chapter 4.

On the other hand, the moment analysis has been widely applied for interpretation of tracer test results for wetlands (e.g. Kadlec, 1996; Lin et al., 2003; Martinez and Wise, 2003b; Sherman et al., 2009) but it yields the drawback that inappropriate interpretation could result from significant errors between the observed tracer breakthrough / RTD and the model. In this study, moment analysis of tracer test results showed that the analysis was capable of capturing the tail but missed the peak of the tracer RTDs in most cases (see section 4.4.3 of Chapter 4 for details). Despite this, the moment analysis is still a useful method for early estimation of TIS model parameterisation as discussed in section 4.4.2.

2.5.5 Nominal residence time and water volume

System nominal residence time is defined as the water volume involved in flow divided by the volumetric flow rate (Kadlec and Wallace, 2009). As stated earlier, system nominal residence time may be affected by the choice of appropriate flow and system volume for computation of actual nominal residence time. There is ambiguity about the choice of the flow rate i.e. whether to use inlet, or outlet, or an average of inlet and outlet flow (Kadlec and Wallace, 2009). When there is local variation in flow and water volume, the appropriate calculation must involve integration of transit times from inlet to outlet (Kadlec and Wallace, 2009). Therefore, for wetland systems (and ponds), the actual nominal residence time across the systems is given as (Chazarenc et al., 2003):

$$\tau_{an} = \frac{V}{Q_i - Q_o} ln\left(\frac{Q_i}{Q_o}\right) \qquad [2.31]$$

where τ_{an} = actual nominal residence time (d); Q_i = inlet flow (m^3/d); Q_o = outlet flow rate (m^3/d). Eqn. 2.31 can be written in another form as (Kadlec and Wallace, 2009):

$$\tau_{an} = \tau_{in}\left(\frac{\ln(R)}{R-1}\right) \qquad [2.32]$$

where τ_{in} = inlet nominal residence time, $\tau_{in} = V/Q_i$ (d); V = total system volume (m^3); R = water recovery fraction, $R = Q_o/Q_i$ (dimensionless). Both the equations (Eqn. 2.31 and Eqn. 2.32) are regarded as the theoretical residence time in plug-flow systems, thus in the case of a TIS system, τ_{an} can be determined as (Kadlec and Wallace, 2009):

$$\tau_{an} = \tau_{in}\left(\frac{1}{N}\sum_{j=1}^{N}\left(\frac{1}{1-\frac{\alpha j}{N}}\right)\right) \qquad [2.33]$$

where α = water loss fraction, $\alpha = 1 - R = 1 - Q_o/Q_i$ (dimensionless); N = total number of tanks; j = tank number counter i.e. $j = 1, 2, ..., N$ (unitless). Computation of this actual nominal residence time (Eqn. 2.31 - Eqn. 2.33) gives the advantages of considering the effects of flow changes and either water losses by evapotranspiration or infiltration, or water gains by rainfall. Computation of actual nominal residence time in accordance with the TIS system will accurately determine the fraction of water involved in the treatment as it takes account of the flow pattern during tracer test, in addition to effect of flow changes between inlet and outlet. Accordingly, the nominal water volume is determined by (Kadlec and Wallace, 2009):

$$V_{nominal} = (LWh)_{nominal} \qquad [2.34]$$

where L = system length (m); W = width (m); h = water depth (m). In practice, it is appropriate to deal with nominal parameters because for instance, water depth is difficult to determine with satisfactory degree of accuracy (Kadlec and Wallace, 2009). Therefore, quantification of system flow rate and volume are the most important parameters to determine during a tracer test.

2.6 TRACER FLOW-PATTERN MODELLING

2.6.1 Introduction to flow modelling approach

Modelling of hydraulic characteristics of a treatment system is important for it allows the quantification of actual time a fraction of water is retained in the system and the average age of water retention, which in turn relates the extent to which treatment has been achieved (Metcalf and Eddy, 2004). In this study, systems' hydraulic characteristics are the key elements that must be appropriately determined from each of the tracer RTDs observed during the field experiments. A modelling approach can be adopted as a means for comparing the actual tracer responses during the tracer tests with the expected theoretical response, to assess system performance under current design (Metcalf and Eddy, 2004). In order to do so, modelling of the tracer RTD curves is applied to determine the main parameters (e.g. mean residence time, variance (spread of tracer) and mode (peak of tracer)) which will then lead to determination of treatment system efficiencies e.g. system volumetric efficiency (e_v), RTD efficiency (e_{RTD}) and the overall hydraulic efficiency (e_λ). Furthermore, modelling is a useful tool to represent flow movement in real systems, for scale up and for diagnosing poor flow (Levenspiel, 1999).

There are different kinds of models to represent whether flow is either close to ideal plug-flow or completely-mixed, or lies between the two, which is regarded as the non-ideal flow condition (Levenspiel, 1999). Because real reactors always deviate from these ideals (plug-flow and completely-mixed), the use of these models may not adequately represent the actual nature of flow movement under which the flow is treated. To account for this non-ideal flow behaviour, the principle of a dispersion model (also known as plug-flow with dispersion, PFD model) and a tanks-in-series (TIS) model may apply (Levenspiel, 1999). Either can be applied, whichever fits the intended use. These models would essentially give identical results for systems with relatively small deviations from plug-flow. Details of these two models are described below.

There are however, several advanced models in addition to these simple flow models, but they are not presented here due to complexity in use. Examples include the finite stage model i.e. zones of diminished mixing (ZDM) model (e.g. Werner and Kadlec, 2000) and one-dimensional transport with inflow and storage (OTIS) model (e.g. Martinez and Wise, 2003a; Keefe et al., 2004). Stage models can also be used, but although they can well represent the tracer response, they are of limited use for evaluation of pollutant removal, and hence wetland design (Kadlec and Wallace, 2009). A more sophisticated approach is the computational fluid dynamics (CFD) flow modelling (e.g. Persson et al., 1999; Koshiaho, 2003; Jenkins and Greenways, 2005; Kjellin et al., 2007; Lightbody et al., 2007). The advantage of CFD modelling is the ability to explore the consequences of alterations in the basin morphology on system efficiency (Kadlec and Wallace, 2009). Therefore, it has been possible to apply quite sophisticated models to represent tracer responses, but that level of detail is not always necessary for interpretation of contaminant removals (Kadlec and Wallace, 2009). For this reason, only a TIS model is used for interpretation of tracer results in this study, a model which is regarded as a reliable and widely used tool in treatment wetlands and ponds (Kadlec and Knight, 1996).

2.6.2 Plug flow with dispersion (PFD) model

The PFD model is typically satisfied for systems that deviate not too greatly from plug-flow (Levenspiel, 1999). In this model, mixing is presumed to follow a diffusion equation and the tracer mass balance equation is represented by a differential equation, which includes both spatial and temporal variability (Fogler, 1992).

$$\mathcal{D}\frac{\partial^2 C}{\partial x^2} - \frac{\partial (uC)}{\partial x} = \frac{\partial C}{\partial t} \qquad [2.35]$$

where u = actual water velocity (m/d); $\mathcal{D}$ = dispersion coefficient (m^2/d) and x = distance from inlet toward outlet (m). Solutions to this mass balance are readily available in Levenspiel (1972) and in accordance with appropriate boundary conditions (Eqn. 2.38 and Eqn. 2.39 below). These boundary conditions are referred to the entrance and exit boundaries of flowing water into and out from a system i.e. whether these boundary conditions are open or closed to diffusion (Kreft and Zuber, 1978; Levenspiel, 1999). The dimensionless parameter which characterises Eqn. 2.35 is the Peclet number, Pe or its inverse the dispersion number, D.

$$Pe = \frac{uL}{\mathcal{D}} = \frac{1}{D} \qquad [2.36]$$

Note that dispersion is a measure of the spreading of the tracer curve from an ideal plug-flow system. If dispersion approaching zero, $D \rightarrow 0$, the system dispersion is negligible, hence approximating plug-flow. If dispersion is considerably larger, $D \rightarrow \infty$, the system is approaching completely-mixed flow conditions.

Systems with a small extent of dispersion are often characterised by a symmetrical shape of RTD curve, whilst a non-symmetrical RTD curve is normally seen for systems with large extent of dispersion (Levenspiel and Turner, 1970). A large dispersion means a large deviation from ideal plug-flow, hence in mathematical terms, a large RTD variance, σ^2. The variance of the RTD is characterised by the dispersive behaviour of the flow created by the distribution of velocities of flow-through (i.e. lateral, longitudinal or vertical mixing) within a system (Kadlec and Wallace, 2009), which can be written in the dimensionless form, σ_θ^2 of:

$$\sigma_\theta^2 = \frac{\sigma^2}{{\tau_m}^2} \qquad [2.37]$$

where σ_θ^2 = dimensionless variance (unitles); σ^2 = system's variance (d^2) and τ_m = mean residence time (d), both of which can be calculated according to moment calculations as shown in Section 2.5.4. Accordingly, system dispersion number, D, for systems with relatively large extent of dispersion ($D > 0.01$), can be calculated according to the appropriate boundary conditions as follows (Levenspiel, 1999):

For closed-closed boundary condition, the relation is given by:

$$\sigma_\theta^2 = 2D - 2D^2\left(1 - e^{-1/D}\right) \qquad [2.38]$$

For open-open boundary condition, the relation is given by:

$$\sigma_\theta^2 = 2D + 8D^2 \qquad [2.39]$$

The boundary conditions appropriate for most treatment wetlands and lagoons, and that gives a tracer curve which is identical to the RTD function, is the closed-closed boundary conditions (Levenspiel, 1972; Fogler, 1992). This implies that no tracer can diffuse back from the wetland into the inlet pipe or up the exit structure at the wetland outlet (Kadlec and Wallace, 2009). In a reactor open to diffusion, like a stream or a river, the hydraulic pattern would be directly influenced by the upstream and downstream mixing conditions and the appropriate boundary conditions is termed the open-open boundary conditions (Fogler, 1992). Therefore, for closed-closed boundary condition, it can be seen that system dispersion number and dimensionless variance are exponentially related as given in Eqn. 2.38. Thus, the greater the dispersion number, the more it deviates from an ideal plug-flow. In theory, poorer hydraulic performance can be anticipated as flow deviates significantly from this ideal.

There is a way of justifying the use of plug-flow with dispersion (PFD) model rather than to use the TIS model, which is based on the system dispersion number, D. Evaluation of system dispersion number may be made to classify the extent of a system dispersion i.e. whether it appears to be small ($D < 0.01$) or large ($D > 0.01$) deviation from plug-flow (Levenspiel, 1999). An acceptable intermediate axial dispersion limit for applying PFD models within treatment wetlands is $D < 0.025$ (Kadlec and Wallace, 2009). Levenspiel (1972) reported $D < 0.01$ for systems with a relatively small extent of dispersion from ideal plug-flow. Regardless of wetlands and lagoons, $0.10 < D < 0.97$ was found, indicating a relatively large amount of dispersion within the investigated mine water treatment systems, hence this model was not chosen for representing the tracer flow-through across the systems. Kadlec (1994) reported $0.07 < D < 0.35$ for free water surface (FWS) wetland systems, which also falls within the relatively large dispersion range. Thus, Kadlec and Wallace (2009) concluded that generally, neither FWS nor horizontal sub-surface flow (HSSF) wetlands are within the acceptable mixing range for the PFD model application, with the exceptions in a few cases of HSSF wetlands. The PFD model is only infrequently applicable to treatment wetlands as it predicts features not seen in practice e.g. unrealistically instantaneous concentration drop at wetland inlet. Therefore, Kadlec and Wallace (2009) again concluded that the PFD model is not an acceptable alternative for most treatment wetland situations.

2.6.3 Tanks-in-series (TIS) model

The TIS fit for residence time distribution is represented by the gamma probability density function (Levenspiel, 1972; Lee and Wade, 1994; Kadlec and Wallace, 2009). This is regarded as a reliable tool for analysing the tracer RTDs, and is characterised by the number of continuously-stirred tank reactors (CSTR) in series and a mean residence time. Gamma distribution function, *g*(*t*) is a two-parameter probability density function, comprising of α (shape parameter) and β (scaling parameter), given as:

$$g(t) = \frac{1}{\beta^{\alpha}\Gamma(\alpha)} t^{\alpha-1} exp\left(-\frac{t}{\beta}\right) \qquad [2.40]$$

Because the distribution of residence time, *E(t)* is typically assumed to follow the hydrodynamic principle of a number of CSTR in series, Eqn. 2.41 can be used to represent the RTD function with a known number of CSTR, n and the residence time, τ_i, (substituting for α and β, respectively from Eqn. 2.40) which can be written as:

$$E(t) = g(t) = \frac{1}{{\tau_i}^{n}\Gamma(n)} t^{n-1} exp\left(-\frac{t}{\tau_i}\right) \qquad [2.41]$$

where *g(t)* = gamma distribution for residence time (d^{-1}); *Γ(n)* = gamma function of *n,*= $\int_0^{\infty} t^{N-1}\, exp(-\mathrm{t})\, dt$, to allow n being accounted as a non-integer variable, or (*n*-1)!, if n is an integer (d^{-1}); n = number of tanks-in-series (unitless); t = time (d); τ_i = mean residence time in one tank (d). Note that this equation is an equivalent form of Eqn. 2.40. Accordingly, the resulting parameters from the gamma distribution function for tracer RTD are given as the following:

i) mean residence time for the whole system, $\tau_m = n\,.\tau_i$

ii) spread of tracer from the mean, $variance = n\,.{\tau_i}^2$

iii) time for the peak tracer, $mode = (n-1)\tau_i$

For a TIS model, the mean residence time for the whole system is the result of a number of equally sized (same volume), well-mixed tanks-in-series and the mean residence time in each tank, τ_i (V_i/Q) (Kadlec, 1994), which can also be written as:

$$\tau_m = \frac{nV_i}{Q} \qquad [2.42]$$

where V_i = volume in each tank (m^3); Q = flow rate (m^3/d), therefore giving $\tau_m = n\tau_i$. Accordingly, Eqn. 2.41 can be written in the form of (by substituting $\tau_i = \tau_m/n$) (Kadlec and Wallace, 2009):

$$E(t) = g(t) = \frac{n^n}{{\tau_m}^n \Gamma(n)} t^{n-1} exp\left(-\frac{nt}{\tau_m}\right) \qquad [2.43]$$

In order to apply the gamma distribution function, which is available as computer spreadsheet tool e.g. GAMMADIST and GAMMALN in Microsoft Excel (Kadlec and Wallace, 2009), the value of n (shape parameter) and τ_i (scaling parameter) are required for the model to fit with the actual tracer test data. Essentially, the n TIS can be determined from system dimensionless variance, σ_θ^2 using the relation given by Levenspiel (1999) for TIS model as follows:

$$\sigma_\theta^2 = \frac{\sigma^2}{{\tau_m}^2} = \frac{1}{n} \qquad [2.44]$$

therefore, $n = \frac{1}{\sigma_\theta^2} = \frac{{\tau_m}^2}{\sigma^2}$, where σ^2 = variance (d^2); τ_m = mean residence time (d). Obviously these parameters (n and τ_i) can be determined from the moment calculations because the first moment, M_1 yields the tracer mean residence time, τ_m for n tanks-in-series, and the second moment, M_2 yields the variance, σ^2, therefore showing the importance of moment analysis for early estimation of the TIS model parameterisation. τ_i is thus simply obtained from τ_m divided by n. Based on Eqn. 2.44, the inverse relation clearly shows that system dimensionless variance is an important indicator to system number of TIS. In theory, a system with large n TIS is influenced by a low system dimensionless variance, which corresponds to a small degree of flow dispersion, and hence a small extent of deviation from plug-flow. This should ideally be indicative of a hydraulically more efficient system. Systems with small extents of dispersion, for $D < 0.025$, corresponds to about 20 TIS (Kadlec and Wallace, 2009).

The resultant n from TIS model in fact represents the number of tanks necessary to model a real system as n ideal tanks-in-series (Levenspiel, 1972). If $n = 1$, the system simply approximates an ideal continuously-stirred tank reactor (CSTR); if n becomes very large, $n \rightarrow \infty$, the system behaves approximately as an ideal plug-flow reactor. On the other hand, the mode of the RTD (corresponding to the peak time) from TIS model can be described from the relation below (Kadlec, 1994).

$$\frac{\tau_{m-}\tau_p}{\tau_m} = \frac{1}{n} \qquad [2.45]$$

where τ_p = peak time (d).

Following Eqn. 2.43, if the n and τ_m are straightforwardly taken from the values calculated from moment analysis to be used in conjunction with the gamma distribution function, then the resulting parameters from this method will give the results termed as TIS model from moment (Kadlec and Wallace, 2009). Conversely, a more robust approach is to use the least squares (LSQ) method to minimise the summation of squared errors between the TIS model and the observed data. Using this method, the n and τ_i (hence τ_m) values are simultaneously solved for gamma distribution function by SOLVER application in Microsoft Excel to produce the best fit to actual tracer data. The results are termed a TIS model from least squares errors (Kadlec and Wallace, 2009). Whenever there is delay in tracer detection, delayed TIS from least squares method is more appropriate, and is detailed below.

2.6.3.1 TIS model with delay

Inclusion of delay or lag time between tracer injection and first tracer detection has been recommended by many authors (e.g. Kadlec et al., 1993; Kadlec, 1994; Chazarenc et al; 2003). This essentially characterises a transport delay of tracer to reach the system outlet, which approximates the plug-flow fraction of water entering the system (plug-flow zone), with a detention time equalling the lag time (Kadlec et al., 1993). The corresponding volume during the lag time is thus regarded as the volume of the plug-flow zone (Kadlec et al., 1993):

$$V_{pf} = Q\tau_{pf} \quad [2.46]$$

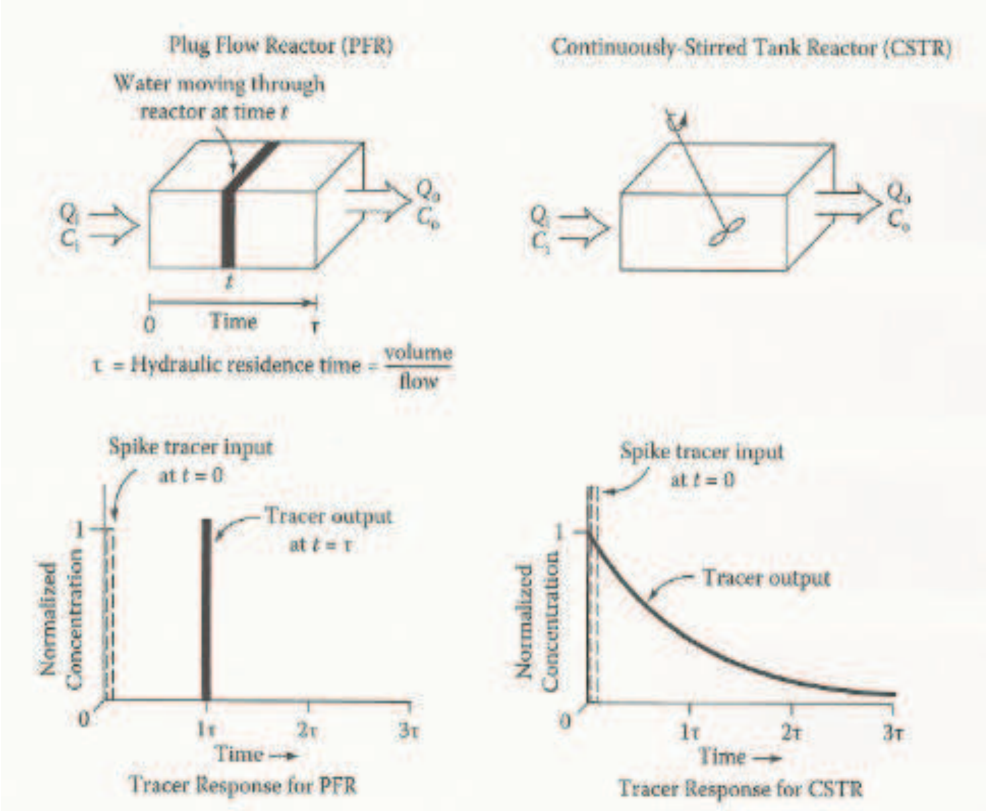
where V_{pf}= volume of plug-flow zone (m^3); Q = flow rate (m^3/d); τ_{pf} = detention time in plug-flow zone (d). Modification of the gamma distribution function is performed in cases with delay in tracer detection, to produce a better fit to actual tracer data. This is termed the delayed TIS model from LSQ (Kadlec et al., 1993; Kadlec and Wallace, 2009).

$$g(t) = \frac{1}{\tau_i(n-1)!}\left(\frac{t-t_D}{\tau_i}\right)^{n-1} exp\left(-\frac{t-t_D}{\tau_i}\right) \quad [2.47]$$

where t_D = delay time (d); τ_i = tracer residence time in one tank (d).

2.6.4 Tracer response in plug-flow reactor (PFR) and continuously-stirred tank reactor (CSTR)

Under plug-flow conditions, the concentration versus time is simply a tracer spike with a very small standard deviation about the mean residence time (Persson, 1999). In other words, a spike input of tracer entering a PF reactor will move through the system with zero mixing and the tracer spike exits the system unchanged (Figure 2.1a) (Kadlec and Wallace, 2009). In a CSTR reactor, the tracer concentration-time distribution is represented by an exponential function (declining tracer output cutve) with a long tail, where the effect of flow dilution progressively reduces the tracer concentration at the outflow (Figure 2.1b) (Persson et al., 1999; Kadlec and Wallace, 2009).



(a) (b)

Figure 2.1 Tracer response in (a) plug-flow reactor and (b) continuously-stirred tank reactor (adapted from Kadlec and Wallace, 2009)

As noted earlier, the residence time distribution within a wetland system may be represented by a TIS model (a model that lies between the idealised extremes of the completely-mixed and plug-flow reactor types). A single CSTR (*n*=1), is an exponential declining function of tracer residence time distribution, while a plug-flow condition is achieved when the number of CSTRs in series increases, approaching infinity (Figure 2.2).

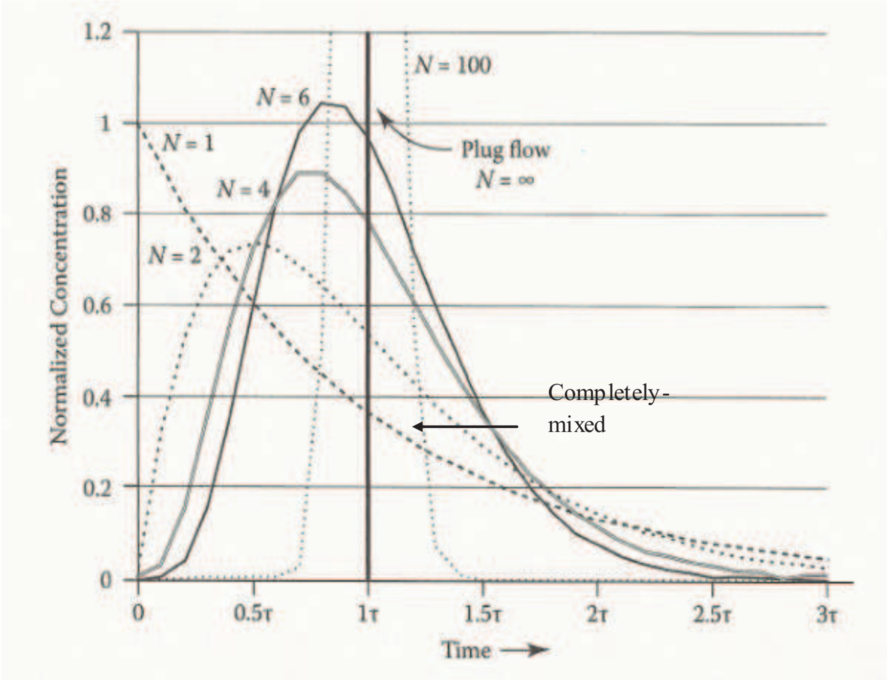
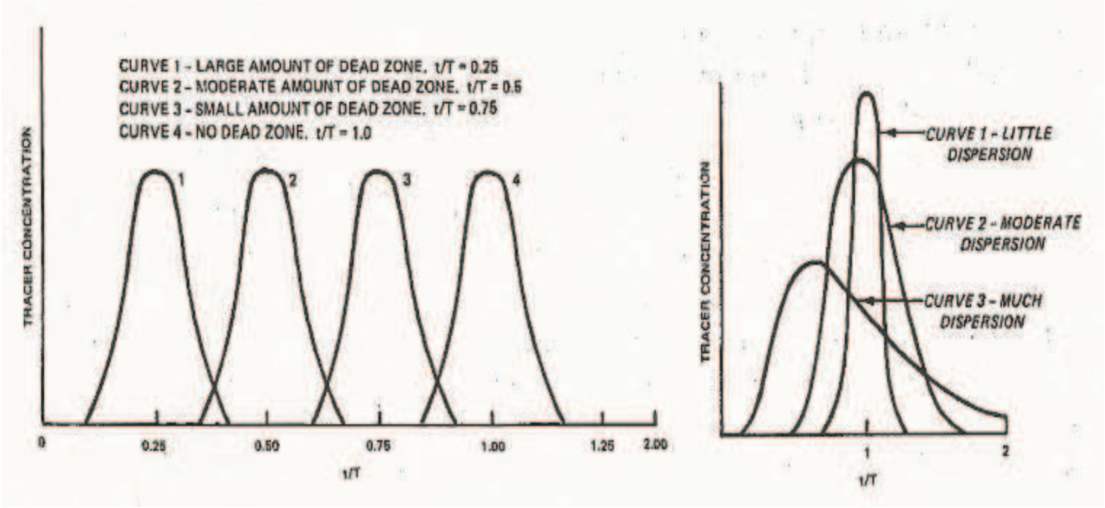


Figure 2.2 Residence time distribution according to tanks-in-series model (adapted from Kadlec and Wallace, 2009)

Between these two conditions, the residence time distribution may take the form of a positively skewed distribution function with the tail of the distribution extending as flow for the entire system approches fully mixed condition (Persson et al., 1999). The extent to which a tracer distribution deviates from an idealised plug-flow is characterised by the spread (standard deviation or variance) of the distribution function. A larger variance may suggest the presence of flow short-circuiting paths and flow re-circulating zones (Persson et al., 1999). This is refected in the degree of mixing of the systems. A large number of CSTRs in series represents a system with a small mixing scale, which has a small RTD spread and approximates plug-flow. As the number of CSTRs decreases, the mixing scale and the spread of the RTD increases (Holland et al., 2004). A large RTD is considered inefficient for a chemical reactor and may be reflected in a low system hydraulic efficiency (Levenspiel, 1972; Persson et al., 1999; Holland et al., 2004; Kadlec and Wallace, 2009). These effects of flow mixing scale (dispersion) and short-circuiting on residence time distribution (RTD) characteristics are shown in Figure 2.3.



(a) (b)

Figure 2.3 Conceptual diagram of the effects of flow (a) short-circuiting and (b) mixing scale (dispersion) on the residence time distribution (adapted from Thackston et al., 1987)

2.7 MEASURE OF SYSTEM HYDRAULIC EFFICIENCY

Hydraulic efficiency is a measure of the ability of a system to uniformly distribute the flow throughout its volume, maximising the pollutants contact time in the system and optimising the ability to attenuate the pollutants (Holland et al., 2004). This also indicates the dispersion characteristics of the system to exhibit the extent of flow deviations from ideal plug-flow (Persson et al., 1999). The hydraulic efficiency of a treatment system, however, is often limited by flow short-circuiting effects and the presence of stagnant dead zones, which results in some fractions of water moving too quickly or slowly towards the system outlet, as described earlier.

Ideally, a hydraulically efficient system will have a longer retention time and be capable of ensuring a well-distributed flow, and thus a better removal efficiency as a consequence. Thackston et al. (1987), Martinez and Wise (2003b), and Mena et al. (2008) among others, expressed hydraulic efficiency for the investigated shallow basins and treatment wetlands as:

$$e_\lambda = \frac{t_m}{t_n} = \frac{V_{eff}}{V} \qquad [2.48]$$

where t_m = actual mean residence time (d); t_n = nominal residence time (V/Q) (d); V_{eff} = system effective volume; (m^3) V = system nominal volume (m^3); Q = flow rate (m^3/d). The presumption for this ratio of actual mean residence time to volumetric nominal residence time is that there is a portion of system volume not involved in the flow-through, most likely due to the presence of stagnant dead zones, resulting in a lower effective system volume than the total volume (Thackston et al., 1987). Consequently, the mean residence time would normally be less than the volumetric nominal residence time.

According to Persson et al. (1999), hydraulic efficiency of wetlands and ponds is computed from system effective volume ratio (e_v) and the amount of mixing, which corresponds to system deviation from ideal plug-flow, expressed as (1 - $\frac{1}{n}$).

$$e_\lambda = e_v\left(1-\frac{1}{n}\right) = \left(\frac{t_m}{t_{an}}\right)\left(1 - \frac{t_m - t_p}{t_m}\right) \qquad [2.49]$$

where $e_v = \frac{t_m}{t_{an}} = \frac{V_{eff}}{V}$, an expression that equals the hydraulic efficiency (Eqn. 2.48); n = number of tanks-in-series (unitless); t_p = peak residence time (d). It can be seen that the second expression of hydraulic efficiency (Eqn. 2.49) is likely more appropriate than the first as it simultaneously takes into account the mixing characteristics of water movement, showing the behaviour of system dispersion for a particular water travel time in the system. Kadlec and Wallace (2009) expressed the term $\left(1-\frac{1}{n}\right)$ as the residence time distribution efficiency (e_{RTD}), therefore hydraulic efficiency for constructed wetlands is as given in Eqn. 2.50 (after Persson et al., 1999), reflecting both the fractions of water involved in the flow-through and the mixing characteristics of water movement characterised by the behaviour of system dispersion.

$$e_\lambda = e_v . e_{RTD} \qquad [2.50]$$

where e_{RTD} = residence time distribution efficiency = $\left(1 - \sigma_\theta^2\right)$; σ_θ^2 = system dimensionless variance, $\frac{\sigma^2}{{t_m}^2}$ (unitless); σ^2 = tracer flow variance. Note that the term $\left(1 - \sigma_\theta^2\right)$ is an equivalent form of $\left(1-\frac{1}{n}\right)$, and thus simply relate the system dimensionless variance, $\sigma_\theta^2 = \frac{1}{n}$, as discussed in section *2.6.3.1.*

With regard to the details presented in section 2.4-2.7 above, it is worth noting that tracer tests offer a means of better understanding the processes controlling the performance of treatment wetlands (and/or systems similar to them) (Kadlec and Wallace, 2009). Undoubtedly, neither ideal plug-flow nor completely-mixed conditions prevail in real wetlands and ponds, and thus a tracer test can be a measure to account for the extent of the non-ideal flow movement across the systems. Much could be gained from such hydraulic tracer test results, an assessment of which enables a better understanding of the actual flow movement carrying pollutant to be treated in a wetland system or pond. A single injection of tracer into system influent and monitoring the outlet concentration is a simple means of accomplishing this. Note again that the aim of conducting a tracer test is to determine the distribution of residence times for the wetlands/ponds which is indicative of the deviation of flow from ideal condition. This deviation is represented by the metric of volumetric and hydraulic efficiencies (e_v and e_{RTD}), the combined metric termed the hydraulic efficiency (e_λ). Furthermore, tracer results enable application of a new generation of models that are better describing systems over a wide range of operational conditions (Kadlec and Wallace, 2009) and is therefore a useful approach to an efficient design of treatment wetlands and ponds. Fundamentals for these have been detailed in section 2.3 to 2.7 above. Examples of the modelling data are presented in Appendix E.

2.8 HYDRAULIC RESIDENCE TIME AND SYSTEM PERFORMANCE

2.8.1 Hydraulic residence time

Hydraulic residence time is one of the principal results derived from tracer tests. The hydraulic residence time is an estimate of the average time water requires to flow completely across a water system. In order to achieve effective treatment, residence time must be greater or equal to the reaction time needed to achieve desired effluent concentration (Interstate Technology and Regulatory Council, 2003). The required residence time is a function of degradation or removal rate to meet the target effluent concentration. The greater the residence time, the greater the proportion of solids that will settle in the system. Therefore, measurement of travel time water takes to flow through a system and its flow behaviour will essentially give an indication of the hydraulic performance of the system under which polluted water is being treated.

There are, however, several possible influences that may affect the distribution of residence time in treatment wetlands and ponds, as presented below.

2.8.2 Physical influences on residence time distribution

Topographical features, preferential flow channels and mixing effects may have an impact on wetland flow and may cause disturbances from ideal flow (Kjellin et al., 2007). The most efficient flow is plug-flow, where the entire volume of the wetland is utilised to the same extent and all water parcels spend the same time in the wetland (Persson et al., 1999). Because ideal plug-flow rarely occur in most wetland systems, the presence of non-ideal flow patterns seems to have a great impact on water travel time, and hence on pollutant removal in the treatment systems (Kadlec and Knight, 1996). There are several possible influences on residence time that can affect the overall system hydraulic performance as given below.

2.8.2.1 Dead zones

Performance of hydraulic efficiency of a wetland can be affected by the presence of dead zones, sometimes termed as zones of diminished mixing (e.g. Holland et al., 2004), in which the area of a wetland is not being optimally utilised for pollutant treatment (Thackston et al., 1987; Kadlec, 1994). The abundance of dead zones may reduce the effective volume within a wetland, in turn lowering the hydraulic efficiency of the system (Holland et al., 2004). In addition, the dispersion and water exchange with stagnant zones can also contribute to the increased spreading of residence time and a longer tail of a tracer breakthrough curve (Kjellin et al., 2007). It can also lead to a secondary peak (e.g. Goebes and Younger, 2005). The residence time distribution may also be affected by the flow short-circuiting within stagnant dead zones and from incomplete mixing of flow within the wetland systems (Martinez and Wise, 2003b).

2.8.2.2 Vegetation distribution

The presence of vegetation may influence the characteristics of wetland flow (Holland et al., 2004). Aquatic macrophytes for instance may enhance lateral (Nepf et al., 1997) and vertical (Nepf and Koch, 1999) diffusion and flow movement in a wetland. Vegetation distribution within a treatment wetland may be associated with the spread in water residence times and the observed multiple peaks in the breakthrough curves

(Kadlec, 1990; Kjellin et al., 2007). The heterogeneity in vegetation may cause an increased mean water residence time as a result of flow retention in stagnant zones within the vegetation and bottom sediment (Kjellin et al., 2007). Additionally, the hydraulic inefficiencies of a treatment wetland may be attributed to the non-uniform distribution of vegetation causing non-uniform resistance to flow (Martinez and Wise, 2003b).

2.8.2.3 Water level

The water level in a treatment wetland, either caused by event-driven factors (i.e. rainfall, floods, surface runoff) or controlled by wetland design and management, may also affect hydraulic efficiency (Holland et al., 2004). A study by Holland et al. (2004) indicated that increasing water depth, which corresponds to changing water levels, can have a direct impact on the residence time. As water depth increased, the residence time distribution demonstrated a marked short-circuiting and a larger mixing scale which in turn decreased the hydraulic efficiency of the wetland. Nevertheless, the study found a longer retention time as a result of the increased water depth, which contributed to a relatively larger benefit to treatment performance.

2.8.2.4 Flow pattern

Flow pattern, such as turbulent diffusion, may influence the diffusive and mixing mechanisms at higher flow rates (Holland et al., 2004). However, minor fluctuations in flow may not significantly affect the distribution of residence time (Holland et al., 2004). Analysis of residence time distribution across various flow rates by Werner and Kadlec (1996) also indicated similar effects. Assuming that the treatment ability of a wetland is spatially uniform, fast-moving water undergoes little interaction with wetland sediment and biota, and hence experiences little treatment, while slow-moving water experiences greater treatment. These fast and slow-moving waters mix at the wetland outlet, giving the wetland effluent an intermediate degree of treatment (Martinez and Wise, 2003b).

2.8.2.5 Bottom topography

Basin morphology may also affect dispersion and flow paths through a wetland, potentially influencing the residence time distribution of the wetland (Koshioho, 2003). The variations in the bottom topography of a wetland could either be the result of natural variations when undisturbed land is used, or deliberately constructed variations (Kjellin et al., 2007). The shallow zones for instance may enhance the development of dense emergent vegetation whilst the deep zones can to some extent act as preferential pathways to improve distribution of water in a wetland, hence a better utilisation of wetland volume (Kjellin et al., 2007; Persson et al., 1999). The bottom topography, however, had only a minor impact on the variations of water residence times compared to vegetation distribution effect (Kjellin et al., 2007).

2.9 IRON REMOVAL IN MINE WATER TREATMENT SYSTEMS

2.9.1 Removal of iron in aerobic environments

Mechanisms of iron removal within passive treatment systems differ between aerobic and anaerobic environments. Processes governing aerobic iron removal are primarily of abiotic (purely chemical) reactions whereas in an anaerobic environment the removal processes are governed by the biotic (microbial) reactions (Hedin et al., 1994). In such an aerobic environment, oxidative removal of iron as oxyhydroxides is regarded as an important process in the passive treatment of iron-rich mine water (Younger et al., 2002). Generally, the oxidation and hydrolysis reactions may decrease the concentrations of dissolved Fe^{2+} and Fe^{3+} when mine water flows through an aerobic environment (Hedin et al., 1994). These reactions depend on the availability of oxygen for oxidation reactions, the pH of the water, and the concentration of ferrous iron in the treatment system (Younger et al., 2002; PIRAMID Consortium, 2003). Of these parameters, pH is a critical factor because it influences both the solubility of metal hydroxide precipitates and the kinetics of the oxidation and hydrolysis processes (Hedin et al., 1994).

2.9.1.1 Oxidative removal of iron

The oxidative removal of iron occurs by means of the following reactions to form the ferric hydroxide precipitates (Younger et al., 2002; Hedin, 2008):

Oxidation: $Fe^{2+} + \frac{1}{4} O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2} H_2O$ [2.51]

Hydrolysis: $Fe^{3+} + 2H_2O \rightarrow FeOOH_{(suspended)} + 3H^+$ [2.52]

Settling: $FeOOH_{(suspended)} \rightarrow FeOOH_{(settled)}$ [2.53]

- ***Oxidation of ferrous iron***

The oxidation of ferrous to ferric iron in passive systems can occur by means of abiotic and/or biotic processes. These oxidation processes are greatly dependent on pH of the water i.e. microbial oxidation is important at low pH (e.g. Athay et al., 2001) while abiotic processes dominate at pH > 5 (Hedin et al., 1994; Younger et al., 2002). The abiotic oxidation can be classified as either homogeneous or heterogeneous oxidation as given below.

Homogeneous oxidation:

At pH below 3.5, the homogeneous oxidation is linearly dependent on the concentration of ferrous iron and dissolved oxygen given as (Stumm and Lee, 1961; Stumm and Morgan, 1970; Sung and Morgan, 1980):

$$-\frac{d[Fe(II)]}{dt} = k[Fe(II)]pO_2 \qquad [2.54]$$

where k is the rate constant and has units of $M^{-2}atm^{-1}min^{-1}$; [FeII] is the concentration of total ferrous iron (M) and pO_2 is the partial pressure of oxygen (atm). At pH greater than 4.5, the oxidation reaction is linearly dependent on the concentration of ferrous iron and dissolved oxygen, and on the square concentration of OH^- (Stumm and Lee, 1961; Stumm and Morgan, 1970; Tamura et al., 1976a; Sung and Morgan, 1980; Millero, 1985):

$$-\frac{d[Fe(II)]}{dt} = k[Fe(II)]pO_2[OH^-]^2 \qquad [2.55]$$

where k is the rate constant and has units of $M^{-2}atm^{-1}min^{-1}$; $[OH^-]$ is the concentration of hydroxyl ions (M); [FeII] is the concentration of total ferrous iron (M) and pO_2 is the partial pressure of oxygen (atm). At constant pH and pO_2, Equation 2.55 reduces to a first-order equation (Sung and Morgan, 1980; Davison and Seed, 1983):

$$-\frac{d[Fe(II)]}{dt} = k_1[Fe(II)] \qquad [2.56]$$

where $k_1 = k[OH^-]^2 pO_2$ and has units of min^{-1}. Equation 2.56 integrates to yield:

$$[Fe(II)] = [Fe(II)]_0 \exp(-k_1 t) \qquad [2.57]$$

Thus a plot of *ln* $[Fe(II)]_0/[Fe(II)]$ versus time will be linear with a slope of k_1. Similarly, a plot of $\log_{10}$ [FeII] versus time will be linear with a slope of $-k_1/2.3$ (Davison and Seed, 1983).

Heterogeneous oxidation:

The catalytic oxidation removal of Fe(II) by ferric oxyhydroxide can be explained by a heterogeneous oxidation process. At constant pH and pO_2, the rate is given as (Tamura et al., 1976b; Sung and Morgan, 1980):

$$-\frac{d[Fe(II)]}{dt} = (k_1 + k_2[FeIII])[Fe(II)] \qquad [2.58]$$

where k_1 is the homogeneous rate constant (min^{-1}) and k_2 is the heterogeneous rate constant, which has units of inverse concentration and time ($M^{-1}min^{-1}$). Additionally, the heterogeneous rate constant is dependent on the surface rate of Fe(III) oxyhydroxide, oxygen concentration in solution and the adsorption constant of ferrous iron onto ferric hydroxide (Tamura et al., 1976b):

$$k_2 = k_s[O_2]K/[H^+] \qquad [2.59]$$

where k_s is the surface rate of Fe(III) oxyhydroxide ($M^{-1}min^{-1}$); O_2 is the concentration of oxygen in solution; K is the adsorption constant of ferrous iron onto ferric hydroxide ($10^{-4.85}$). At lower pH values, the surface rate is slow and the adsorption of ferrous iron is less favourable, hence slower oxidation rate. However, this autocatalysis process could be noticeable only for pH around 7 and above (Sung and Morgan, 1980). At high pH values such as those created in chemical treatment systems, the homogeneous reaction dominates (Hedin, 2008). Additionally, the extent of Fe(II) sorption increases with increasing reaction time, pH and decreasing Fe(II)-to-sorbent ratio (Park and Dempsey, 2005; Nano and Strathmann, 2006).

It is worth noting that the kinetics of Fe(II) oxidation is highly pH dependent in which reaction rates increase with increasing pH and hydrolysis of the Fe(II) ion (Millero, 1985; Barnes et al., 2009). pH is still an important control on the rates of Fe(II) oxidation within the circum-neutral range (Park and Dempsey, 2005). For instance, the half-life of Fe(II) is changing from days to seconds over the circum-neutral pH range (D.J. Sapsford, Cardiff University, pers. comm.). Thus, this may have implications on the variations in iron removal rates often seen even in the net-alkaline mine water pH range, such as those observed between the lagoons and wetlands studied.

- ***Hydrolysis of ferric iron***

The rate of ferric iron hydrolysis is rapid at pH greater than 4 (e.g. Singer and Stumm, 1970), where the dissolved ferric iron is removed from the solution by the formation of iron oxyhydroxide. In contrast, the rate is very slow at pH below 3 (Younger et al., 2002). Within this low pH range, ferrous iron is oxidised to ferric iron by microbial oxidation, but the formation of solid hydroxide iron is limited by the slow kinetics of hydrolysis at this low pH level (Younger et al., 2002).

- ***Settlement of ferric oxyhydroxide solids***

The processes governing iron settlement within a passive treatment system can be attributed to the following mechanisms (Younger et al., 2002):

i) Settlement of ferric hydroxide from aqueous suspension. This process predominates where neutralised and thoroughly oxidised mine waters are retained in ponds
ii) Physical filtration of colloidal ferric hydroxide from solution by fixed solids (e.g. plant stalks and roots, fibrous wetland materials or non-biological filter media)
iii) Formation of iron plaque on roots and rhizomes of wetland plants. Ferrous iron dissolved in the sediment pore waters oxidised in the vicinity of the roots and rhizomes and precipitates as ferric hydroxide coatings (iron plaques) on the plant material (e.g. Batty, 1999)
iv) In situ accretion of ferric hydroxide by means of surface-catalysed oxidation of ferrous iron (SCOOFI). The sequence of SCOOFI process may include (e.g. Jarvis and Younger, 2001):
    a. Adsorption of dissolved ferrous iron by existing ferric hydroxide present in the substrate
    b. Ferric hydroxide surface itself acts as a powerful catalyst for the oxidation of the adsorbed ferrous iron to ferric iron
    c. In situ hydrolysis of the ferric iron forming new surface layer of ferric hydroxide which can then adsorb more ferrous iron and reinitiate the cycle

2.9.2 Rate limiting processes for iron removal in aerobic mine water treatment systems

In general, the investigated mine water treatment systems are naturally alkaline (rather than generated through pre-treatment with limestone e.g. Hedin et al., 1994) and the primary pollutant of concern is iron. In such cases, passive treatment is reliably adopted for alkaline iron-contaminated waters by means of precipitation of iron as oxyhydroxide solids, while pH is maintained at 6-8 by bicarbonate buffering (e.g. Hedin et al., 1994; Stark et al., 1994; Dempsey et al., 2001; Nuttall, 2002; Younger et al., 2002; Hedin, 2008). Under aerobic and alkaline conditions such as those investigated in this study, oxidative removal of iron becomes the most important process, and is generally explained by the three steps; i) oxidation of ferrous to ferric iron ii) hydrolysis of ferric to a suspended iron oxyhydroxide solid iii) precipitation (settlement) of ferric oxyhydroxides solids as discussed earlier.

The rate limiting process for iron removal depends primarily on pH of the mine water and the concentration of iron and dissolved oxygen (Watzlaf et al., 2001; Dempsey et al., 2001; Younger et al., 2002). The oxidation step is generally considered rate limiting for mine water treatment systems and in many cases for acid mine drainage (Hedin, 2008). Younger et al (2002) reported that at pH values between 3 and 6, iron removal is limited by the oxidation process. Stumm and Lee (1961) also found that iron oxidation is the controlling factor for the removal of iron up to a pH of about 7. Generally, the oxidation process often limits the removal of iron at pH greater than 6 and within available iron concentrations of > 10-20 mg/L. Conversely, the iron removal becomes limited by solid settlement at lower iron concentrations i.e. less than 10 mg/L (Younger et al., 2002), such as those typically occurring at the subsequent treatment unit (e.g. wetland following settlement lagoon) and at the final discharge of a treatment scheme (e.g. Hedin, 2008). For instance, the relative importance of the mechanism of iron settling compared to iron oxidation within a passive treatment system was observed in Marchand passive treatment scheme in Pennsylvania (which consists of a series of settling ponds, followed by a treatment wetland and subsequent mitigation wetland). Even though the removal of 85% of iron within the passive treatment system resulted from the iron oxidation process, particularly in the treatment ponds, the settling of iron within the wetland was regarded as the controlling mechanism on the final discharge quality from the treatment scheme (Hedin, 2008). Clearly, this settlement rate dominance over oxidation in such a wetland system was likely due to the presence of substantially lower ferrous iron in the system i.e. lower than the detection limit, the fact that most iron entering the wetland has been largely oxidised and hydrolysed in the treatment ponds, leaving most of the remaining iron in the form of suspended (particulate) iron for settlement.

2.9.3 Reaction rate model for pollutant removal

Following the flow models for tracer responses as discussed in section 2.6, the corresponding reaction rates for pollutant removal are detailed in this section.

2.9.3.1 Zero-order removal

Assuming that the kinetics of pollutant removal is zero-order (independent of concentration), under steady-state condition, the general reaction rate is given by (Levenspiel, 1972):

$$\frac{dC}{dt} = -k_o \qquad [2.61]$$

where C = pollutant concentration; t = residence time; k_o = zero-order rate constant. Applying this for the removal of pollutant within a system, and assuming a constant flow rate, Q over the entire system area, A the reaction can be written as (Tarutis et al., 1999):

$$Q\frac{dC}{dA} = -k_o \qquad [2.62]$$

Integration of Eqn. 2.62 gives the zero-order pollutant removal which is written as (Levenspiel, 1972):

$$\frac{Co}{Ci} = 1 - \frac{k_o A}{C_i Q} \qquad [2.63]$$

Rearrangement of Eqn. 2.63 and solving for zero-order rate constant, k_o is given as (Hedin, 1994):

$$k_o = \frac{Q[C_i - C_o]}{A} \qquad [2.64]$$

where k_o = zero-order removal constant (g/m^2/d); Q = flow rate (m^3/d); C_i = inlet concentration; C_o = outlet concentration (g/m^3); A = system area (m^2). Note that the k_o in units g/m^2/d is the area-adjusted removal rate as introduced by Hedin et al. (1994).

2.9.3.2 First-order removal

According to the first-order kinetics, the rate of pollutant removal is dependent on pollutant concentration (Kadlec and Wallace, 2009, Tarutis et al., 1999). Because iron removal in wetlands/lagoons (i.e. oxidation, precipitation and settlement) is believed to be first-order with pollutant concentration, zero-order kinetics seems to be less representative of the actual rate of pollutant removal. Thus, according to the first-order chemical kinetics under plug-flow condition, the general reaction rate is given by (Levenspiel, 1972):

$$\frac{dC}{dt} = -kC \qquad [2.65]$$

where C is pollutant concentration, t is residence time and k is first-order rate constant. Integration of Eqn. 2.65 yields the first-order pollutant removal which can be written as (Levenspiel, 1972):

$$\frac{Co}{Ci} = exp^{[-k_v t]} \qquad [2.66]$$

where C_o = outlet pollutant concentration (g/m^3); C_i = inlet pollutant concentration (g/m^3); k_v = volumetric removal rate constant (d^{-1}); t = residence time (d). This approach has been widely applied for removal of biochemical oxygen demand (BOD), nutrients and total suspended solids (Kadlec and Knight, 1996). It can be seen from Eqn. 2.66 that according to the first-order kinetics, pollutant removal is exponentially related to residence time i.e. increase in hydraulic residence time may increase the removal of pollutant (Goulet et al., 2001). Rearrangement of Eqn. 2.66 yields an exponential relationship of pollutant removal efficiency and the residence time which is written as (Tarutis et al., 1999; Goulet et al., 2001):

$$\frac{C_i - C_o}{C_i} = 1 - exp^{[-k_v t]} \qquad [2.67]$$

Goulet et al. (2001) have investigated seasonal metal removals within a wetland treating agricultural and urban wastewater according to this first-order removal and found that a longer residence time has a great impact on metal retention. Nevertheless, the first-order removal model failed to fit the metal retention during summer, fall and winter seasons, and the authors therefore concluded that the removal model is inadequate to predict metal retention on a seasonal basis.

Applying the first-order kinetics for the removal of pollutant within a system e.g. wetland, and assuming a constant flow rate, Q over the entire system area, A the reaction can be written as (Tarutis et al., 1999):

$$Q\frac{dC}{dA} = -k_1 C \qquad [2.68]$$

Integration of Eqn. 2.68 gives the first-order pollutant removal which is written as (Levenspiel, 1999):

$$\frac{Co}{Ci} = exp^{\left[-\frac{k_1 A}{Q}\right]} \qquad [2.69]$$

Rearrangement of Eqn. 2.69 and solving for first-order rate constant, k_1 can be written as (Tarutis et al., 1999):

$$k_1 = \frac{Qln\left(\frac{C_i}{C_o}\right)}{A} \qquad [2.70]$$

where k_1 = first-order removal constant (m/d); Q = flow rate (m^3/d); C_i = inlet concentration; C_o = outlet concentration (g/m^3); A = system area (m^2). Note that this expression is termed the areal first-order removal model, and has been recommended as an improvement method for the design and sizing of wetlands receiving abandoned mine drainage (Tarutis et al., 1999). Note that Eqns. 2.63 and 2.69 above are the derivation of the reaction rates for pollutant removal based on the assumption of ideal plug-flow system. Nevertheless, as noted earlier plug-flow is rarely the case in real system, therefore reliance on this presumption may lead to inaccurate prediction of pollutant treatment within the system. Eqn. 2.69 can be written in accordance with another ideal flow condition, the completely-mixed system which is given as (Levenspiel, 1999):

$$\frac{Co}{Ci} = \frac{1}{\left[1+\frac{k_1 A}{Q}\right]} \qquad [2.71]$$

However, this model may also be inappropriate for use in pollutant removal prediction because actual wetlands or lagoons typically behave as non-ideal systems (i.e. plug-flow with dispersion or a completely-mixed tanks-in-series), therefore neither plug-flow nor completely-mixed pollutant removal principle may adequately apply in most systems (Levenspiel, 1992; Kadlec and Wallace, 2009). According to a tanks-in-series model, the modified first-order removal can be written as (Levenspiel, 1999; Persson and Wittgren, 2003; Kadlec and Wallace, 2009):

$$\frac{Co}{Ci} = \frac{1}{\left[1+\frac{k_{TIS} A}{Qn}\right]^n} \qquad [2.72]$$

where k_{TIS} = TIS first-order removal constant (m/d); n = number of tanks-in-series (unitless). Solving for TIS removal rate constant from Eqn. 2.72 gives (Persson and Wittgren, 2003):

$$k_{TIS} = \frac{Qn\left[\left(\frac{C_i}{C_o}\right)^{\frac{1}{n}} - 1\right]}{A} \qquad [2.73]$$

The kinetics of the tanks-in-series (TIS) removal model originates from the principle that pollutants are being treated through a number of a series of completely-mixed tanks. The model apparently represents a non-ideal pattern of flow carrying polluted water, which is to compensate for the drawback of models assuming ideal plug-flow or completely-mixed conditions. Note that this TIS removal model is principally based on the first-order removal kinetics which is dependent on pollutant concentration. As evidenced by Goulet et al. (2001), the failure of first-order removal model to predict metal retention was attributable to the seasonal variations within the investigated wetland system that favour the occurrence of non-ideal flow patterns. Deviation from plug-flow has affected the degree of treatment received, and thus resulted in the failure of the first-order removal model to describe performance. It has been noted earlier that ideal flow conditions such as plug-flow and completely-mixed flow are rarely satisfied in actual treatment wetlands and/or lagoons. Kadlec (2000) also criticised the use of first-order removal for the design of sewage treatment wetlands, fundamentally because the plug-flow assumption is rarely the case in actual systems, and that the extent of treatment received differs for fast and slow moving water, suggesting the effects of non-ideal flow behaviour. The flow movement within the investigated mine water treatment systems have been shown to follow the principle of a number of completely-mixed tanks-in-series (TIS flow model) as discussed in section 4.4 of Chapter 4, and may better describe the pollutant removal in such systems. Wallace et al. (2008) stated that the first-order TIS model is considered one of the best compromises between both non-ideal hydraulics and pollutant removal. This model, however, has not been widely adopted by practitioners due to its complexity and the data required to adequately apply the model for sizing of a treatment system (Jamieson et al., 2007).

2.10 DESIGN AND SIZING OPTIONS FOR MINE WATER TREATMENT SYSTEMS

2.10.1 Design and sizing of passive mine water treatment systems

Design and sizing of passive systems should ideally be based on the reaction rates of pollutant removal processes as they relate to both the chemical and hydraulic conditions (Younger et al., 2002). According to Kadlec and Wallace (2009), there are three ways of estimating performance and sizing of treatment wetlands/ponds. This could either be based on pollutant and hydraulic loading of the system, adoption of first-order removal models, or the use of regression equations that link several treatment performance parameters. To date, sizing tools for wetlands treating mine water discharges within the UK Coal Authority's mine water treatment systems is still based on zero-order removal rate, that subsequently gives the area required for the system. The use of estimated retention time has also been widely applied to the design of settlement lagoons (PIRAMID Consortium, 2003). The use of the zero-order removal model, also known as the area-adjusted removal method, for sizing of mine drainage treatment systems has been recommended by Hedin et al. (1994). Despite being widely used for mine water treatment system design, criticisms of the use of this method have been fundamentally because it takes no account of pollutant concentration effects on the removal rate (Tarutis et al., 1999; Kadlec and Wallace, 2009).

Adoption of a first-order removal model that considers the effect of pollutant concentration on the rate of removal is likely more reliable for sizing of wetlands treating mine water discharges (Tarutis et al., 1999). However, it should be noted that the first-order removal model (Eqn. 2.70) is in fact derived from the assumption of plug-flow system, which is rarely the case in actual mine water treatment wetlands and lagoons. Therefore, Kadlec and Knight (1996) extended the applicability of first-order removal based on several assumptions including the plug-flow. On the other hand, Kadlec (2000) criticised the use of first-order expressions for the design of sewage treatment wetlands, reasoning that the plug-flow assumption does not apply for such systems and that the contaminant removal processes differ between the fast- and slow-moving zones within the wetland. Goulet et al. (2001) investigated the applicability of first-order removal for a wetland treating agricultural and urban runoff, and found poor fits of the model to most of the observed data. The reason for this is that the seasonal variations greatly affected the ideality of the flow i.e. causing non-ideal flow patterns during summer and fall, thus affecting the extent of treatment received by the pollutants. Younger et al. (2002) have shown that the use of first-order removal formula based on Tarutis et al. (1999) may result in four times larger system area for an aerobic wetland than if designed using the area-adjusted removal formula (although this may vary from site to site). This reflects the fact that acquiring such a large land area needed particularly in the UK where land availability is limited is often of issue (Younger et al., 2000).

Therefore it is possible that the use of relative reaction rate for pollutant removal according to a tanks-in-series model would be a better option for the design and sizing such systems (e.g. Persson and Wittgren, 2003). This approach does take account of the flow pattern across a system, in addition to the first-order kinetics for iron removal. However, use of first-order removal formula requires a reliable removal rate constant value to appropriately design the systems.

2.10.2 Derivation of system sizing tools for mine water treatment systems

The use of a particular model for the sizing of wetland and/or lagoon is essentially dependent on the kinetics of pollutant removal i.e. whether removal rate is dependent or independent of pollutant concentration, and the ideality of the system i.e. whether to assume ideal (plug-flow or completely-mixed) or non-ideal flow (e.g. plug-flow with dispersion or series of completely-mixed) system, as discussed earlier. The principles for derivation of sizing formulas of treatment system regardless of ideal or non-ideal conditions are discussed in the following paragraphs.

Assuming that the pollutant removal within a system is independent of pollutant concentration (zero-order kinetics) and under steady-state condition yields the following expression (Levenspiel, 1972):

$$\frac{C_o}{C_i} = 1 - \frac{k_o A}{C_i Q} \qquad [2.74]$$

where Co = outlet concentration (g/m^3); Ci = inlet concentration; k_o = zero-order removal rate (g/m^2/d); A = system's area (m^2); Q = flow rate (m^3/d). Rearrangement of Eqn. 2.74 above for determining the system area produces an expression written as (Hedin et al., 1994):

$$A = \frac{Q[C_i - C_o]}{k_o} \qquad [2.75]$$

where k_o = zero-order removal rate constant (g/m^2/d), known as the area-adjusted removal as introduced by Hedin et al. (1994). If pollutant removal is dependent on pollutant concentration (first-order kinetics) and in accordance with the plug-flow model yields (Levenspiel, 1999):

$$\frac{C_o}{C_i} = exp\left[-\frac{k_1 A}{Q}\right] \qquad [2.76]$$

where k_1 = first-order removal constant (m/d). Rearrangement of this equation results in system area given as (Tarutis et al., 1999):

$$A = \frac{Qln\left[\frac{C_i}{C_o}\right]}{k_1} \quad [2.77]$$

Note that this equation is the first-order removal as suggested by Tarutis et al. (1999) as the improvement model to the area-adjusted removal, which is essentially based on the plug-flow assumption. Taking into account the non-ideality of a system that behaves as a number of completely-mixed tanks-in-series, and assuming first-order removal kinetics yields (Levenspiel, 1999; Persson and Wittgren, 2003):

$$\frac{C_o}{C_i} = \frac{1}{\left[1+\frac{k_{TIS}\,A}{Qn}\right]^n} \quad [2.78]$$

where k_{TIS} = first-order TIS removal constant (m/d), same unit as the first-order removal constant based on plug-flow model. Rearrangement of Eqn. 2.78 and solving for system area gives :

$$A = \frac{Qn\left[\left(\frac{C_i}{C_o}\right)^{\frac{1}{n}}-1\right]}{k_{TIS}} \quad [2.79]$$

where k_{TIS} = first order removal rate (m/d); n = number of CSTR in series. It can be seen that this expression does gives an area determination which strongly relies on the number of CSTR, n in series rather than only the concentration, flow and a constant removal rate as that of zero and first-order, plug-flow principle. Clearly, n is an indication of the system hydraulic characteristics i.e. the extent of flow deviation from ideal system, therefore showing a more realistic representation of the actual hydraulic performance as well as the intended pollutant treatment during sizing of the system.

2.10.3 Applicability of system sizing formula

The use of either zero or first-order removal principle for the sizing of treatment system requires the knowledge of pollutant concentration, flow rate and the removal rate constant i.e. k_o, k_1 (Tarutis et al., 1999). Moreover, in order to apply the tank-in-series pollutant removal model, the n, number of CSTR in series needs to be known in addition to the removal rate constant, k_{TIS}. The recommended values for k_o relies on the nature of the polluted mine discharges to be treated i.e. whether influent water is net-alkaline or net-acidic (Hedin et al., 1994). The area-adjusted removal rate constant, k_o has been empirically developed by Hedin et al. (1994) for wetland systems receiving net-alkaline mine water from abandoned mine workings, which is

20 g/m^2/d for iron and 1 g/m^2/d for manganese removal. In cases of influent mine water being net-acidic in nature, the suggested value for acidity removal is 7 g/m^2/d, also for abandoned mine discharges. These constant removal rates have been succesfully used for the design and sizing of wetlands treating abandoned mine discharges under net-alkaline and net-acidic conditions within UK passive mine water treatment systems (Younger et al., 2002; PIRAMID, 2003). The value of first-order removal constant, k_1 as proposed by Tarutis et al. (1999) is 0.18 m/d for iron removal, even though reliance on this value for use in design of constructed wetlands is not certain, as the k_1 was derived from natural wetlands varying in system chemistry and ecosystem characteristics. Yet, the k_1 value typically deviates from this constant value, particularly for systems differing in inflow characteristics from which the k_1 was derived e.g. Kadlec (2000) and Goulet et al. (2001). Thus, the first-order removal principle may only be used if a reliable k_1 value is available, or by relating the k_1 with various wetland physical, chemical and biological attributes (Tarutis et al., 1999). This is somewhat related to recent work by Sapsford and Watson (2011), in which a pH-dependent first-order removal rate constant have been developed for typical mine water conditions in the UK, and are found to be in the range of 0.04 d^{-1} (pH 6)-372 d^{-1} (pH 8) for first-order oxidation rate constant, and 12.5 d^{-1} for first-order sedimentation rate constant. This retention time-based approach seems to be appropriate for it takes into account the chemical characteristics of mine water i.e. pH, dissolved oxygen and temperature, and is based on the first-order kinetics for iron removal.

2.11 SUMMARY

Current design practice for aerobic wetlands treating net-alkaline mine waters in UK applications are based on the zero-order kinetics for pollutant removal i.e. the commonly used area-adjusted removal as recommended by Hedin et al. (1994). Lagoons are design to allow nominal 48 hours of retention time. However, there have been limited studies that investigate the effectiveness of the use of these methods in UK applications. A knowledge that iron removal under aerobic conditions follows first-order kinetics model for pollutant removal has been the basis for a recommended alternative method for the design of such systems (i.e. first-order removal model by Tarutis et al, 1999). Both of these approaches are based on the plug-flow assumption, which is not the case in real systems. An increasing knowledge of the hydraulic behaviour (e.g. flow pattern across a treatment system) requires a better understanding of the hydraulic factors relating to treatment system performance. Such an assessment has not been widely explored in UK mine water treatment systems. The extent to which actual systems deviate from an ideal flow pattern is the subject of study here. Therefore, it is the intention of this study to evaluate the conditions under which mine water treatment systems perform well in terms of hydraulic efficiency and efficient rates of contaminant removal, and evaluate the appropriateness of current, and alternative system sizing methods in light of the new insights gained.

Apparently, one of the limitations of the current design practice for passive mine water treatment systems is that the hydraulic residence time is not being accounted for in the performance assessment of such systems. This has significantly led to limited understanding of this hydraulic behaviour of the treatment systems which, together with the knowledge of the geochemical processes governing pollutant removal, are central in the assessment of the overall treatment system performance. Such an understanding will be useful for improvement of existing treatment system performance and in the design of future systems. Assessment of the hydraulic behaviour (e.g. residence time and hence the flow pattern) across the treatment systems can be accomplished by means of conducting tracer tests. Fundamental issues and theories relating to tracer test implementation have been detailed in section 2.3-2.7. Thus, this study attempts to investigate this hydraulic flow behaviour in actual mine water treatment systems and how this may have an impact on pollutant removal and on the design of such systems. Theoretical background for iron removal processes and the bases for design of such systems have been detailed in section 2.9-2.10.

As noted earlier, the hydraulic flow behaviour through a mine water treatment system is a significant measurement of system hydraulic performance. However, its relationship to pollutant removal has not been widely assessed. It is believed that greater hydraulic efficiency (i.e. longer residence times) should result in an improved rate of pollutant removal. Most of the previous tracer studies (not only in mine water) put their emphases on the interpretations of the tracer used as a sole means for characterising hydraulic behaviour of the systems rather than developing the link between hydraulic and geochemical factors governing treatment system performance (e.g. Lin et al., 2003; Edwardson et al., 2003; Cox et al., 2003; Wolkersdorfer et al., 2005). Thus this study will focus on the effect of different hydraulic flow patterns as they relate to treatment performance efficiencies of the mine water treatment systems studied. Evaluation of system hydraulic assessment is presented in Chapter 4, while the geochemical factors pertaining to treatment performance efficiency is discussed in the earlier parts of Chapter 5 (sections 5.2-5.3). The link between hydraulic and geochemical factors governing treatment system performance is discussed in section 5.4 of Chapter 5, followed by the implications for design of such systems. Theoretical background and fundamentals behind these hydraulic and geochemical factors in relation to passive mine water treatment system performance have been provided in this chapter.

CHAPTER 3

METHODOLOGY

3.0 INTRODUCTION

This chapter details the methods undertaken during the field and laboratory works throughout the study. The field works include water sampling for water quality analysis and a series of tracer tests for assessment of mine water treatment system hydraulic performance (section 3.1 and section 3.2). The laboratory works include the analytical determination of water quality and tracers (section 3.3) and laboratory column experiment for assessment of iron oxidation and settlement rates in mine water (section 3.4).

3.1 FIELD SAMPLING AND MEASUREMENTS

3.1.1 Field sampling and experiments

In line with the objectives of the study, a series of tracer tests were undertaken between July 2008 and July 2010 at eight passive mine water treatment systems operated by the UK Coal Authority. These include field tracer experiments conducted at the mine water treatment sites (Table 3.1) located within Northern England and part of southern Scotland, which consist of mine water treatment wetlands and settlement lagoons (as described in Chapter 1). Sampling for water quality analysis and water samples for laboratory column analysis was also undertaken during each field trip (methods detailed in section 3.1.3).

Table 3.1 Locations of mine water treatment systems where sampling and tracer tests were undertaken

Site	County	Passive treatment	Tracer test
Lambley	Northumberland	Wetland	July 2008, Nov 2009, Apr 2010
*Acomb	Northumberland	Settlement lagoon, Wetland	Feb, Jun 2009
Whittle	County Durham	Settlement lagoon, Wetland	Feb 2010
Allerdean Mill	Northumberland	Settlement lagoon, Wetland	Dec 2008, Apr 2009
*Bates	Northumberland	Settlement lagoon, Wetland	July 2009
Strafford	South Yorkshire	Settlement lagoon, Wetland	Aug 2009
Mousewater	West Lothian	Settlement lagoon, Wetland	July 2010
Cuthill	West Lothian	Settlement lagoon, Wetland	July 2010

Tracer tests conducted at both settlement lagoon and wetland at each site except *tracer tests conducted at settlement lagoon only

Several factors needed to be taken into account when choosing the potential treatment sites, including:

- The nature of the treatment system – passively treat mine water with alkaline pH (enable the assessment of system performance whenever pH and dissolved oxygen are not limiting)
- Site-specific restrictions – was it possible to inject the intended tracers without interfering with surrounding areas e.g. nearby receiving systems and public
- Site security – was it secure to leave equipment over the duration of tracer test
- Feasibility – easily accessible for deployment of tracer test and the number of influent and effluent points (e.g. monitoring a tracer test at treatment system with multiple influents and/or effluents may be difficult)

3.1.2 In –situ field measurements

Prior to commencement of any sampling and tracer experiment, major physicochemical parameters were first measured using a calibrated Myron L Ultrameter for pH, redox potential (Eh) in units mV, electrical conductivity (EC) in units µS/cm and water temperature in units ^{o}C. Calibration for pH was performed in the laboratory using VWR Colour-key buffer solutions at pH 4.0, 7.0 and 10.0 to an accuracy of ±0.01 pH units. Conductivity was calibrated using calibration standard at 1413 µS/cm to an accuracy of 1%. Sample alkalinity was measured using a HACH digital test kit with 1.6 N sulphuric acid titrated into a 100 mL sample with Bromocresol Green Methyl-Red indicator (to pH 4.5 end point). Alkalinity was measured in units mg/L as $CaCO_3$. Several measurements were taken and average values determined (see Appendix C).

3.1.3 Water sampling

Samples for water quality analysis were collected in pre-washed (soaked overnight in 10% HNO_3 (v/v), washed three times with tap-water, then three times with 18.2 Ω MilliQ deionised water) polypropylene bottles. 125 mL bottles were used for collection of mine water samples at each inlet and outlet of treatment system for analysis of major ions and metal concentrations:

- Unfiltered samples (acidified with 1% by volume concentrated HNO_3) were collected for total cations and metal analysis

- Filtered (with 0.2 µm cellulose nitrate membrane filters) and acidified (with 1% by volume concentrated HNO_3) samples collected for dissolved cations and metal analysis
- Unacidified samples collected for anions analysis
- Additionally, filtered samples (with 0.2 µm cellulose nitrate membrane filters) for Fe speciation were collected (acidified with 1% by volume concentrated HCl) for analysis of dissolved Fe (II) and Fe (III)

Samples of water from each inlet and outlet of treatment system were also collected in 20 L polyethylene carboys for laboratory analysis of iron oxidation and settlement rates. All samples were kept in the cold room at 4°C prior to analysis and analysed within 1 week of sampling. Efforts were made to ensure that samples for Fe speciation were analysed on the same day as collection to prevent rapid Fe^{2+} oxidation and hydrolysis of Fe^{3+}. The 0.2 µm filters were used as colloidal solids (e.g. Fe and Al hydroxides) may pass through the 0.45 µm filters (Appelo and Postma, 2005; Hedin, 2008). Replicate samples were taken periodically for analytical precision check at 10% accuracy in accordance with Quality Assurance/Quality Control (QA/QC) procedures detailed in APHA (1988). Reliability of sample analyses was tested by charge balance calculations. An electro-neutrality within ± 5% was considered to be of suitable accuracy but up to ± 10% is acceptable (Appelo and Postma, 2005) (see Appendix C).

3.1.4 Flow measurements

This section details the choice of flow measurement methods for point discharges of mine water i.e. open channels and pipes such as those encountered in the investigated treatment systems. Appropriate methods were chosen based on site-specific conditions at each discharge and the intended level of accuracy. Knowledge of the expected flows and limitations of each method may also help in selecting appropriate technique.

3.1.4.1 Bucket and stopwatch

This method is the simplest approach for measuring flow for mine water discharges through a pipe or a channel. Measurements were made using a bucket of a known volume (typically around 10L) and a stopwatch to record the time to fill the bucket. Measurements were done at least 3 times (average was taken) for accuracy of measurement and ensured that water filled the bucket without having it overflow. Flow rate was simply calculated as the time needed to fill the volume:

$$Q = \frac{V}{\Delta t}$$

where Q = flow rate (L/s); V = volume of bucket (L); Δt = time to fill the bucket (s). Measured flow rate was taken within 5-10% precision, which is typically acceptable for discharges ≤ 1L/s (PIRAMID Consortium, 2003) or up to 3 L/s (Brassington, 2007) or 8 L/s (Wolkersdorfer, 2008).

3.1.4.2 Thin-plate weirs

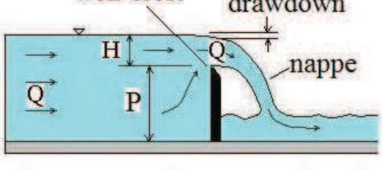
Weirs are control structures constructed by restricting the size and depth of the channel. This creates a raised upstream sub-critical flow, critical flow over the weir and super-critical flow downstream. For small streams or narrow man made channels, thin-plate or sharp-crested weirs are typically used. When measuring the flow, upstream head is related to the discharge over the crest of the structure where flow passes through critical conditions (Shaw, 1994; BS 3680-4A:1981) (see Figure 3.1). Thin-plate weirs can either be a V-notch or a rectangular-notch. A 90° V-notch weir is typical although ½ 90° notch or ¼ 90° notch may be used for more accurate lower flow measurements. A rectangular thin-plate weir is particularly appropriate for higher flows (i.e. > 20 L/s) (PIRAMID Consortium, 2003). Proper weir installation can reach up to 1% precision in use. The flow over the weir is proportional to the head of water above the weir notch on the upstream side. For a 90° V-notch, the flow was determined using the formula below (Brassington, 2007):

$$Q = 1.342H^{2.48}$$

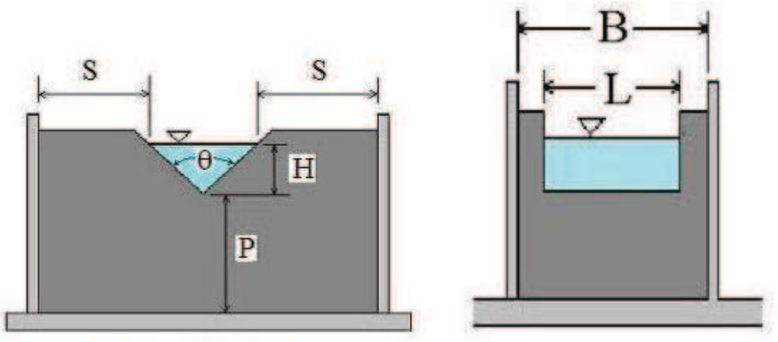
where Q is flow (m^3/s), H is the head of water above the apex of the 'V' (m). The flow over a ½ 90° notch or ¼ 90° is half that over the 90° notch respectively. Alternatively, flow over a rectangular thin-plate weir can be determined as (Brassington, 2007):

$$Q = L[1.83(1 - H)\,H^{1.5}]$$

where L is the width of the rectangular weir (m).



(a)



(b) **(c)**

Figure 3.1 Schematic diagram of (a) flow over sharp-crested weir (Q=flow direction, H=water head, P=height of weir crest) (b) V-notch thin-plate weir (c) rectangular notch thin-plate weir (adapted from Bengtson, 2010)

The water heads were ascertained using water levels data recorded by an Eijelkamp CTD Diver. The Diver semi-continuously measured the water and atmospheric pressure, temperature and conductivity at a point behind a 90° V-notch weir where the water was not disturbed by the sharp notch. The Diver was then adapted to a LoggerDataManager (LDM) software for transfer and reading of the measurements. The actual water heads were taken as the difference between the atmospheric pressure recorded by a BaroDiver and the levels recorded by the CTD Diver for use in the equations above. The CTD Diver is capable of measuring the pressure to an accury of ±0.2 cmH_2O, temperature of ±0.2 ^{o}C and conductivity to 1% accuracy. Measured flow rate (L/s) was taken within 10% precision. When installing the Diver (typically attached to a fixing post), it is important that the Diver benefits from maximum water depth and flow, and that there is sufficient circulation around the Diver's sensor (ensure that the Diver measures the surrounding water). When measuring the flow, it is also essential that the measuring locations are free from contaminants e.g. iron hydroxide precipitates which are often the case in ferruginous mine water that can interfere with the measuring devices.

3.1.4.3 Velocity-area method

Velocity-area method was used whenever alternative methods were not possible e.g. in an open channel at the inlet of treatment system. Even though the width of the channels are relatively small for use of the velocity-area method (i.e. 1 m wide), efforts were made to ensure that flow rates were measured to an accuracy of 10%. Of the entire channel width channel was subdivided into sub-sections (approximately equal interval size) where the water depth and velocity of each sub-section was measured. The water depth was measured using a graduated pole and the flow impeller was set at 0.6 of the depth measured downstream from the surface (this is where theoretically the mean velocity occurs). The velocity was measured using a Valeport Model 801 Electromagnetic Flow Meter suspended in the water pointing in an upstream direction (Figure 3.2). A flat sensor was used for water depth <15 cm and a cylindrical sensor used if depth was >15 cm.

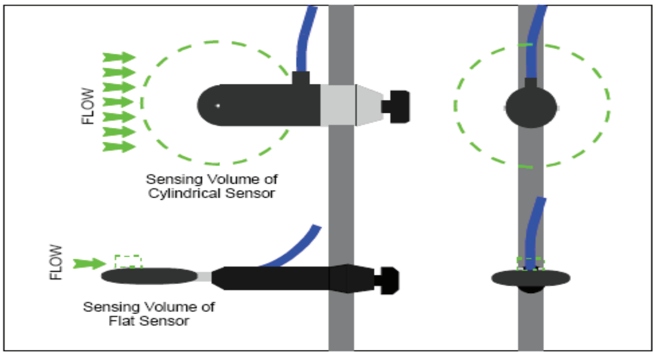


Figure 3.2 Velocity measurement using a flow meter (adapted from Valeport Limited, 1999)

Velocity measurement was allowed for 30 seconds before the reading was recorded with standard deviation less than 10%. Channel width, width of the sub-section, water depths and velocities at the boundaries of a sub-section were recorded. The flow rate was calculated as the sum of average velocity multiplied by the cross-sectional area of each sub-section. Mean-section method was used to calculate the flow rate as given in the formula below (Shaw, 1994) and is illustrated in Figure 3.3:

$$Q = \sum_{i=1}^{n} \frac{(v_{i-1} + v_i)}{2} \frac{(d_{i-1} + d_i)}{2} (b_i - b_{i-1})$$

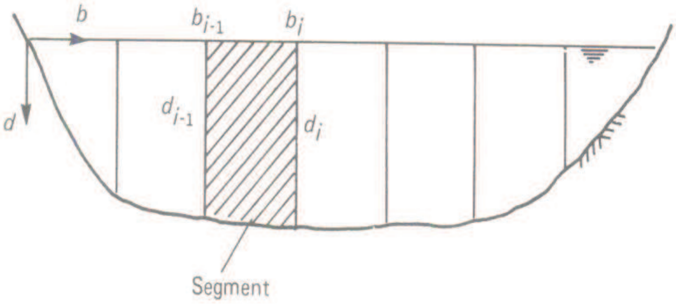


Figure 3.3 Mean-section method of flow measurement (adapted from Shaw, 1994)

3.1.4.4 Flow measurement methods during site monitoring

As described in section 3.1.4, flow measurement method was dependent on site-specific conditions at the discharge. The flow measurement methods used at point discharges of mine water at the investigated treatment systems are summarised in Table 3.2. Flow data are included in Appendix D.

Table 3.2 Flow measurement method at each influent and effluent point of the mine water treatment schemes investigated

Site	**Treatment unit**	**Measurement point**	**Flow measurement device/method**
Lambley	Wetland	Influent	Flow impeller
		Effluent	V-notch weir
Acomb	Lagoon	Influent	Historic flow pumping data*
		Effluent	Historic flow pumping data*
Whittle	Lagoon	Influent	Historic flow pumping data*
		Effluent	Historic flow pumping data*
	Wetland	Influent	Historic flow pumping data*
		Effluent	V-notch weir
Allerdean Mill	Lagoon	Influent	Bucket and stopwatch
		Effluent	Flow impeller
	Wetland	Influent	Flow impeller
		Effluent	V-notch weir
Bates	Lagoon	Influent	Flow impeller
		Effluent	Flow impeller
Strafford	Lagoon	Influent	Flow impeller
		Effluent	Flow impeller
	Wetland	Influent	Flow impeller
		Effluent	V-notch weir
Mousewater	Lagoon	Influent	Flow impeller
		Effluent	Flow impeller
	Wetland	Influent	Flow impeller
		Effluent	V-notch weir
Cuthill	Lagoon	Influent	Flow impeller
		Effluent	Flow impeller
	Wetland	Influent	Flow impeller
		Effluent	V-notch weir

*Flow pumping rate from the Coal Authority (note that at some sites pumps operate intermittently and therefore the mean flow rate for the tracer test period is reported)

3.2 TRACER TEST

3.2.1 Tracer test implementation

The hydraulic residence times of mine water within the investigated treatment systems were determined by conducting tracer tests. Background concentrations were pre-determined from samples taken prior to the tracer experiments (Lin et al., 2003; Wolkersdorfer et al., 2005) so that any changes due to tracer addition could be detected and that the actual mass recovered could be precisely determined. The method employed for the tracer test was the slug tracer injection, where a known amount of tracer was injected into the inlet of the treatment system and complete mixing with the flow was assumed (Kilpatrick and Cobb, 1985). The method is also preferable to the constant-rate injection because of the simplicity of the injection and the fact that less tracer is required (Kilpatrick and Cobb, 1985). To ensure maximum mixing, the tracers were dissolved with the mine water and were poured directly into the turbulent zone at the inlet discharge point (Figure 3.4). Throughout the full series of tracer experiments three types of tracer have been employed; sodium bromide, Na-fluorescein and sodium chloride. Dual-tracer tests were conducted whenever possible for verifying the results (Sherman et al., 2009).

(a) **(b)**

Figure 3.4 Example of (a) tracer injection point at the inlet of a treatment system (b) injection of Na-fluorescein dye and sodium bromide tracers

Samples of mine water were automatically collected by Aquamatic Auto Cell P2 Autosamplers equipped with 24 x 1L polyethylene bottlers (Figure 3.5a) at specific time intervals (estimated based on the system nominal residence time). More than one autosampler was used in cases where longer nominal residence time was expected.

The tracer test typically takes between 24-72 hours, depending on the system nominal residence time. Autosamplers were installed at the inlet (for monitoring iron concentration (and other metals) throughout the tracer test duration and for monitoring background concentration of tracer i.e. bromide). On-site measurement for bromide was not available, but other tracers i.e. Na-fluorescein and NaCl were measured in the field. Outlet autosamplers were installed (for capturing the recovered tracer and for monitoring iron concentration (and other metals) at the effluent). Thus, the removal of iron during the monitored residence time could be determined from the average of iron concentrations monitored at the influent and effluent of system. Samples for water quality analysis (as described in section 3.1.3) were also collected during the tracer tests. Data are included in Appendix C.

(a) **(b)**

Figure 3.5 (a) Collection of water samples using Aquamatic Auto Cell P2 Autosamplers and Na-fluorescein measurement using a Seapoint fluorimeter (b) An Eijelkamp CTD Diver used for semi-continuously recording the water and atmospheric pressure, temperature and conductivity (also for flow measurement as in this case at a point behind the V-notch weir)

Bromide was analysed in the laboratory using a calibrated Dionex 100 Ion Chromatograph (see section *3.3.1.2*). Na-fluorescein was continuously measured in the field using a calibrated Seapoint fluorimeter (detection limit 0.2 μg/L) which was set up to take the concentration readings at 5 minute intervals (Figure 3.5a) and was connected to a Dataron Data Bank data logger for data transfer. Alternatively, the Na-fluorescein was also analysed in the laboratory using a Varian Cary Eclipse Fluorescence Spectrometer (see section 3.3.3), whenever on-site measurement was not possible and/or for verifying the results). The sodium chloride tracer was measured as electrical conductivity which was recorded using an Eijelkamp CTD Diver (Figure

3.5b) at 5 minutes intervals. Flow rate during tracer experiment was measured using various methods as described in section 3.1.4.

3.2.2 Estimation of tracer amount

Following the details in section 2.3.3 of Chapter 2, the amounts of tracer used here were initially estimated by considering the following criteria:

- sufficiently added mass of tracer could at least be detected at the sampling points above the detection limit (Wolkersdorfer, 2005)
- at the time of 95% tracer mass, the tracer would still be detectable above the background concentration (Lin et al., 2003)
- tracer test should last until at least 10% of initial tracer mass added have been recovered (Kilpatrick and Cobb, 1985)
- assuming a complete mixing of tracer with the mine water

Table 3.3 Amount of tracer used during tracer tests; dual-tracer approach typically employed for verifying results

Site	Treatment unit	Tracer	Amount
Lambley	Wetland	NaBr	2.054 kg
		Na-fluorescein	51.34 g
		NaCl	20 kg
Acomb	Lagoon	NaBr	2.165 kg
Whittle	Lagoon	NaBr	1.32 kg
		Na-fluorescein	19.8 g
	Wetland	NaBr	1.44 kg
		Na-fluorescein	10.82 g
Allerdean Mill	Lagoon	Na-fluorescein	48.54 g
	Wetland	NaBr	0.223 kg
		Na-fluorescein	26.5 g
Bates	Lagoon	Na-fluorescein	175 g
Strafford	Lagoon	Na-fluorescein	65 g
	Wetland	Na-fluorescein	33 g
Mousewater	Lagoon	NaBr	6.5 kg
		Na-fluorescein	60 g
	Wetland	NaBr	2.016 kg
		Na-fluorescein	82 g
Cuthill	Lagoon	NaBr	1.089 kg
		Na-fluorescein	23 g
	Wetland	NaBr	0.823 kg
		Na-fluorescein	20.6 g

This was simply estimated given the detection limit of the analytical technique, background concentration of the tracer and with a known system volume; the test was designed in such a way that the tracer amount could be detected with an increase in background concentration and assuming a complete mixing of tracer with the mine water (Kruse et al., 2007; Wolkersdorfer, 2008). Comparison of tracer amount was also made upon the various mathematical equations previously adopted in tracer tests (see Appendix B for example of tracer mass estimation). The amounts of tracer were also compared to that of the amount and assumptions used in previous tracer experiments to verify the results (as summarised in Table 2.6 Chapter 2). The amounts of tracer used for the tracer test are given in Table 3.3.

3.2.3 Selection of tracer

A review of literature from previous tracer studies was conducted during the early stage of the study to determine the potential type of tracer to be used in tracer test. The advantages and limitations (see section 2.3.3 of Chapter 2) of adopting any particular tracer were taken into account prior to selection of the appropriate tracer. Three potential tracers (sodium bromide (NaBr), sodium chloride (NaCl) and Na-fluorescein) were then chosen for assessment of tracer performance during a trial tracer test following their practicality in use during a tracer test by Workersdorfer et al. (2005) at the Bowden Close treatment system, County Durham (which consists of two RAPS and an aerobic wetland). In selecting a suitable tracer, factors such as conservative behaviour and sorption and degradation effects of the tracer, were primary considerations. Bromide is generally considered as one of the best hydrologic tracers due to its nonreactive (conservative) behaviour in most environments, its low background concentration levels, ease of measurement, low cost and relatively low toxicity (Bowman, 1984; Davis et al., 1980; Whitmer et al., 2000). Chloride is commonly used because it is simple to detect using conductivity probes, is highly soluble in water, relatively inexpensive and does not adsorb to negatively charged soil minerals (Wood and Dykes, 2002; Flury and Papritz, 1993). Fluorescein is used because it is visibly detected in low concentrations and considered resistant to adsorption on organic and inorganic materials (Smart and Laidlaw, 1977).

A trial tracer test was carried out at a selected site (Lambley wetland, 21 months after commissioning during the test), employing these types of tracers to assess their compatibility for use in mine water treatment system, and particularly for determining the hydraulic residence time. The results of the trial tracer test were then evaluated for the selection of the appropriate tracer to be used in the subsequent tracer experiments.

3.2.3.1 Trial tracer test

A series of trial tracer tests employing multiple tracers; Fisher Scientific Laboratory reagent grade NaBr, Na-fluorescein and sodium chloride (NaCl) was conducted during the early stage of the study between 29/07/2008 and 06/08/2008. The objective of this test was to compare the performance of the different tracers in actual mine water application. These consist of simultaneous NaBr and Na-fluorescein injection and a separate NaCl injection

- ***Simultaneous sodium bromide (NaBr) and Na-fluorescein injection***

The simultaneous injection of NaBr and Na-flourecsein was initiated on 29/07/2008 at 13:30 pm. The amounts of tracer added were initially designed so that the peak tracer concentrations could be detected even if complete mixing with the mine water occurred (Kruse et al., 2007). Based on the assumptions that 1 mg/L of bromide (Kruse et al., 2007) and 50 µg/L of Na-fluorescein (Wolkersdorfer et al., 2005) peaks could be expected during the tracer test, a mass of 3.102 kg of bromide and 120.45 g of Na-fluorescein had been calculated for the tracer injection. The 3.102 kg of NaBr (2.41 kg of bromide) were dissolved in 17 litres of water in the field prior to injection. The 120.45 g of Na-fluorescein were dissolved in 2 litres of deionised water in the laboratory to facilitate the dye mixing with the mine water.

After injection of the tracers, inlet samples were subsequently collected at hourly intervals for 24 hours, and outlet samples at 20 minute intervals for 16 hours. The basis for the assigned interval times was the previously calculated time to fill of the wetland of 6.9 hours (Kruse et al., 2007). Both the inlet and outlet autosamplers were logged at the same time at 13:30 pm on 29/07/2008. However, the sample sequence terminated at 13:30 pm on 30/07/2008 for inlet autosampler and at 05:10 am on 30/07/2008 for outlet autosampler. Approximately 250 mL of samples were collected in each of the polyethylene bottle to be taken back to laboratory for analysis of bromide. Na-fluorescein was continuously measured in the field using a fluorimeter; commenced logging at 12:44 pm on 29/07/08 and lasted for 25.5 hours before being taken back to the laboratory.

- ***Sodium chloride (NaCl) injection***

Following the NaBr and Na-fluorescein injection, NaCl was also used in the trial tracer test. The injection of NaCl was conducted a day after the simultaneous tracer injection to avoid possible interference on conductivity due to other salt addition i.e. bromide (Käss, 1998). The salt was dissolved in the mine water prior to injection. 20 kg of NaCl was injected and measured as conductivity which was recorded for 1 week to ensure all NaCl salt was carried through the system. Conductivity was measured as a proxy for direct determination of Na^+ and Cl^- (Käss, 1998). The conductivity was measured using an Eijelkamp CTD Diver. Background conductivity was measured a day before NaCl injection at the inlet to the system, and during the tracer test, for comparison with concentrations recorded by the CTD Diver at the outlet.

The trial tracer test showed that despite three different tracers essentially identical results were obtained. Thus, in the following tracer tests either can be used. However site-specific factors were also taken into account because tracers may behave differently in different systems. Results of the trial tracer test are discussed in section 4.2.1 of Chapter 4.

3.2.4 Tanks-in-series (TIS) model

In this study, the tracer residence time distributions (RTDs) have been modelled based on the tanks-in-series (TIS) mode, which is believed to represent a good approximation of most wetland conditions. The use of this model for wetland systems' hydraulic modelling is recommended by Kadlec and Wallace (2009), the model is simple and can be used with any kinetics (Levenspiel, 1972), and is a widely applied tool for treatment wetlands and ponds (Kadlec and Knight, 1996). The TIS model lies between the two commonly known ideal systems (i.e. plug-flow and completely-mixed), neither of which appear to be the case in real wetland conditions (Kadlec and Wallace, 2009). Based on the TIS model, the number of tanks-in-series, *n*, for tracer RTD is determined. This represents the ideal *n* TIS for RTD as in non-ideal systems (Levenspiel, 1972) such as observed from the systems studied. The *n* TIS essentially indicates the spread of tracer residence time from the mean, thus showing how the flow would deviate from ideal plug-flow.

Application of the TIS model to actual RTD data obtained from field experiments was used to yield the actual mean residence time of the tracer flow-through, and the corresponding hydraulic parameters, for evaluation of treatment system performance. This TIS hydraulic model is flexible enough to describe both mixing and preferential flow paths commonly encountered in treatment wetlands (Kadlec and Wallace, 2009). Analysis of system hydraulic characteristics was undertaken using the TIS model obtained from three different approaches, whichever fits the data well; i)TIS from moment, ii)TIS from least squares errors and iii)delayed TIS from least squares (after Kadlec and Wallace, 2009). Comparison of the model was also made upon model improvement and modification (based on Kadlec and Wallace, 2009) to produce better results.

3.3 LABORATORY ANALYTICAL ANALYSES

3.3.1 Water quality analysis

3.3.1.1 Cation analysis

Analyses of cations included measurement of major cations (Ca, Mg, Na, K) and metals (Fe, Mn, Al, Zn and Si) concentrations in the mine water samples. Total and dissolved cation concentrations were analysed using a calibrated Varian Vista MPX Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES). Calibration of machine was performed using blank and standard solutions (each solution was made up using VWR SpectrosoL stock solutions in a 1% by volume HNO_3 solution).

Table 3.4 Standard solutions and detection limits for ICP-OES

Element	**Concentration (mg/L)**		**Detection limit (mg/L)**
	Std 1	**Std 2**	
Al	2	5	0.05
Ca	10	20	0.02
Fe	5	10	0.01
K	25	50	0.1
Mg	5	10	0.02
Mn	2	5	0.01
Na	5	10	0.1
Zn	2	5	0.01
Si	10	20	0.1

Proportions of elements in each standard and detection limits for the machine are shown in Table 3.4. Dilution was performed (up to 1:50 dilution factor) using 18.2 Ω

MilliQ deionised water to obtain readings within the measurable range of concentrations. Blank and standards were run periodically (i.e. every 10 samples) to ensure QA/QC of the analysis at 10% accuracy (APHA, 1988).

3.3.1.2 Anion analysis

Analyses of anions included measurement of major anions (Cl^- and SO_4^{2-}) for water quality analysis and bromide for analysis of tracer transported through the treatment systems during tracer experiments. The anion concentrations were analysed using a calibrated Dionex 100 Ion Chromatograph. The machine was calibrated using blanks and against 10 mg/L chloride and 20 mg/L sulphate standard solutions for water quality analysis. Calibration standard solutions of 1, 2 and 3 mg/L bromide were used for analysis of tracer. Dilution was performed using 18.2Ω MilliQ deionised water. Standards were run periodically (i.e. every 10 samples) to ensure QA/QC of the analysis at 10% accuracy (APHA, 1988).

3.3.1.3 Analytical quality checks

Reliability of sample analyses was tested by charge balance calculations. This can be determined from the sum (in meq/L) of major cations (Ca, Mg, Na, K) and any other metal(s) with high concentration, and sum of major anions (Cl, SO_4, HCO_3), which should ideally be equivalent. An electro-neutrality of ± 10% was considered to be of suitable accuracy, albeit ± 5% was preferable (Appelo and Postma, 2005; Younger, 2007). The charge balance was calculated using the following formula (Younger, 2007):

$$Electroneutrality(\%) = \left[\frac{\sum cations\,(\frac{meq}{L}) - \sum anions(\frac{meq}{L})}{\sum cations\,(\frac{meq}{L}) + \sum anions\,(\frac{meq}{L})}\right] x\ 100$$

The charge balance calculation indicates electro-neutrality for water analyses from each treatment site within the acceptable range of ± 10% (see Appendix C).

3.3.2 Fe speciation analysis

The Fe speciation analysis was performed according to the modified ferrozine method (Viollier et al., 2000). Standard solutions for the method of 1, 2 and 3 mg/L of Fe (III) were made up using Fe (III) stock solution (Fe (III) chloride in 0.01M hydrochloric acid). Reagents used with the ferrozine method are:

- Reagent A – Ferrozine (0.01M ferrozine in 0.1M ammonium acetate solution)
- Reagent B – Reducing agent (1.4M hydroxylamine hydrochloride in 2M hydrochloric acid)
- Reagent C – Buffer (10M ammonium acetate solution adjusted to pH 9.5 with ammonium hydroxide)

Ferrozine reagent reacts with divalent iron to form a stable orange/red colour complex with a maximum absorbance at 562 nm. If Fe (III) is present in solution it can also react with ferrozine, thereby interfering with the colour. Standards and samples were analysed using a calibrated UV-Vis spectrophotometer measured at 562 nm wavelength to give the absorbance readings. Reaction of standards or samples with Reagent A was recorded as absorbance A_1. Absorbance after the reduction steps (reaction with Reagent B and Reagent C) was recorded as absorbance A_2 (detailed procedures in Viollier et al. (2000)). Each recorded absorbance (A_1 and A_2) was plotted against concentration of iron (standard Fe (III) solutions), each of which yields the slope of the plot (M_1 and M_2). Concentration of Fe (II) and Fe (III) were calculated using the following equations (adapted after Viollier et al., 2000):

$$Fe(II) = \frac{A_2 - 0.8A_1}{M_2 - 0.8M_1}$$

$$Fe(II) = \frac{A_1\,M_2 - A_2M_1}{M_2(1.25M_2 - M_1)}$$

where;

A_1 = absorbance after addition of reagent A

A_2 = absorbance after reduction of Fe (III)

M_1 = slope of plot A_1 versus concentration of iron

M_2 = slope of plot A_2 versus concentration of iron

3.3.3 Fluorescence analysis

Whenever on-site measurement of fluorescein was not possible, samples were taken back to the laboratory for fluorescence analysis. Measurement of fluorescence was carried out using a calibrated Varian Cary Eclipse Fluorescence Spectrometer. The machine was calibrated using blank and standard solutions made up to 1, 5, 10, 50 and 100 µg/L fluorescein and measured at 475 nm excitation wavelength and 530 nm emission wavelength. Fluorescence was measured as absorbance, each sample was read 3 times and the average reading was taken. The absorbance readings were plotted against fluorescein concentrations (standard solutions) to obtain the calibration curve and was used for determining the fluorescein concentrations of the mine water samples.

3.4 LABORATORY EXPERIMENT

3.4.1 Column tests

Laboratory column tests were undertaken to observe the time- and concentration-dependent removal of iron when pH and dissolved oxygen are not limiting. A column test was conducted for each of the influent and effluent water collected from the treatment sites, and tested in the laboratory. During the experiment, the water was well aerated and pH was monitored to be within the circum-neutral range. pH was set at 6.5, 7.0 and 7.5 for influent of lagoon, effluent of lagoon/influent of wetland, and effluent of wetland, respectively. Semi-continuous measurements (readings every 5 minutes) of turbidity, pH, dissolved oxygen and temperature in each 5 litre polyethylene vessel of 200 mm diameter were made using a calibrated YSI 6-series Multiparameter Water Quality Sonde (model 6820 V2), suspended (approximately 5 cm below the water level) in the vessels for 24 hours. The Sonde was connected to a computer installed with an EcoWatch Sonde Interface Software to monitor real-time turbidity measurements (and other parameters). Supernatant samples were collected using a 5 mL syringe every 5, 10 and 30 minutes, depending on the real-time turbidity measurements during the first 6 hours of experiment. Samples were collected as follows:

- Unfiltered 5 mL supernatant samples collected every 10 minutes during the first 6 hours (5 minutes during the first 2 hours) and acidified with 1% by volume of concentrated HNO_3 for analysis of total iron
- 5 mL of filtered (0.2 μm supor membrane) supernatant samples collected every 30 minutes and acidified with 1% by volume of concentrated HNO_3 for analysis of dissolved iron
- 5 mL of filtered (0.2 μm supor membrane) supernatant samples collected every 30 minutes and acidified with 1% by volume of concentrated HCl for Fe speciation analysis (Fe(II) and Fe(III))

Samples for Fe speciation were subsequently analysed on the same day of the experiment, whilst samples for total and dissolved iron were kept in the cold room at $4^{o}C$ and were analysed within 1 week of experiment. Accordingly, the underlying assumptions of these tests are (Roetting et al., 2009):

- Filtered iron concentration represents the dissolved fraction of water samples, which at pH about 6-8 is predominantly ferrous iron (Hedin, 2008)
- pH and oxygen concentration are constant during experiments
- Settlement rate of iron oxyhydroxide is related to the turbidity of the water column, since turbidity is primarily due to suspended iron

3.4.2 Reaction rates calculation

The oxidation rates of ferrous to ferric hydroxides were observed by measuring the changes in ferrous iron concentration over time. This was obtained by plotting $\log_{10}$ [FeII] versus time, according to a pseudo first-order expression (Sung and Morgan, 1980; Davison and Seed, 1983). The oxidation rates were subsequently calculated from the slope of the plot multiplying by -2.3. In a similar manner, pseudo first-order kinetics was assumed to describe the settlement rates of ferric hydroxides as a function of suspended iron. The settlement rates were obtained by plotting $\log_{10}$ [$Fe_{particulate}$] versus time, according to a pseudo first-order expression. Iron settlement rates were then calculated from the slope of the declining portion of the plot multiplying by -2.3 (Davison and Seed, 1983).

CHAPTER 4

RESULTS AND DISCUSSION:

HYDRAULIC PERFORMANCE OF MINE WATER TREATMENT SYSTEMS

4.0 RESULTS AND DISCUSSION: HYDRAULIC PERFORMANCE OF MINE WATER TREATMENT SYSTEMS

4.1 INTRODUCTION

This chapter presents the factors that govern the hydraulic performance of mine water treatment systems. This includes the analysis and interpretation of tracer test results from treatment wetlands and lagoons receiving net-alkaline, iron-rich mine water. The different residence time distributions (RTDs) observed from the tracer tests and the possible influences on the RTDs are discussed in section 4.3. Section 4.4 details the results of the modelling approach used to precisely evaluate the RTDs in order to account for the flow pattern across the systems. Such an approach enables characterisation of hydraulic performance within the system and how these hydraulic characteristics may be affected by several factors. Comparisons between lagoons and wetlands hydraulic performance are discussed.

The hydraulic factors influencing treatment performance were assessed by means of conducting tracer tests to experimentally determine the actual residence time within the treatment system. This is because hydraulic performance in passive treatment systems is often associated with the hydraulic residence time within the system. The relative importance of residence time for measuring hydraulic performance of passive / semi passive treatment systems has been discussed in many studies (e.g. Thackston et al., 1987; Kadlec, 1996; Persson et al., 1999; Goulet et al., 2001; Martinez and Wise, 2003a). However, to date this issue has not been investigated at UK mine water treatment systems. Much could be gained from such an investigation, in particular an understanding of the coupled relationships between the hydraulic and geochemical factors that influence the overall treatment performance.

4.2 EFFECTS OF FLOW VARIABILITY ON RESIDENCE TIME CALCULATIONS

4.2.1 Dynamic and average flow

In implementing a tracer test, flow rate is an important variable that must be precisely measured, since it determines the likely concentration of tracer measured at the

Table 4.1 Comparison of tracer recovery (M_0), mean residence time (M_1) and tracer flow variance (M_2) using dynamic and average flow. $Q_{dynamic}$ = dynamic flow, $Q_{average}$ = average flow, and W = wetland, L = lagoon

Tracer test	**Tracer**[*]		$Q_{dynamic}$			$Q_{average}$	
		M_0[a] (%)	M_1[b] (d)	M_2[b] (d^2)	M_0[a] (%)	M_1[b] (d)	M_2[b] (d^2)
Lambley (W) 2007	Br	84.43	0.258	0.009	85.70	0.256	0.008
Lambley 2008	Na-fluorescein	119.67	0.501	0.031	112.80	0.501	0.031
	NaCl	97.42	0.507	0.028	94.23	0.509	0.029
	Br	89.24	0.434	0.013	86.39	0.433	0.013
Lambley 2009	Na-fluorescein	96.36	0.406	0.022	96.43	0.406	0.022
	Br	75.88	0.366	0.012	74.72	0.367	0.012
Lambley 2010	Na-fluorescein	112.69	0.462	0.034	112.49	0.462	0.034
	Br	87.78	0.438	0.019	86.01	0.439	0.020
Strafford (L)	Na-fluorescein	69.69	0.795	0.375	69.69	0.795	0.375
Strafford (W)	Na-fluorescein	103.57	0.390	0.032	106.99	0.388	0.030
Whittle (L)	Na-fluorescein	-	-	-	119.29	0.329	0.060
	Br	-	-	-	95.96	0.247	0.024
Whittle (W)	Na-fluorescein	113.64	0.120	0.007	115.84	0.119	0.007
	Br	82.56	0.085	0.002	81.61	0.087	0.002
Allerdean Mill (L)	Na-fluorescein	-	-	-	76.58	0.998	0.323
Allerdean Mill (W)	Na-fluorescein	-	-	-	67.40	0.107	0.003
Mousewater (L)	Na-fluorescein	-	-	-	76.00	0.297	0.328
	Br	-	-	-	84.72	0.161	0.016
Mousewater (W)	Na-fluorescein	94.33	0.716	0.053	95.52	0.713	0.052
	Br	77.78	0.687	0.050	77.91	0.686	0.050
Cuthill (L)	Na-fluorescein	-	-	-	67.68	0.286	0.052
	Br	-	-	-	67.66	0.520	0.080
Cuthill (W)	Na-fluorescein	71.99	0.464	0.017	72.66	0.468	0.018
	Br	67.98	0.441	0.013	68.99	0.444	0.014
Bates (L1)	Na-fluorescein	-	-	-	155.24	0.619	0.129
Bates (L2)	Na-fluorescein	-	-	-	65.78	1.144	0.219
Mean		91.69	0.418	0.023	89.78	0.439	0.063
S.E		4.06	0.044	0.004	4.27	0.051	0.018

[a] Mass recovery is given in term of percentage (kg mass recovered/kg mass added)

[b] Note that the tracer mean residence time (M_1) and variance (M_2) presented in the table are calculated based on moment analysis which were later improved using gamma distribution function for TIS model

[*] The use of different tracers and their performance during tracer test are discussed in section *4.3.1.4*.

system outlet. Measurement of outlet tracer concentration, following injection at the inlet at a known time, enables calculation of the residence time, and analysis of how this tracer flow spreads across the system (the variance). Therefore variability of flow clearly has an influence on the outcome of a tracer test.

Calculation of system residence time distribution assumes a steady-state flow condition, which is never the case in actual systems due to event driven factors such as rainfall, evaporation and flow pumping (Werner and Kadlec, 1996). Therefore, it is important that this effect is considered in assessing the residence time distribution, which reflects the actual hydraulic behaviour of a system. As detailed in section 2.5.4 of Chapter 2, computation of tracer recovery (M_0), mean residence time (M_1) and tracer flow variance (M_2) (which are the important parameters from tracer residence time distribution) are largely dependent on the tracer concentrations and flow measurements. Kadlec (1994) reported M_0, M_1 and M_2 can be different using either dynamic (timely data) or average (of the timely data) outflow. In this section, comparisons are made between dynamic and average flow (measured flow taken within 10% precision), with corresponding tracer concentrations, to yield the M_0, M_1 and M_2. These parameters were calculated using moment analysis as described in section 2.5.4 of Chapter 2. Note that computations of these parameters were later improved using a tracer flow analytical modelling, whereby the moment calculation provide an early estimation values for the modelling approach. A comparison of dynamic and average flow values is presented in Table 4.1. Apparently, only slight differences are seen between the two methods for computing M_0, M_1 and M_2, the evidence for which is only a small difference of mean values for these parameters (differences are not significant, $p>0.05$ for all parameters). This probably reflects the fact that the outflows of the treatment systems were consistent throughout the duration of the tracer tests.

The main cause of any dynamic flow within the treatment systems was likely to be caused by the flow pumping system (which provides system inflow) switching on and off (i.e. at Lambley, Allerdean Mill, Bates and Cuthill), and possibly by internal flow obstructions such as internal weirs or channels (present at most schemes) and the presence of small islands created as planting blocks (present at some schemes e.g. Strafford wetland). These can possibly result in fluctuations of flow from steady-state conditions (Kadlec, 1994). Despite these fluctuations, the outflows have not significantly changed during passage through the systems, and the evidence from the tracer tests supports this. Therefore, in such cases, the use of either dynamic or average outflow takes reasonable account of the actual behaviour of tracer and flow movement across the system.

It is worth noting that the $Q_{average}$ is only considered valid in cases where there is less than 1% difference between net water loss and gain (Kadlec, 1994). In this study the difference between mean inflow and outflow (which is assumed to correspond to the water mass balance i.e. water gain and loss) is 2.2% (see Table 4.2), although this net water loss and gain might be meaningful on site to site basis. The difference ranges between 0.22% up to 41.67%. Therefore using $Q_{dynamic}$ is thought to be more appropriate for computing M_0, M_1 and M_2. Kadlec (1994) reported 1-3% net water losses at a constructed free water surface wetland receiving pumped river water in north-eastern Illinois, United State and the flow in their study was determined from the pumping rate rather than the mean flow. Kadlec and Wallace (2009) extended that the $Q_{average}$ is considered appropriate to within 4% difference between inlet and outlet. In this study, whenever complete timely flow data are available, computation of M_0, M_1 and M_2 are made using the dynamic flow.

4.2.2 Nominal residence time

The tracer nominal residence times were precisely determined by taking into account the variability of flow between system inlet and outlet. It is important that appropriate flow is used when computing the nominal residence time, for it approximates the water mass balance by either water gain or loss within the system. Ideally, if water is gained (i.e. rainfall) tracer concentration will be diluted and flow movement will tend to accelerate, hence shorter residence time. In contrast, if water is lost (i.e. evapotranspiration or infiltration) tracer will become more concentrated and move more slowly to the outlet, hence resulting in longer residence time (Kadlec and Wallace, 2009). There is however, ambiguity about the choice of the flow i.e. whether to use inlet, outlet, or the average of inlet and outlet (e.g. Kadlec, 1994; Kadlec and Wallace, 2009). Therefore, comparisons are made using different inflow and outflow rates for computation of the estimated nominal residence time, τ_n and are compared to τ_{an}, which is presumed to be the actual nominal residence time (Kadlec, 1994; Chazarenc et al., 2003), as presented in Table 4.2. Methods for calculating the τ_n and τ_{an} have been detailed in section 2.5.4 and 2.5.5 of Chapter 2.

Table 4.2 Nominal residence time using different flow rates; Q_i = inflow, Q_o = outflow and Q_{avg} = average of Q_i and Q_o W = wetland, L = lagoon

Tracer test	Tracer	Q_i (L/s)	Q_o (L/s)	$^a\tau_n$ (d)			$^b\tau_{an}$(d)
				V/Q_i	V/Q_o	V/Q_{avg}	
Lambley (W) 2007	Br	81.86	84.83	0.266	0.257	0.262	0.260
Lambley 2008	Na-fluorescein	81.45	81.66	0.318	0.317	0.318	0.318
	NaCl	81.45	81.14	0.320	0.321	0.321	0.321
	Br	81.45	81.91	0.322	0.320	0.321	0.321
Lambley 2009	Na-fluorescein	76.89	78.34	0.327	0.321	0.324	0.323
	Br	76.89	78.38	0.328	0.321	0.325	0.324
Lambley 2010	Na-fluorescein	78.91	76.57	0.317	0.327	0.322	0.323
	Br	78.91	76.58	0.317	0.327	0.322	0.323
Strafford (L)	Na-fluorescein	14.04	14.04	1.562	1.562	1.562	1.564
Strafford (W)	Na-fluorescein	14.04	19.89	0.348	0.175	0.262	0.225
Whittle (L)	Na-fluorescein	25	23.07	0.604	0.655	0.630	0.642
	Br	25	23.07	0.604	0.655	0.630	0.642
Whittle (W)	Na-fluorescein	23.07	21.85	0.230	0.243	0.237	0.240
	Br	23.07	21.83	0.228	0.240	0.234	0.237
Allerdean Mill (L)	Na-fluorescein	9.67	6.53	1.162	1.721	1.442	1.554
Allerdean Mill (W)	Na-fluorescein	7.91	8.26	0.328	0.314	0.321	0.317
Mousewater (L)	Na-fluorescein	36.72	31.9	2.057	2.368	2.213	2.285
	Br	36.72	31.9	2.057	2.368	2.213	2.285
Mousewater (W)	Na-fluorescein	31.9	34.37	0.777	0.721	0.749	0.742
	Br	31.9	34.37	0.777	0.721	0.749	0.742
Cuthill (L)	Na-fluorescein	10.72	10.61	1.176	1.188	1.182	1.185
	Br	10.72	10.61	1.176	1.188	1.182	1.185
Cuthill (W)	Na-fluorescein	10.61	7.48	0.623	0.883	0.753	0.771
	Br	10.61	7.48	0.623	0.883	0.753	0.771
Bates (L1)	Na-fluorescein	78.69	83.32	0.926	0.867	0.897	0.881
Bates (L2)	Na-fluorescein	58.55	83.32	1.227	0.867	1.047	0.983
Mean		41.92	42.88	0.676	0.721	0.699	0.698
S.E		41.92	5.972	0.099	0.116	0.107	0.111

$^a\tau_n$ calculated as V/Q; where V is the system volume (m^3) and Q is either Q_i, Q_o, *or* Q_{avg} (L/s)

$^b\tau_{an}$ calculated as $\tau_{in}\left(\frac{1}{N}\sum_{j=1}^{N}\left(\frac{1}{1-\frac{\alpha j}{N}}\right)\right)$, in accordance with a TIS system (Chazarenc et al., 2003; Kadlec and Wallace, 2009;)

It is clearly shown in Table 4.2 that in cases where Q_o is greater than Q_i (water gain) inflow based nominal residence time, τ_n (V/Q_i), is relatively greater than the presumed actual nominal residence time, τ_{an}. In contrast, the outflow based nominal residence time, τ_n (V/Q_o), will give an underestimate of the τ_{an}. Conversely, when Q_o is lower than Q_i (incoming water is lost), inflow based nominal residence time, τ_n (V/Q_i), is relatively lower than the τ_{an}. The outflow based nominal residence time, τ_n (V/Q_o), for such a water loss case results in an overestimate of the τ_{an}. The use of average inflow and outflow, τ_n (V/Q_{avg}), will give the same effect as using the inflow based nominal residence time (V/Q_i), but with a lesser percentage of difference with τ_{an} i.e. values closer to the actual nominal residence time are derived.

The τ_{an} computation is considered the most reliable quantification of nominal residence time because it takes into account the changes of flow between system inlet and outlet, while at the same time considering the kinetics of flow movement across the system. Note that the τ_{an} computed here is derived based on the concept of water gain and loss for a tank-in-series (TIS) system, as it will be shown later in section 4.4 that the flow movement within the investigated systems approximates a TIS flow model. It is shown here (Table 4.2) that erroneous values of τ_n are derived when using either Q_i or Q_o for computation of system nominal residence time. Specifically, there is a 3.15-3.30% difference of mean value compared to the τ_{an} regardless of whether $Q_o > Q_i$ or $Q_o < Q_i$. Q_{avg} gives a much closer value of τ_n compared to τ_{an} (0.15% difference of mean values), and these differences are not significant ($p>0.05$).

Differences between measured inflow and outflow are assumed to be indicative of the effects of evapotranspiration / infiltration and rainfall, which may influence the actual nominal residence time. Overall, the differences between Q_i and Q_o for the systems studied are insignificant ($p>0.05$) with exceptions in only a few cases, and no significant losses of water were observed, perhaps partly because all systems are lined with HDPE liner, and therefore infiltration loss is unlikely. Water gain was presumed to be the result of surface or groundwater runoff, particularly during rainfall events (e.g. high outflow during tracer test at Strafford). In essence, computation of actual nominal residence time is essential for determining accurate system volumetric efficiency because volumetric efficiency is determined from the ratio of actual tracer mean residence time, τ_m to actual nominal residence time, τ_{an} which is why it is necessary to accurately calculate both. In all cases, the actual nominal residence time to be used in the following computation of hydraulic performance metric is determined from τ_{an}, as described in section 2.5.5 of Chapter 2.

4.2.3 Effective volume ratio

System effective volume, e_v can be calculated by the ratio of tracer mean residence time, τ_m to nominal residence time, τ_{an}. However, appropriate use of nominal residence time will give the most accurate quantification of the effective system volume as stated earlier. As shown in Table 4.3, the ratio is calculated by using tracer mean residence time ($Q_{dynamic}$ basis) divided by different nominal residence times for comparison i.e. e_v (τ_n basis) or e_v (τ_{an} basis).

Clearly, computation of effective volume ratio using either τ_n (Q_i basis) or (Q_o basis) corresponds with the resulting e_v (i.e. higher τ_n (Q_i basis) or (Q_o basis) will result in higher e_v, and vice versa). However, by this means, the resulting e_v apparently reflects only the fraction of either incoming or exiting flow within the system, therefore a large erroneous e_v will result if Q_i and Q_o are greatly different. On the evidence of tracer test results (Table 4.3), e_v computed using τ_n (Q_i basis) and (Q_o basis) is 1.4% and 2.1% different, respectively (of the mean value) from computed e_v using actual nominal residence time, τ_{an}. On the other hand, the τ_n (Q_{avg} basis) gives e_v which is close (0.71% difference of mean value) to the computed e_v (τ_{an} basis), thus a better quantification than using either τ_n (Q_i and Q_o basis). Generally, the differences between e_v (τ_n basis) and e_v (τ_{an} basis) are insignificant ($p>0.05$) with exceptions in only a few cases within these treatment systems, principally due to a fairly consistent flow throughout the tracer tests as discussed earlier.

Notwithstanding this, computation of e_v using actual nominal residence time is still considered the most appropriate approach, for it takes into account the changes of both the fractions of incoming and exiting flow across the system as discussed earlier. Therefore, this computation has the advantages of considering not only the changes in flow rates during passage through the system but also the effect this has on the kinetics of flow movement across the system (i.e. based on a TIS flow movement). Thus it gives a reliable computation of actual nominal residence time, and hence e_v.

Table 4.3 Effective volume ratio, e_v calculated using different nominal residence time. τ_m are values of mean residence times ($Q_{\text{dynamic basis}}$) from Table 4.1; τ_n (V/Q_i, V/Q_o, and V/Q_{avg}) and τ_{an} are nominal residence times as calculated in Table 4.2. W = wetland, L = lagoon

Tracer test	**Tracer**		**e_v (τ_n basis)**		**e_v (τ_{an} basis)**
		$\tau_m/(V/Q_i)$	**$\tau_m/(V/Q_o)$**	**$\tau_m/(V/Q_{avg})$**	**τ_m/τ_{an}**
Lambley (W) 2007	Br	0.970	1.004	0.987	0.99
Lambley 2008	Na-fluorescein	1.575	1.580	1.578	1.575
	NaCl	1.584	1.579	1.582	1.579
	Br	1.348	1.356	1.352	1.352
Lambley 2009	Na-fluorescein	1.242	1.265	1.254	1.257
	Br	1.116	1.140	1.128	1.130
Lambley 2010	Na-fluorescein	1.457	1.413	1.435	1.430
	Br	1.381	1.339	1.360	1.356
Strafford (L)	Na-fluorescein	0.509	0.509	0.509	0.508
Strafford (W)	Na-fluorescein	1.121	2.228	1.489	1.733
Whittle (L)	Na-fluorescein	0.545	0.502	0.524	0.512
	Br	0.409	0.377	0.393	0.385
Whittle (W)	Na-fluorescein	0.566	0.494	0.530	0.511
	Br	0.595	0.521	0.558	0.534
Allerdean Mill (L)	Na-fluorescein	0.859	0.580	0.692	0.642
Allerdean Mill (W)	Na-fluorescein	0.326	0.341	0.334	0.338
Mousewater (L)	Na-fluorescein	0.144	0.125	0.135	0.130
	Br	0.078	0.068	0.073	0.070
Mousewater (W)	Na-fluorescein	0.921	0.993	0.957	0.965
	Br	0.884	0.953	0.919	0.926
Cuthill (L)	Na-fluorescein	0.243	0.241	0.242	0.241
	Br	0.442	0.438	0.440	0.439
Cuthill (W)	Na-fluorescein	0.751	0.530	0.641	0.607
	Br	0.713	0.503	0.590	0.576
Bates (L1)	Na-fluorescein	0.668	0.714	0.690	0.703
Bates (L2)	Na-fluorescein	0.932	1.319	1.126	1.163
Mean		0.835	0.864	0.840	0.846
S.E		0.088	0.109	0.094	0.098

Based on the comparisons, it is clear that e_v (τ_{an} basis) is preferable over other methods and is used in the following computation of the overall system hydraulic efficiency, e_λ, which will be discussed in section 4.4. e_v is apparently an important hydraulic performance metric which shows the fraction of system volume that is being effectively used. For instance, as shown in Table 4.3, e_v in excess of 1.0 are seen in Lambley and Strafford wetlands and one of Bates lagoon, suggesting that the actual mean residence times are comparatively greater than the nominal residence times in these systems, whereby the total volume of each system is being optimally used during the long retention of water through the system. These may be attributed to the complexity of vegetation distribution, for example at Lambley wetland and other factors such as system layout and internal obstructions which are further discussed in section 4.4.4 and 4.4.5. In contrast, much lower e_v i.e. 0.07 is seen in Mousewater lagoon, whereby the mean residence time is much lower than nominal residence time due to flow short-circuiting effect. These hydraulic performance characteristics of wetlands and lagoons are discussed in detail in section 4.4.

4.3 TRACER TEST RESULTS

4.3.1 Trial tracer test

A trial tracer test was carried out at the Coal Authority's Lambley wetland, employing a multi-tracer approach using NaBr, Na-fluorescein and sodium chloride (NaCl). The objective of this test was to assess the comparability of the different tracers for use in mine water, particularly for determining the hydraulic residence time. The test was conducted during the early stage of this study, between 29/07/2008 and 06/08/2008. The tests consisted of simultaneous NaBr and Na-fluorescein injection and a separate NaCl injection. The results of the trial tracer test were then evaluated for the selection of appropriate tracer to be used in the subsequent tracer experiments.

4.3.1.1 Sodium bromide

During the test, the flow rate varied between 67.25-91.61 L/s with a mean flow of 81.91 L/s. Based on the mean flow and the volume of the system, the nominal residence time was approximately 7.70 hours (0.32 days). The breakthrough curve of bromide and flow rates after 16 hours of bromide detection is shown in Figure 4.1. Bromide was first detected after 4.66 hours (0.194 days) of NaBr injection, and the breakthrough curve shows that bromide peaks at approximately 9.67 hours (0.403 days) at a concentration of 1.014 mg/L. The tracer mean residence time was 11.06 hours (0.461 days), a relatively longer retention than the nominal residence time

(0.321 days). Residence time must be greater or equal to the reaction time needed to achieve desired effluent concentration in order to achieve effective treatment within a wetland (Kadlec and Knight, 1996). Factors contributing to the longer residence time were likely the establishment of vegetation in the system and the absence of significant preferential flows, which were prevalent in a previous test undertaken soon after site commissioning (discussed in section *4.3.2.1*). The recovery of bromide over the 16 hour test was 87.70% (2.11 kg of the 2.41 kg of bromide injected). The incomplete recovery of tracer is concluded to be due to the fact that bromide concentration was still decreasing when the test finished. Thus, a significant mass of bromide was still held within the wetland.

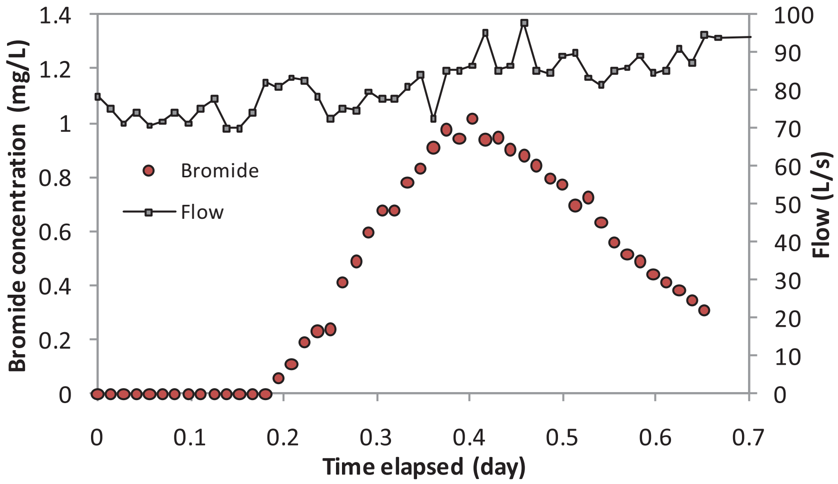


Figure 4.1 Bromide breakthrough curve of Lambley wetland for 16 hours monitoring commenced at 12:00 pm on 29/07/2008

4.3.1.2 Na-fluorescein

120 g of Na-fluorescein was injected into the wetland which was then distributed by the 3 inlet channels that were designed to uniformly spread the incoming water through the wetland (see Figure 4.2). However, visual observations showed that tracer dispersal was biased towards one of the three inlet channels suggesting some preferential flow in the distribution structure. The concentration of the tracer was measured by the fluorimeter which was logged to start capturing the concentration readings for a 24 hour duration. The flow during the Na-fluorescein tracer test was in the range of 68.66-101.21 L/s, with a mean flow rate of 81.66 L/s.

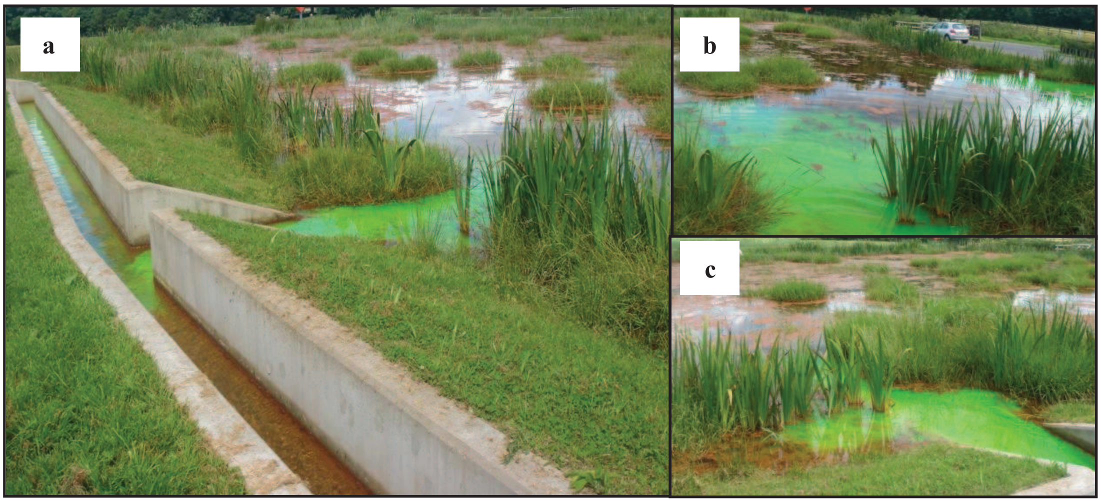


Figure 4.2 (a) Na-fluorescein injection into the inlet channels of Lambley wetland (b) Na-fluorescein moves more rapidly through one channel (c) The dye tracer moves more slowly through another inlet channel due to presence of ochrous sludge in front of the inlet structure

The breakthrough curve of the Na-fluorescein obtained from the experiment (Figure 4.3) can be considered as an ideal tracer plot; the tracer concentration detected when the test finished was less than 10% of the tracer peak (4.9 μg/L of 87.25 μg/L tracer peak concentration) (Kilpatrick and Wilson, 1989). As shown in Figure 4.3, the first Na-fluorescein detection was observed 3.67 hours (0.153 days) after the injection of tracer and the peak concentration was observed after 10.7 hours (0.423 days). The mean tracer residence time was 11.76 hours (0.490 days) which was also greater than the nominal residence time of 0.318 days.

Of the total amount of Na-fluorescein injected, a mass recovery of 119.97% was obtained in the wetland. This unusual tracer recovery was principally thought to be a function of potential inaccuracies in flow rate measurements. The very noisy stage and flow records appear to be a feature of turbulence in the stilling well where the CTD-Diver was located and may impart large error (>10%) margins on measured flows, and therefore calculation of tracer mass recovery. Spot measurements of flow rate (e.g. bucket/stopwatch or impeller measurements) would improve flow records in future studies, as would a longer approach channel to the V-notch weir, which would minimise turbulence. Furthermore, the presence of background fluorescence (suspended sediment and / or natural fluorescence background) may also cause the tracer recovery to be apparently in excess of 100% (Smart and Laidlaw, 1977).

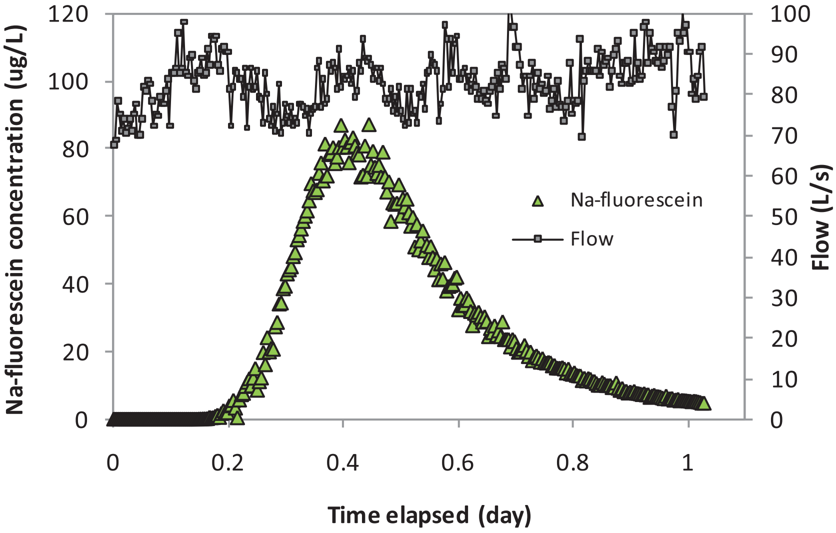


Figure 4.3 Na-fluorescein breakthrough curve for the Lambley wetland over 24 hours monitoring commenced at 12:00 pm on 29/07/2008

4.3.1.3 Sodium chloride

Figure 4.4 indicates that an increase in conductivity could be observed some 10 hours after NaCl injection, albeit the background conductivity is noisier than either bromide or Na-fluorescein concentrations. Because of the ease of recording conductivity, readings were logged at 5 minute intervals for a period of 1 week. Of the 1 week conductivity measurement, the possible portion of conductivity plot that corresponds to the NaCl injection is as shown in Figure 4.4 (small diagram). The inset diagram in the figure in particular illustrates the elevation of conductivity in the effluent water during the tracer test. The peak detection of conductivity was observed after 10.39 hours (0.433 days) of NaCl injection and the mean residence time was 12.17 hours (0.507 days). The background conductivity measured prior to the NaCl injection was found to be 0.433 mS/cm and was used as the baseline reading of the conductivity. The amount of NaCl (in mg/L) was taken as 0.891 of the measured conductivity (in µS/cm) at 15°C for calculation of the recovered tracer (Brassington, 2007). As will be discussed later, the highly fluctuating background conductivity as shown in Figure 4.4 may somehow result in erroneous calculation of the recovered tracer (i.e. significant drop of conductivity below baseline after two days of injection, and a sudden rise of conductivity above baseline and a drop again during day 5). For these reasons, the NaCl tracer was not preferable to be used in the following tracer tests. During the tracer test, the flow ranged between 67.26-90.64 L/s, and the mean flow was 81.14 L/s.

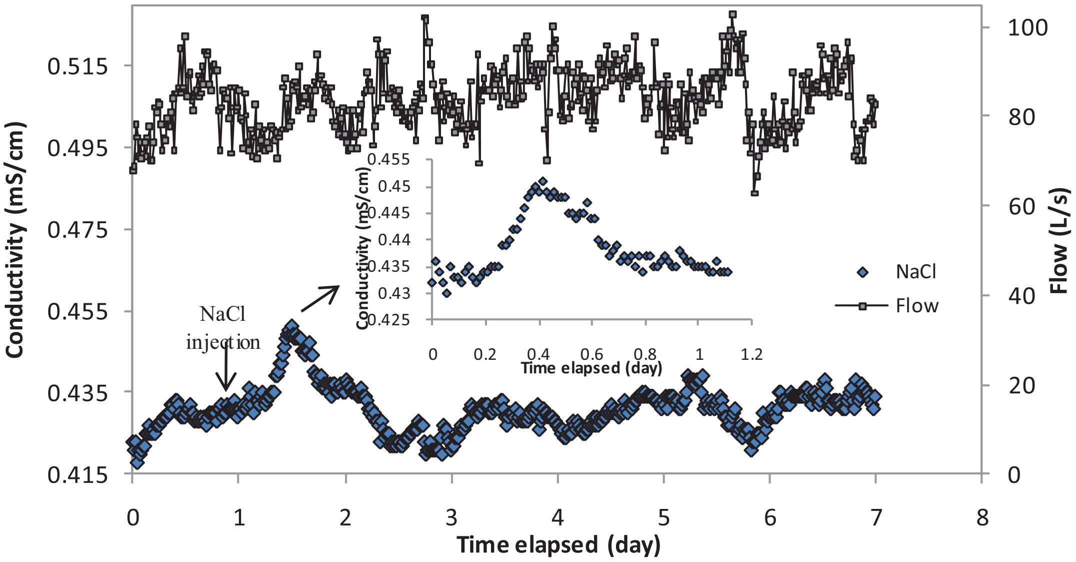


Figure 4.4 Conductivity plot of Lambley wetland outlet from 12:00 pm 29/07/2008 to 13:00 pm 06/08/2008. Sodium chloride injection was conducted at 14:15 pm on 30/07/2008. Peak conductivity was detected after 10 hours of injection (insert plot)

4.3.1.4 Comparison of tracer performance

Because flow-rate remained consistent throughout, the performance of the three tracers used can be compared directly even though the NaCl tracer was not synchronous with the other two tracers. Summary performance data for the three tracers are shown in Table 4.4 while Figure 4.5 shows a normalised tracer residence time distribution (RTD) to compare the results from the different tracers.

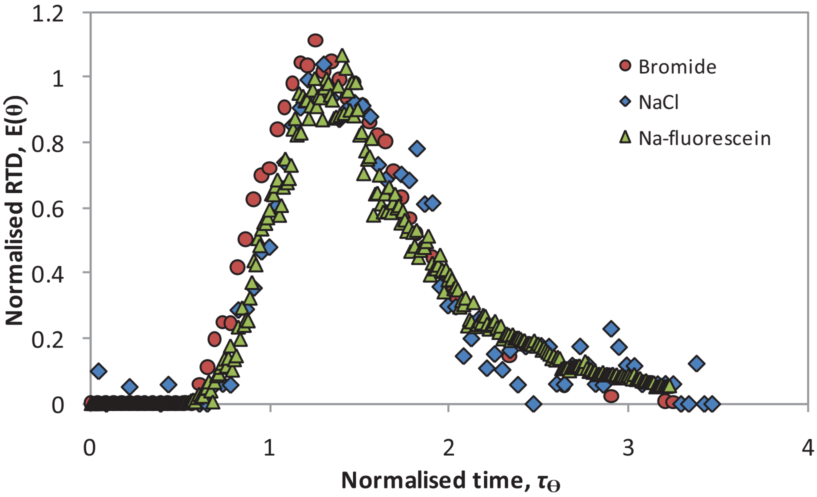


Figure 4.5 Normalised RTD curve for bromide, Na-fluorescein and NaCl to indicate the performance of the different tracers. All tracers show nearly identical peak and mean residence time

Table 4.4 Comparison of different tracer performance in Lambley wetland treatment system

Tracer	**Bromide**	**Na-fluorescein**	**NaCl**
Mean Flow rate (L/s)	81.91	81.66	81.14
Nominal residence time (d) [a]	0.321	0.318	0.321
Duration of tracer injection (d)	0.67	1	7
First detection (d)	0.194	0.153	0.194
Peak residence time (d)	0.403	0.423	0.433
Mean residence time (d)[b]	0.461	0.490	0.507
Tracer recovery (%)[c]	87.70	119.67	97.42

[a] Calculated as $\tau_{an} = \tau_{in}\left(\frac{1}{N}\sum_{j=1}^{N}\left(\frac{1}{1-\frac{\alpha j}{N}}\right)\right)$ (after Kadlec and Wallace, 2009) as detailed in section 2.5.5 Chapter 2.

[b] Calculated as $\tau_{m} = \int_0^\infty tE(t)\,dt = \frac{\int_0^\infty tQ(t)C(t)dt}{\int_0^\infty Q(t)C(t)dt} \cong \frac{\sum_{i=1}^{n} tQ_i(t)C_i(t)\Delta t}{\sum_{i=1}^{n} Q_i(t)C_i(t)\Delta t}$ (after Kadlec, 1994) as detailed in section 2.5.4 Chapter 2.

[c] Calculated as the percentage of total mass recovered from the amount of tracer added

The RTD plot is used to aid comparative interpretation of tracer performance i.e. tracer concentrations, flow rates and duration of tests (Levenspiel and Turner, 1970; Levenspiel, 1972). This has been detailed in section 2.5.2 and 2.5.3 of Chapter 2. Note that tracer mass recovery is sensitive to the long tail of the concentration curve such as those tracers investigated here (Figure 4.5). Curl and McMillan (1966) found that such tails are well represented by an exponential decay. Therefore the bromide breakthrough curve (from the tracer test which was terminated early before the concentration had reached the background) as shown in Figure 4.1, was extrapolated using an exponential decay for estimation of the remaining portion of the curve (Curl and McMillan, 1966; Thackston et al., 1987). The recoveries of tracer were obtained by the zeroth moment analysis (Eqn. 2.15) to yield the total mass of tracer that has been recovered at the exit of the wetland (Martinez and Wise, 2003a; Werner and Kadlec, 1996). As presented in Table 4.4, bromide indicates 87.70% of mass recovery, NaCl of 97.42% and Na-fluorescein of 119.97%. The anomalous recovery of Na-fluorescein was probably due to the flow rate monitoring issues described earlier although fluorescence interference could be possible. It was reported that suspended sediment in water could raise background fluorescence and reduce effective dye fluorescence because of light absorption and scattering by the sediment particles (Smart and Laidlaw, 1977). Natural plant pigments have also been reported to be the cause of fluorescence interference (Rabinowitch, 1951).

On the other hand, the lower recovery of bromide is thought simply to be due to the test being terminated before bromide concentrations had returned to background, though sorption onto wetland sediment and uptake by wetland vegetation cannot be ruled out (Lin et al., 2003). However, bromide sorption onto sediment is less significant because soils and sediments are thought to have negative surface charges that repel the negatively charged Br^- ions (Korom, 2000), and therefore in principle it moves as fast as water in soil (Flury and Papritz, 1993). Additionally, bromide has been widely used to study the movement of water through soil in the laboratory and field (e.g. Bowmen, 1984; Gish et al., 1986; Jury et al., 1986; Starr et al., 1986). Despite this, bromide losses through wetland systems have been observed, as it is readily taken up by plants (e.g. Owens et al., 1985; Jemieson and Fox, 1991; Schnabel et al., 1995; Eckhardt et al., 1996; Whitmer et al., 2000). Given that the reeds in the Lambley wetland have matured during the tracer test, this could be a possible explanation of the bromide losses in the wetland.

In general, the three tracers gave nearly identical results in terms of hydraulic residence time and consistently high tracer mass recoveries. The peak residence times appeared almost at the same time; 0.403, 0.423 and 0.433 days (9.67, 10.15 and 10.39 hours) for bromide, Na-fluorescein and NaCl, respectively. The mean residence times were also very similar; 0.461, 0.490 and 0.507 days (11.06, 11.76 and 12.16 hours). The mean residence times are greater than their nominal residence times by 24-57%, the highest resulting from the NaCl injection. This comparatively longer mean to nominal residence time of the NaCl was probably due to the density effect of the salt (higher solution density than the water) given the large amount of the tracer added (20 kg). This potentially results in retention of salt in the lower depths of the wetland prior to full mixing, and therefore a longer time for the tracer to leave the system. This effect has been suspected by many practitioners/researchers (e.g. Käss, 1998; Schmid et al., 2004; Kadlec and Wallace, 2009).

When comparing the performance of these three tracers, it is difficult to identify categorically the most reliable tracer given the similarity of results gathered at the Lambley site. Although only 87% of the tracer mass added was recovered, bromide had the advantage that background concentration within the wetland was negligible and interpretation of the tracer recovery was therefore more straightforward. The cause of the mass recovery of Na-fluorescein being greater than 100% is unknown. Although the immediate cause of this appears to be the very high concentrations of

Na-fluorescein, which were above the expected peak for quite a long period, the reason for the high concentrations is unclear. This could lead to inaccurate interpretation of the residence time determined based on the recovered Na-fluorescein tracer. For the NaCl tracer, the fluctuation in the baseline conductivity measured throughout the test affected the calculated recovery of the tracer. It was found that during the NaCl injection the conductivity dropped significantly below the baseline making it difficult to identify the exact conductivity portion attributable to the salt addition and what portion was due to the increase in conductivity caused by other ions present in the water. Despite the higher tracer recoveries of Na-fluorescein and NaCl, bromide was still considered the most conservative tracer in water. However, due to the consistent performance of the tracers, and from experience of conducting tracer tests, the selection of tracer appears to be best made based on site-specific considerations. For example, at Acomb lagoon, due to proximity of the treatment scheme and the nearby community, bromide is preferable over Na-fluorescein because the dye can be visibly seen by the public, which is not desirable. As in the case of Bates treatment scheme, in which the mine water is very saline, Na-fluorescein is used because a comparably large amount of salt (of which bromide) might be needed to avoid interference with other salts presence in high concentrations (e.g. chloride). In any cases following the trial tracer experiment, NaCl is not preferable because a large amount will be needed in order to raise the background level (due to the dissolved cations in the water measured as conductivity), which in turn can lead to a sink of the salt tracer due to density stratification (Käss, 1998).

4.3.2 Tracer residence time distribution (RTD) of wetland systems

4.3.2.1 Residence time distribution of Lambley wetland over 4 years since commissioning

Discussion on a year-to-year basis of wetland performance is presented in this section, taking a wetland system, Lambley, as an example to demonstrate performance of the wetland over four years of operation (2007-2010) since site commissioning. This site monitoring was also conducted within the four different seasons to account for the seasonal variations in the wetland system (Table 4.5) which, it is recognised, complicates interpretation of tracer test results.

Table 4.5 Seasonal and yearly variation in water chemistry and hydraulics of Lambley wetland from 2007-2010. Note: Metal concentrations are not shown in this table and are reserved for section 5.2 of Chapter 5.

Variable	Inlet/Outlet	Feb 2007[a] (winter)	July 2008 (summer)	Oct 2009 (fall)	Apr 2010 (spring)
Water chemistry					
pH	In	7.73	6.65	6.09	6.35
	Out	6.96	6.40	6.65	6.65
Temperature (ºC)	In	9.8	17.5	11.2	11.7
	Out	8.4	17.0	9.2	11.9
Alkalinity (mg/l $CaCO_3$)	In	171	164	151	162
	Out	164	162	154	149
Conductivity (µS/cm)	In	441.2	440.8	462.1	459.0
	Out	423.3	434.2	447.2	442.2
Eh (mV)	In	-71	-24	77	-14
	Out	-59	32	71	-5
Hydraulics					
System area (m^2)		6845	6845	6845	6845
System volume (m^3)[b]		2163	2238	2169	2163
Length to width ratio (L/W)		3.4	3.4	3.4	3.4
Water depth (m)		0.316	0.327	0.317	0.316
Flow (L/s)		81.86	81.45	76.89	78.91
Tracer recovery (%)[c]		84.83[*]	87.70[*] 119.67[†] 97.42[‡]	75.88[*] 118.94[†]	87.78[*] 108.59[†]

[a] Data from Kruse et al. (2007)
[b] Calculated as system area (m^2) x water depth (m)
[c] Calculated as the percentage of total mass recovered from the amount of tracer added
[*] Denotes bromide, [†] denotes Na-fluorescein and [‡] denotes NaCl tracer, respectively

It was found that there was no significant variation of water chemistry for the Lambley wetland over the four monitoring seasons (or years) except temperature and Eh ($p<0.05$). As anticipated, significant temperature difference was seen between winter and summer seasons (the lowest, 8.4 ºC, at the outlet during winter 2007 and the highest, 17.5 ºC, at the inlet during summer 2008). Eh was significantly different for winter 2007 and fall 2009. For the pH, even though differences are not statistically significant, this variation in pH may have a significant influence on the rates of iron removal (i.e. Fe(II) oxidation, see section *2.9.1.1* of Chapter 2). Note that discussion of iron removal is provided separately in section 5.3 of Chapter 5.

Individual illustrations of tracer RTD for each monitoring year from 2007 to 2010 at Lambley wetland are shown in Appendix F (Figure F.1). The use of different tracers was to ensure accurate measurement of tracer flow movement across the system and to make sure of the tracer conservancy. Despite this, for comparison, the tracer RTDs are presented in the form of normalised RTD curves (Figure 4.6) to illustrate the effect on tracer RTDs from the different experimental conditions, i.e. tracer concentrations, flow rates and duration of test between the years of monitoring, and are illustrated on the same scale (refer to section 2.5.3 of Chapter 2 for explanation on the normalisation procedures). Tracer recoveries are shown in Table 4.5.

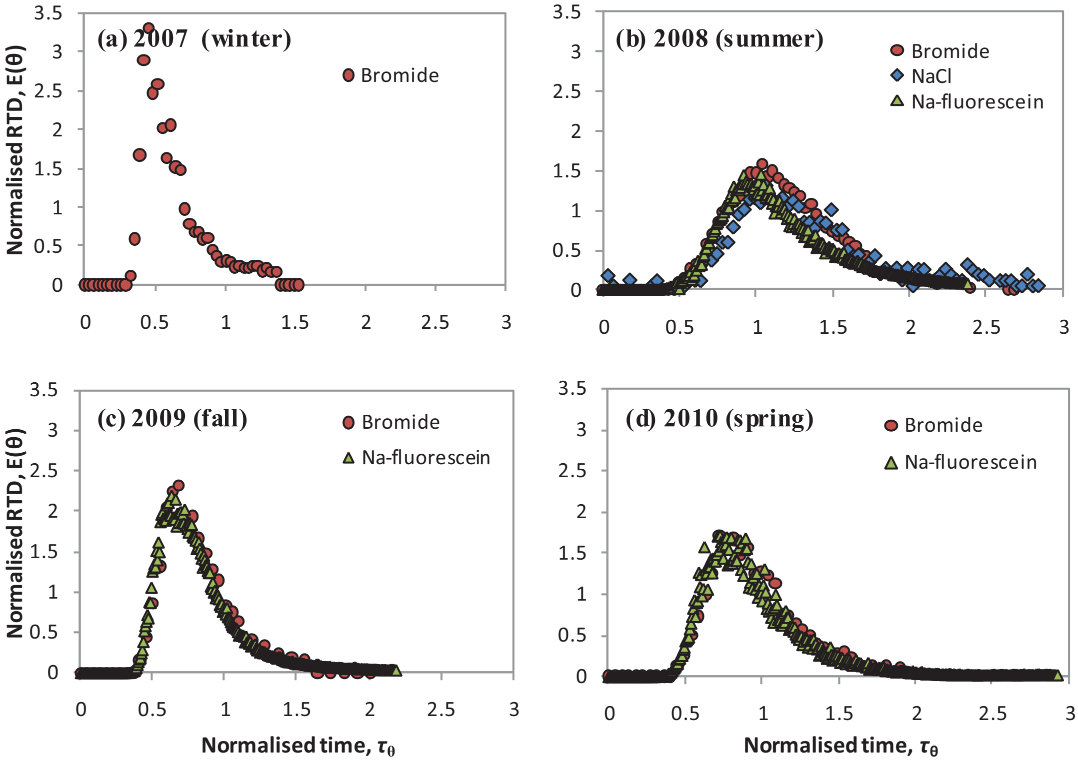


Figure 4.6 Normalised RTD curves for Lambley wetland to compare the year-to-year changes of flow movement across the system

Significantly different RTD shapes are clearly seen in Figure 4.6, demonstrating the changes in flow movement within the wetland system over the 4 years of site monitoring. Multiple sharp peaks are observed in February 2007 (Figure 4.6a; see Appendix F for clarity) indicating apparent short-circuiting effects, whereby the tracer takes preferential flow paths as it moves through the system. It appears that the very sparsely-populated reeds during their early colonisation resulted in significant flow channelling effects in the wetland. The multiple peaks in the breakthrough curves observed by Kjellin et al. (2007) were also associated with the vegetation distribution and the spread in water residence times within a treatment wetland receiving treated sewage water from a sewage treatment plant in Eskilstuna, Sweden. The study concluded that the heterogeneity in vegetation may also cause an increased mean water residence time as a result of flow retention in stagnant zones within the vegetation and bottom sediment. Residence time monitoring during the second year of the wetland operation (Figure 4.6b, July 2008) indicated much improved results, whereby considerably less dispersed RTD curves were observed compared to 2007. Importantly, similar RTD shapes were found despite the use of different tracers, indicating consistent performance of the wetland during the period of the tracer test, and strengthening confidence in these results. It can be seen that during this stage of wetland operation, the flow streaming effects have been removed, which in part at least appears to be due to the maturity of the reed colonies, which ensures a more even flow distribution across the system. Further monitoring of the system residence time during the third year of wetland operation (Figure 4.6c, November 2009) demonstrated an intermediate shape of RTD between the tracer flow patterns observed in 2007 and 2008. The relatively dispersed RTD curves than those observed in 2008 could represent the re-occurrence of flow short-circuiting across the wetland system. As in 2008, the two different tracer RTDs observed in 2009 are closely matched (Figure 4.6c), showing the consistency of wetland performance throughout the tracer test and the reliability of the results. The most recent tracer monitoring in April 2010 (Figure 4.6d) indicated RTD shapes which were rather dispersed than the year before, showing an improvement of flow distribution across the wetland. Likewise, the two RTD shapes are essentially the same.

It can be seen that the shape of tracer RTDs for 2007 and 2009 exhibit an early sharp peak, and the flow patterns are relatively dispersed than those seen in 2008 and 2010 (Figure 4.6a and Figure 4.6c, respectively). This indicates that there are some fractions of water moving faster through the system, but also a fraction that moves more slowly. Assuming that the treatment ability of a wetland is spatially uniform, fast-moving water undergoes little interaction with wetland sediment and biota, and hence undergoes less effective treatment, while slow-moving water experiences greater treatment. These fast and slow-moving waters mix at the wetland outlet, giving the wetland effluent an intermediate degree of treatment (Werner and Kadlec, 1996; Martinez and Wise, 2003a). In 2007, the sparsely-populated reeds could be the cause of some fractions of water being transmitted rapidly through the poorly vegetated system (hence the very sharp early peak), but also with a rather long time for the later water fractions to exit the system. For 2009, the streaming effect could also be attributable to the movement of some fractions of fast moving (upper layer) water through the densely-populated reeds, and in particular channelisation created by the dead vegetation within the mature reed colonies that had developed in the 3 years of wetland operation. Clearly, these short-circuiting effects appear to be significant both during early reeds colonisation and again when reeds become more mature and therefore dense (albeit the pattern may also relate to effects of different seasons). This perhaps has implications for maintenance e.g. periodic reed clearance to ensure flow is distributed more uniformly. On the other hand, reasonably well-distributed flows were seen in 2008 and 2010 (less dispersed RTD curves), possibly indicating the complexity of the role of wetland vegetation to sustain efficient hydraulic performance over its operation, coupled with the seasonal effect on the reeds' growth. Notwithstanding this, a long RTD tail was seen despite a more distributed flow, suggesting that retention of a fraction of the inflow as more slowly-moving water in such wetland systems is inevitable, irrespective of the stage of reed development. Kjellin et al. (2007) concluded that factors such as dispersion and water exchange within stagnant zones were shown to contribute to the spread of residence times, particularly to the long tail of the observed breakthrough curves.

In essence, the significant improvement of the hydraulic performance of the wetland seen during the second year of the wetland operation (i.e. longer residence time; as will be shown later in section *4.4.4.2*, this is consistent with improved system hydraulic efficiency) implies that this wetland system reached optimal performance after 2 years of operation. Performance had slightly decreased by the third year, and later slightly improved during the fourth year of wetland operation. Whether this trend will continue is uncertain, and can be confirmed by further monitoring in future years. Clearly, the influence of vegetation on flow patterns indicates that seasonal or ecological succession may influence the characteristics of wetland flow (Holland et al., 2004). Additionally, the hydraulic inefficiencies of a treatment wetland may be attributed to the non-uniform distribution of vegetation causing non-uniform resistance to flow (Martinez and Wise, 2003a). As shown here, the reeds' growth was to a large extent influenced by the seasonal variation (growing or non-growing season) and / or the age of the wetland system itself (year-to-year reed development) (see Figure 4.7). This appears to have greatly influenced the wetland RTDs, given the consistent flow through the system throughout the monitoring period. However, this qualitative link between vegetation effect and the hydraulic performance of the wetland was only through the observations of the treatment system over the four years monitoring, though a quantitative assessment of such a variation would appear to be more useful (one of the limitations of the results presented here). As part of a wider programme of investigation of the design and performance of mine water treatment wetland systems, multiple systems in the UK were monitored to assess the possible influences on residence time, and ultimately determine how the residence time may have an impact on the overall system hydraulic performance. In this way it is hoped that recommendations for improved design of such systems may be made. Nevertheless, this investigation of the variability of RTD at the Lambley system has provided a rare insight into temporal changes in hydraulic performance.

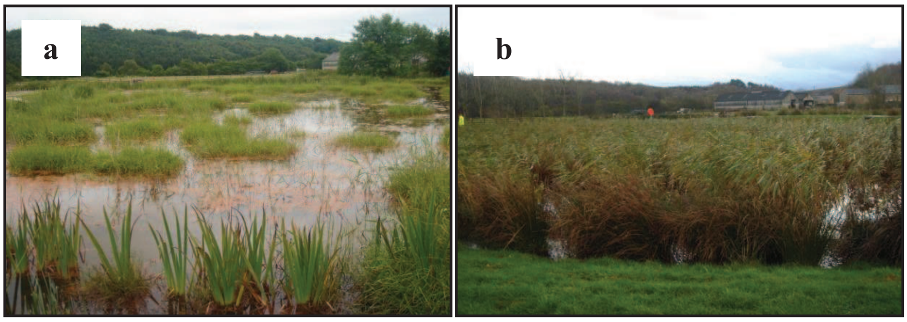


Figure 4.7 Images of wetland vegetation growth at Lambley wetland (a) sparsely-vegetated reeds during early colonisation (b) maturely-developed reeds

4.3.2.2 Residence time distribution of other wetlands

The actual tracer RTDs for the wetland systems are shown in Appendix F (Figure F.2). The normalised forms of these tracer RTDs, for comparison of the different RTD shapes within the investigated wetland systems, are shown in Figure 4.8 and are plotted on the same scale.

Table 4.6 Summary of hydraulic characteristics of wetland systems

Variable	Inlet/ Outlet	Whittle[a]	Whittle	Allerdean Mill	Strafford	Mousewater	Cuthill
Season of monitoring		winter	winter	spring	summer	summer	summer
Age of system (years)		5.0	8.0	1.5	0.8	5.8	7.0
System area (m^2)		2400	2400	1066	1690	8400	2744
System volume (m^3)		721	458	224	423	2142	571
Length-to-width ratio (unitless)		5.5	5.5	2.1	5.7	3.5	3.5/5.3#
Water depth (m)		0.3	0.19	0.21	0.25	0.26	0.21
Flow (L/s)		25	23.07	7.91	14.04	31.9	10.61
Tracer recovery (%)[b]		60.3*	82.56* 113.64†	67.40* 76.58†	103.57†	77.98* 94.33†	67.98* 71.99†

aData for Whittle (first wetland), data from Kruse et al. (2007)
bCalculated as the percentage of total mass recovered from the amount of tracer added
*Denotes bromide and †denotes Na-fluorescein, respectively
#L-shaped wetland, L:W ratio of first cell/L:W ratio for second and third cell

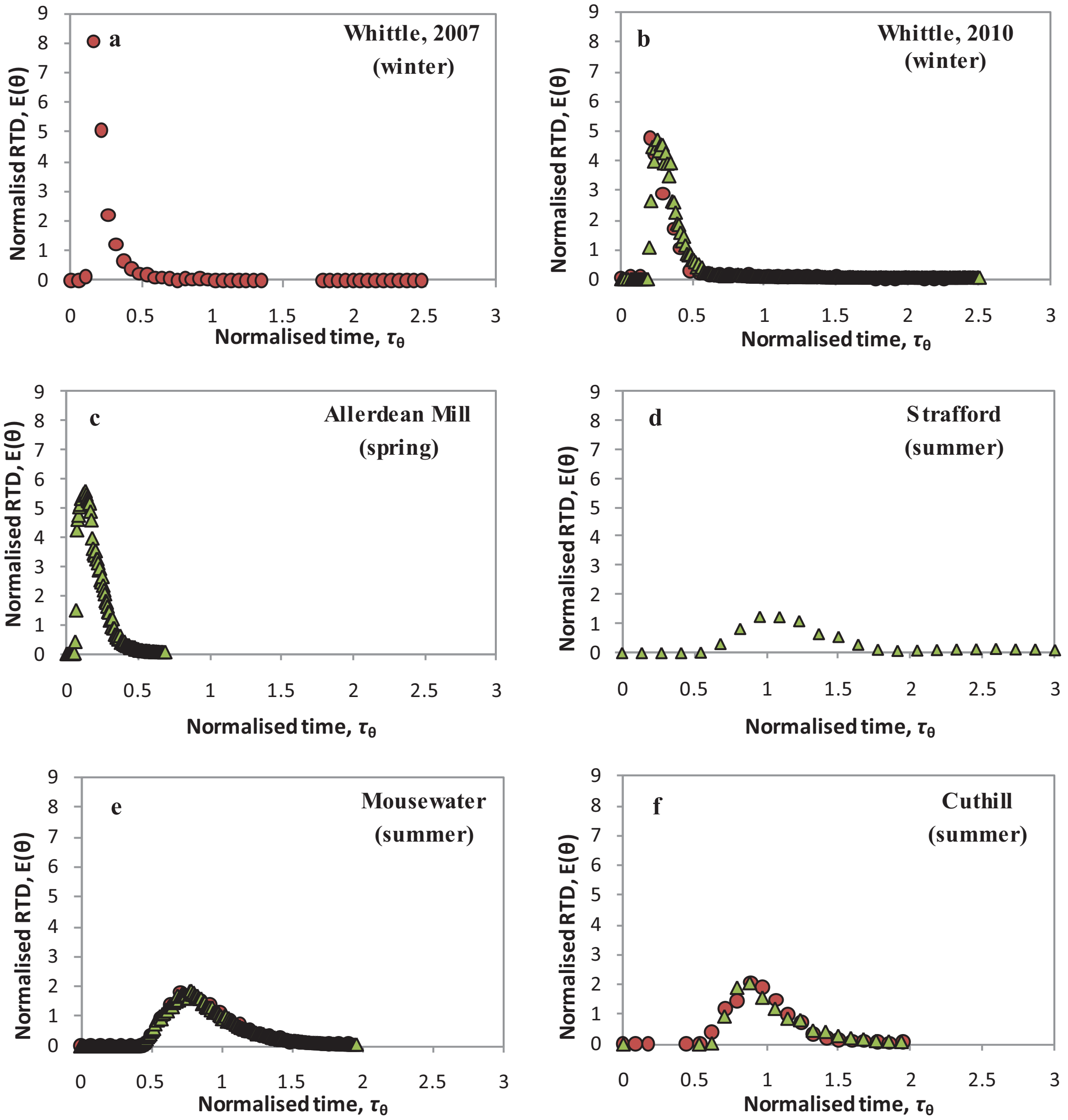


Figure 4.8 Normalised tracer RTD curves for wetland systems, plotted on the same scale for comparison. Red circles denote bromide tracer, green triangles denote Na-fluorescein tracer

Discussion of the different systems is presented here, to show how residence time may differ between systems due to other factors (i.e. design configurations, season and age of operation) in addition to the role of vegetation (seems to have an influence on the residence time as noted earlier, albeit the effect of seasons complicates interpretation). A summary of the hydraulic characteristics of the wetlands investigated is given in Table 4.6. The flow rate for these wetland systems ranges from 7.91 L/s to 31.9 L/s (measured during the tracer tests). These include a range of lagoons' volume between 224 – 2142 m^3. The age of the wetlands during tracer tests ranges between 0.8 – 8 years.

Whittle

On the evidence of these tracer RTD results, the Whittle wetland clearly has an RTD curve pattern which is very narrow and exhibits a very long RTD tail (Figure 4.8a and Figure 4.8b, respectively). Note that the tracer tests at Whittle wetland were conducted at different cells of three nearly identical wetland cells, which operate in series i.e. in Cell 1 during tracer test in 2007 and in Cell 3 during tracer test in 2010 (see section *1.6.1.3* of Chapter 1 for layout of Whittle wetland cells). In 2010 the tracer test was undertaken in the third wetland cell because the first two cells were undergoing remediation work following a leakage found in the first wetland cell. Despite this, a very similar RTD shape was seen in both wetland cells (although with a slightly lower peak and a slightly wider curve in 2010 compared to 2007). There are several possible influences that may explain these sharp and narrow RTDs seen in both wetland cells as follows:

- The Whittle wetland was commissioned in 2002, and therefore during the first tracer testing, in 2007, the wetland had been in operation for almost 5 years, so the wetland reeds were well established. As such, it can be anticipated that development of preferential flow paths and flow short-circuiting may appear within these maturely-developed reeds and within the dead vegetation and ochre build-ups at the bottom of the wetland. The very sharp peak of tracer RTD in 2007 may therefore be due to significant short-circuiting effects created by a significant fraction of fast-moving water across this mature wetland.
- The fairly similar RTD shapes observed in both wetland cells may suggest the likely feature of seasonal effect during the tracer tests in winter seasons (both in February 2007 and February 2010) where the apparent streaming effects could be due to channelisation created through the mature reeds and possibly due to presence of large amount of dead plant materials and reeds during winter seasons.
- The significant role of the mature wetland reeds on the wetland flow movement may be coupled with the high length to width ratio of the wetland (see Table 4.6), causing a slower moving water through the wetland
- The long RTD tails seen in both wetland cells were presumably be attributable to the retention of the remaining wetland flow (despite leakage in 2007) in the lower water layer within the reed colonies i.e. due to presence of dead zones

within the accumulated dead plant materials and vegetation debris and in the case of mine water within the precipitated iron hydroxides. The abundance of dead zones may reduce the effective volume within a wetland, in turn lowering the hydraulic efficiency of the system (Holland et al., 2004).

Nevertheless, it should be noted that distinguishing between the influences of the first three of these is difficult, and in reality the reason for the sharp and narrow peak may be a combination of all influences. Several physical influences on residence time distribution have been listed in section 2.8.2 of Chapter 2.

Allerdean Mill

The Allerdean Mill wetland (Figure 4.8c) also shows a reasonably narrow RTD curve. Note that the tracer test was conducted at the first of three wetland cells in series, and the tracer was recovered from only one of two outlet channels from the wetland cell. No tracer data are available from the other outlet channel due to a malfunctioning auto-sampler during the tracer test. Only about 35% of measured tracer was recovered from one of the outlet channels but the total tracer recovery was ascertained from the ratio of flow leaving through each channel. The reasons for the narrow RTD curve are possibly as follows:

- The wetland at Allerdean Mill was in its second year of operation during the tracer test. It is possible that the relative maturity of the reeds may contribute to flow short-circuiting effects. This, however, would be in contrast to the Lambley wetland during its second year operation, during which flow was distributed well without significant short-circuiting effect.
- It therefore appears more likely that flow channelling at Allerdean Mill is a result of the multiple outlets from the wetland cell, which result in poor mixing of flow prior to exit from the system (*cf.* Lambley wetland, which only has one outlet channel). Note that at the Allerdean Mill, the wetland cell studied comprises 3 inlet channels and 2 outlet channels, it may be possible for channelling effects to occur within the system. The narrow peak suggests that this may be the case, with water potentially transmitted via a channelised flow path.
- There is however uncertainty about the seasonal effect on the reeds' growth that could possibly lead to channelisation during the spring tracer test.

- The relatively short RTD tail suggests that retention of mine water within dead zones was less evident than at Whittle, perhaps as a consequence of the low length to width ratio at Allerdean Mill, though it is not possible to be certain.

Strafford

In contrast to the Allerdean Mill wetland, the Strafford wetland indicates a flatter RTD curve with a longer tail (Figure 4.8d). The wetland was only in its first year of operation since site commissioning; the wetland was very sparsely-populated with reeds during the tracer test. This flatter and wider RTD curve could be due to the presence of 'islands', which were constructed as planting blocks in the wetland, resulting in flow recirculation effects, and hence a more well-distributed flow within the wetland (flatter RTD curve), leading to long retention of a large proportion of the water before exiting the system (long RTD tail) (Persson and Wittgren, 2003). The dispersion and water exchange with stagnant deep zones (i.e. such as created by the planting blocks) can also increase the spreading of residence time and a longer tail of a tracer breakthrough curve (Kjellin et al., 2007). Despite the sparsely-populated reed colonies the Strafford wetland flow was notably well-distributed (*cf.* as was the case of Lambley wetland during its first year operation) within this small open water body wetland. It appears that the creation of the planting blocks in the wetland may assist in ensuring a greater degree of flow mixing across the system.

Mousewater

The Mousewater wetland is characterised by a reasonably wide RTD curve (Figure 4.8e). Visual observations at the treatment site indicate a wetland system which is mature, with significant reed development across the system. The Mousewater wetland was at the end of its fifth year of operation at the time of the tracer test but, possibly because of the very large size of the wetland system (8400 m^2 of treatment area), flow is well-distributed within it despite the dense stands of reeds. This was probably coupled with a low length to width ratio of the wetland, ensuring a better flow distribution across the full width.

Cuthill

The RTD shape for Cuthill wetland is fairly similar to the Mousewater wetland RTD (Figure 4.8f). The Cuthill system was nearing the seventh year of operation at the time of the tracer test with a mature reeds' growth. The wetland has an unusual L-shaped geometry (see section *1.6.1.8* of Chapter 1 for detail layout) and it is uncertain whether this would have any direct influence on the good flow distribution shown in Figure 4.8f. Evidence from other systems suggests that the presence of large volumes of vegetation debris usually results in flow short-circuiting, but there is no evidence of this at Cuthill. The reasonably well-distributed flow in the Cuthill and Mousewater wetlands may be governed to some extent by seasonal effects i.e. during the summer season when vegetation grows well. These conditions may possibly favour a more even flow distribution in the system.

Clearly there are multiple influences on the wetland residence time distribution as discussed above:

- Wetland vegetation appears to be a key influence that affects the movement of flow through whether the sparsely- or densely-vegetated reeds across the wetlands (see Figure 4.9)
- Similarly, seasonal variation during the tracer test may be important i.e. summer or winter (growing or non-growing season) which has great influences on the reeds' growth thus also affecting the flow movement
- The age of wetland seems to have a great influence whether reeds development over years of operation may ensure a more distributed flow or conversely may impart a flow short-circuiting effect
- Additionally, the wetland length to width ratio may also important in whether governing a preferential flow path or capable of distributing the flow across its full width

These are therefore the possible inter-related influences which characterise the distribution of residence time within these investigated wetland systems. Nevertheless, it s difficult to exactly identify the influence of one compared to the other in such wetland cases. This has also been seen in other wetland flow studies e.g. Martinez and Wise (2003a), Worman and Kronnas (2005) and Kjellin et al. (2007) amongst others that there appears to be several possible influences on wetland water residence time and flow patterns in both field experiment and simulation study.

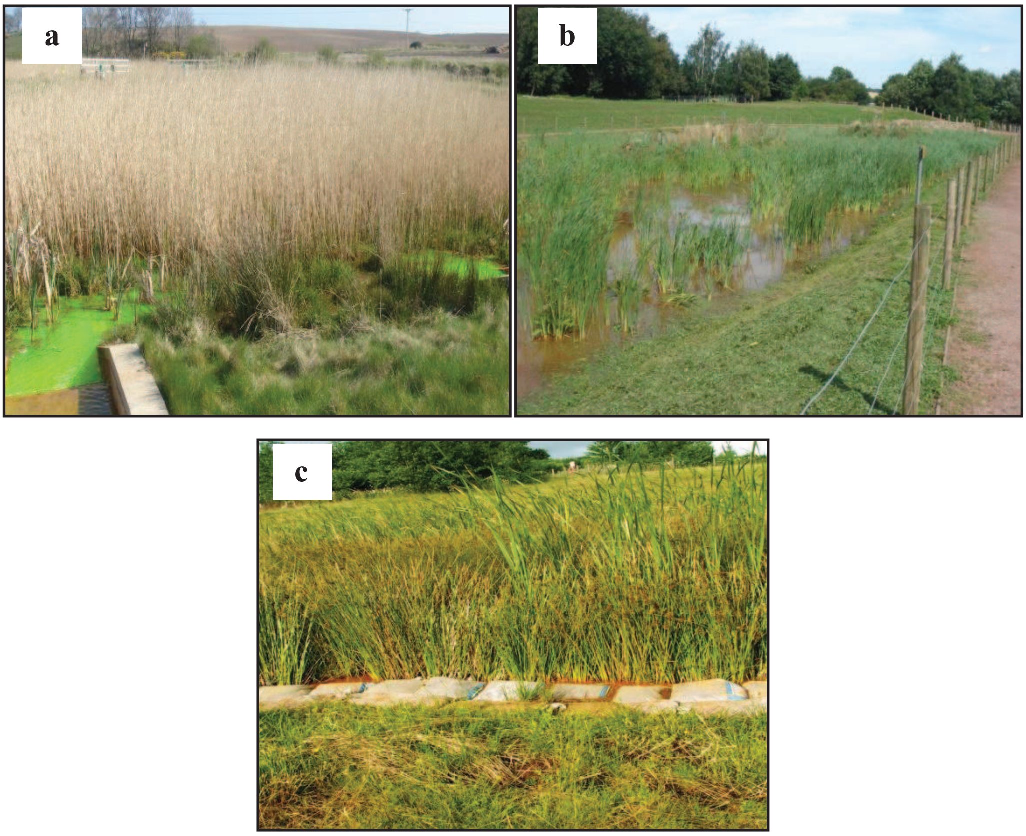


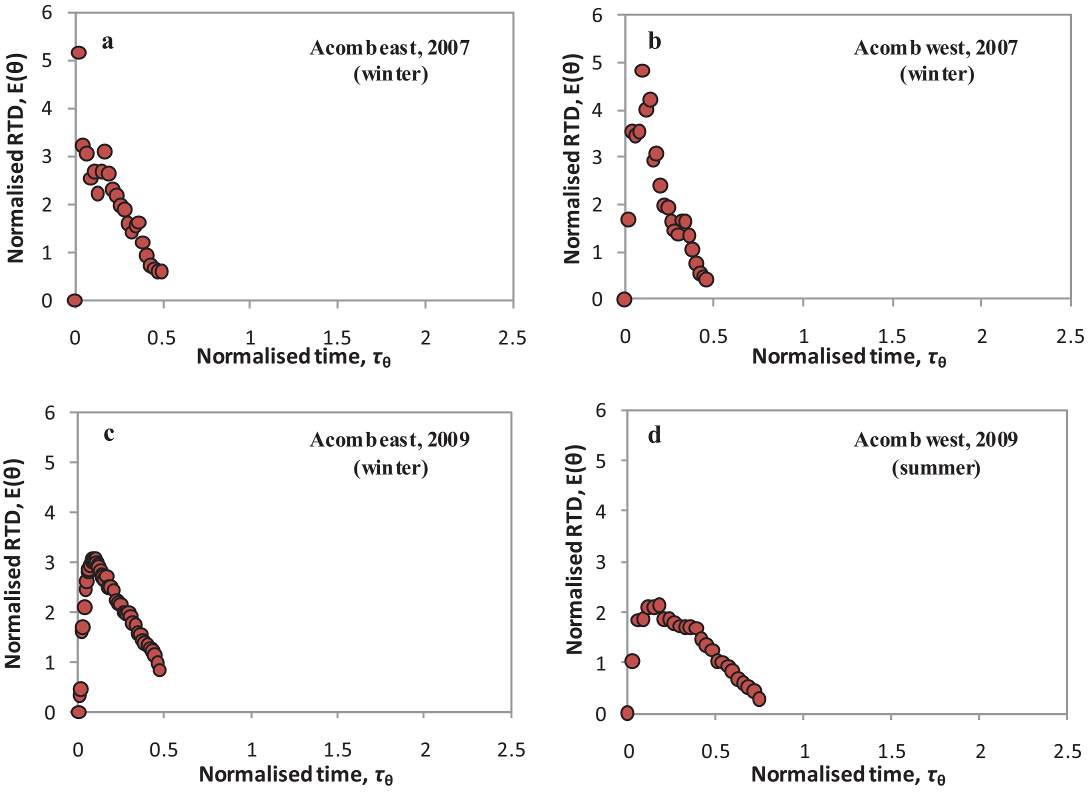
Figure 4.9 Images show wetland vegetation (a) Re-development of reeds after winter seasons at Allerdean Mill wetland (b) sparsely-vegetated reeds during first year operation at Strafford wetland (c) maturely-developed reeds at Whittle wetland

4.3.3 Tracer residence distribution time (RTD) of lagoon systems

As with the wetland systems, actual tracer RTDs for the investigated mine water treatment lagoons are shown in Appendix G (Figure G.1). Similarly, the normalised RTD curves are presented and plotted on the same scale for comparison of the observed tracer RTDs between systems, as shown in Figure 4.10. As with the wetland systems, discussion on a site-by-site basis is presented here, to illustrate the possible influences on lagoon residence time distributions. A summary of lagoon hydraulic characteristics is given in Table 4.7.

Of these 7 treatment sites investigated, 4 of them have already in their fifth year's operation or more. Visual observations indicate large amount of ochre builds-ups present in places within the treatment system. The flow rate for these lagoon systems ranges from as low as 5.8 L/s to as high as 78.7 L/s (measured during the tracer tests). These include a range of lagoons' volume between 1050 – 6527 m^3. Engineered design aspect of these treatment lagoons has a range of length-to-width ratio of between 1.2 to 4.7, and depth ranges from 1.6 to 3.0 m. Whenever possible, dual-tracer test is conducted for verifying the results, however this often limited by site-specific restrictions on the use of intended tracer as discussed earlier.

Generally, the lagoon systems indicate tracer RTD curves which are very narrow, characterised by an early sharp RTD peak as shown in Figure 4.10. Note that most of these lagoons serve as a pre-treatment unit(s) for settlement of iron-rich mine water prior to final polishing treatment in a wetland. It might be anticipated that the occurrence of stagnant dead zones caused by accumulation of settled iron hydroxide solids and debris on the bottom of the lagoons may be an important factor for the reduction of effective water depth in the lagoons, although several other factors may also be significant for the generally lower hydraulic performance of the lagoons (this will be further discussed in section 4.4.5).



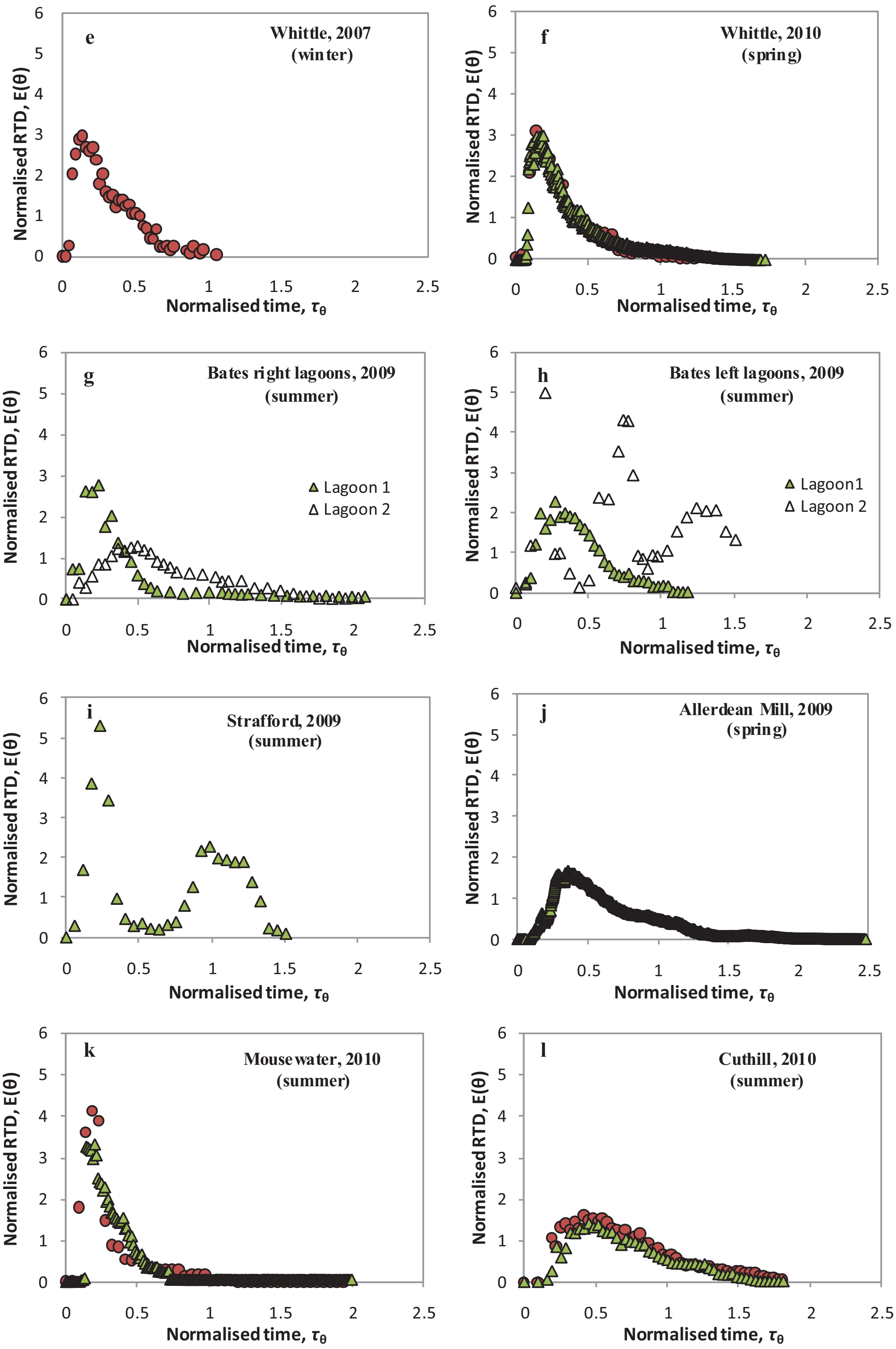


Figure 4.10 Normalised tracer RTD curves for lagoon systems plotted on the same scale for comparison. Red circles denote bromide tracer, green triangle denote Na-fluorescein tracer

Table 4.7 Summary of hydraulic characteristics of lagoon systems

Variable	**Acomb^a East**	**Acomb^a West**	**Acomb East**	**Acomb West**	**Whittle^a**	**Whittle**	**Bates Right L1**	**Bates Right L2**	**Bates Left L1**	**Bates Left L2**	**Strafford**	**Allerdean Mill**	**Mousewater**	**Cuthill**
Season of monitoring	winter	winter	winter	summer	winter	spring	summer	summer	summer	summer	summer	spring	summer	summer
Age of system (years)	5	5	7	7	5	8	5.8	5.8	5.8	5.8	0.8	1.5	5.8	7.1
System area (m^2)	375	375	375	375	900	900	2850	2850	2850	2850	850	883	3036	726
System volume (m^3)	1050	1050	1050	1050	1305	1305	6242	6242	6242	6242	2040	1325	6527	1089
Length-to- width ratio (unitless)	1.5	1.5	1.5	1.5	3.0	3.0	2.0	2.0	2.0	2.0	4.5	4.7	1.2	3.2
Water depth (m)	2.8	2.8	2.8	2.8	1.65	1.65	2.2	2.2	2.2	2.2	2.4	1.6	2.2	2.0
Flow (L/s)	6.25	5.8	6.25	6.5	25	25	78.69	78.69	58.55	58.55	14.04	9.67	36.72	10.72
Tracer recovery (%)^b	82.14*	82.14*	61.75*	77.74*	82.05*	95.97* 119.29†	130.62†	155.24†	69.19†	65.78†	69.69†	76.58†	84.72* 76.00†	67.66* 77.68†

[a] Data from Kruse et al. (2007)

[b] Calculated as the percentage of total mass recovered from the amount of tracer added

[*] Denotes bromide and [†] denotes Na-fluorescein, respectively

Acomb

Tracer tests at Acomb lagoon were conducted at both east and west lagoons during winter 2007, and repeated in the east lagoon during winter 2009 and in the west lagoon during summer 2009. No tracer data are available from the west lagoon during winter 2009 because of the malfunctioning of auto-sampler during the test, and therefore it was repeated during summer 2009. During the tracer test in 2007, the effect of reduced effective water depth was apparent in Acomb east lagoon (Figure 4.10a); visual inspection showed that the lagoon had a greater build-up of settled ochre, reaching the water surface level in places (Kruse et al., 2009). This may create a flow short-circuiting effect as the effective depth is reduced substantially, resulting in the very early sharp RTD peak, followed by another two peaks observed over the duration of the tracer test (see Appendix G (Figure G.1a) for clarity). This effect was also evident in Acomb west lagoon. However, the flow into this lagoon is slightly lower, and the build up of ochre is also less, which may explain the longer time before the tracer peak is observed i.e. water flows more slowly to reach the outlet (Figure 4.10b).

Wider RTD curves are seen at Acomb during tracer tests conducted in 2009 (Figure 4.10c and Figure 4.10d) compared to 2007. This was expected, since the 2009 test followed ochre sludge removal from the east lagoon and part of west lagoon in July 2008. Additionally, the relatively wider curve in the west lagoon could possibly be coupled with seasonal effect during summer 2009 tracer test; convective mixing became significant during summer season to provide a more distributed flow across the system given a relatively small lagoon system. Therefore, within these lagoons of similar size, the effect of ochre sludge removal seems to be important in the distribution of residence time across the system as observed by relatively wider RTDs seen in 2009 (compared to 2007). Seasonal effects may also be important but it is hard to determine with certainty given the intervention to remove sludge between the two tracer tests.

Whittle

As with the wetlands, short-circuiting effects are also apparent in the Whittle lagoons. However, given a relatively large system (hence the volume) this could be the likely reason for the comparatively wider curves seen in Whittle compared to Acomb lagoon

(Figure 4.10e and Figure 4.10f), because flow is distributed slightly more uniformly across this large, elongated lagoon. Note that the Whittle lagoon system consists of two lagoons operated in parallel, both exiting through a single outlet channel. Preferential flow could be occurring through these parallel systems, but mixed at the system outlet before exiting the lagoon. These mixing and re-circulation effects of water within the system may result in retention of large volumes of water. Given a high length-to-width ratio of this lagoon, this may also assist in maintaining large amounts of effective volume whilst also resulting in longer RTD tails in the lagoon.

Bates

The Bates treatment system exhibited fairly distinct tracer RTDs for each of the lagoons, despite 4 identical lagoon shapes at this site. The Bates lagoon system comprises two sets of lagoons which operate in parallel (right and left side from the pumping station). Each side consists of two identical lagoons which operate in series before entering a wetland. On the right side of the treatment system both lagoons have notably longer RTD tails than the left side lagoons (Figure 4.10g compared to Figure 4.10h). Given that the flow split is relatively higher to the right side, comparatively greater volumes of water were transmitted through these lagoons, which allowed for greater retention of more slowly moving water fractions given a deep lagoon system. However, it is noticeable that the first lagoon (to the right side) indicates an RTD curve which is more skewed, with a more dispersed flow pattern than seen in the subsequent treatment lagoon, which is relatively less dispersed. This is not surprising because the first lagoon receives mine water with an initially high iron concentration; under such alkaline and aerobic conditions rapid oxidation and precipitation of iron will occur, thus leaving substantial amounts of settled iron hydroxides at the bottom of the lagoon, reducing its depth. This may in turn create an abundance of dead zones (reduces effective water depth of lagoon), which will favour the occurrence of flow short-circuiting across the system. In contrast the second lagoon in series receives a relatively lower iron concentration, following settlement of most ferric iron in the first lagoon, and therefore a more effective depth can be expected without significant flow streaming. Notwithstanding these differences, the high length-to-width ratios and depths of the lagoons allows for greater retention of water, possibly explaining the relatively long RTD tails seen in both right side lagoons.

The same effect would be expected to be seen in the left side lagoons. The first lagoon receives a smaller proportion of the total flow compared to the right side and, as such, water moves more slowly across the system, with a more distributed flow and hence a less dispersed flow pattern (Figure 4.10h). Nevertheless, the second lagoon on the left side indicates apparent preferential flow paths across the system, as shown by three distinct RTD peaks. Field observation showed that the lagoon was highly turbid in nature, suggesting the presence of high oxyhydroxide iron concentration and may therefore suggest that substantial ochre build-up is occurring, resulting in the apparent reduction in depth and consequent preferential flow paths.

Strafford

The Strafford lagoon also shows an apparent preferential flow path effect across the system, as shown in Figure 4.10i. During the tracer test the Strafford treatment system was only in its first year of operation since site commissioning. It is noticeable that there appear to be two significant flow paths across the treatment lagoon (i.e. bimodal RTD curve). One possible reason typically associated with this effect is flow streaming effects. It is possible that this effect is attributed to the stagnant dead zones with ochre build-ups within the reeds planted along the margins of the lagoons, which are intentionally provided to improve the aesthetics of the scheme. Field observation showed that some amount of Na-fluorescein tracer was trapped within this vegetation and only moved slowly to the system outlet. Therefore, while much of the tracer was retained within these zones, fast moving water may create a significant short-circuiting effect and preferential paths in the surface layer. This effect may be exacerbated by the retention of flow within the dead zones and possibly because of the uneven bottom topography of the newly-constructed treatment scheme, where ochre build-ups were present in places.

Allerdean Mill

The flatter RTD shape and the very long RTD tail observed in the Allerdean Mill lagoon was presumably due to water moving slowly across the parallel elongated lagoons at this site (Figure 4.10j). The high length-to-width ratio lagoons may retain a significant portion of water along their length since they receive a reasonably low flow.

Cuthill

As with the Allerdean Mill lagoon, a relatively less dispersed RTD with a long tail is also seen in the Cuthill lagoon (Figure 4.10l). However, the Cuthill lagoons are relatively smaller than the Allerdean Mill lagoons, and they receive a higher flow rate. This could explain the slightly more distributed flow across the Cuthill system. Similarly, the relatively lower length-to-width ratio of the Cuthill lagoon could possibly result in the shorter RTD tail seen in the system compared to Allerdean Mill.

Mousewater

The Mousewater lagoon indicates an RTD curve which is very dispersed and exhibits a long tail (Figure 4.10k). This lagoon has a unique shape, separated by a concrete dividing wall to enable continuous lagoon operation on one side whilst draining down the parallel side to allow removal of ochre sludge. The system configuration may favour the development of preferential flow paths as the high flow water moves through these parallel lagoons. The flows through the two sides mix at the outlet, with retention of some fractions of the water volume, and thus a long RTD tail. Retention of the slowly moving water within stagnant zones would be possible given the fairly large volume and depth of the lagoon.

4.3.4 Comparison of wetlands and lagoons RTDs

There appear to be multiple influences that possibly affect the distribution of residence time in the wetland and lagoon systems (i.e. the different RTD shapes) observed in this study. Because generally more than one influence may be present, it is difficult to know exactly the effect of one compared to the other. For instance, in most wetlands vegetation appears to be a key influence, but this is also greatly influenced by the seasonal variation (growing or non-growing season), while the age of the system itself may also be of great importance (i.e. the sparsely- or maturely-developed reeds). It is anticipated that vegetation and seasonal variations have a greater influence on wetland RTD compared to lagoons.

In contrast, for lagoon systems vegetation is clearly not an important influence on the RTD. The RTD shapes in lagoons are typically associated with stagnant dead zones in deeper parts of lagoons, which favour development of flow streaming effects and/or preferential flow paths through these zones. This reduced effective lagoon depth seems to have a great influence on lagoon RTD. Development of such dead zones is most likely due to the build up of ochre, which may impart a short-circuiting effect. Therefore while much of the lower/deeper water layer may be retained within these stagnant zones, short-circuiting may be simultaneously occurring in the upper/surface layer. In contrast, in most wetland systems, short-circuiting is typically favoured by the channelling effect caused by densely populated reed stands or by accumulated dead vegetation. The relatively shallow depth of wetlands exacerbates these problems. As evidenced during the tracer tests, the lagoon RTDs tend to exhibit greater short-circuiting effects than the wetland RTDs (see Figure 4.10 compared to Figure 4.6 and Figure 4.8). This is characterised by a relatively early narrow curve with sharp peak(s), and occurs in most lagoons investigated.

Notwithstanding these vegetation and depth effects, the wetland and lagoon RTDs are both influenced by the age of the system, typically associated with the maturity of vegetation in the case of wetlands, and with depth reduction due to ochre build-up in the case of lagoons. This is particularly important for wetlands, since the year-to-year changes in vegetation growth appear to have such a great influence on the RTD. Similarly for lagoons, over years of operation the number and importance of dead zones will increase due to accumulated ochre. Given that most lagoons serve as the pre-treatment unit(s) prior to wetland treatment, and also that lagoons are typically deep, this abundance of dead zones within settled ochre may result in further short-circuiting with long-term operation if the ochre sludge is not dredged out. An obvious recommendation is therefore to ensure regular sludge dredging if efficient performance is to be maintained. Likewise, the length-to-width ratio seems to have a great influence in both wetland and lagoon systems such that this design configuration will either aid in distributing the flow across the full width or conversely result in preferential flow path. It will be shown later (in section *4.4.5.1*) that a greater length-to-width ratio has a significant influence on the greater lagoon hydraulic efficiency, although this effect is coupled by the greater lagoon depth as well.

These multiple influences were also seen in other wetlands and ponds studies. For instance, Martinez and Wise (2003a) reported the different residence time distribution of a wetland treating domestic wastewater in Florida. Differences were attributed to non-uniform distribution of vegetation, suboptimal cell shapes, variable microtopography of the wetland cells, and other landforms in the cell bottoms creating short-circuited channels. Persson and Wittgren (2003) reported several design aspects which can affect the hydraulic conditions and performance of ponds that receive wastewater from agricultural areas, including the length-to-width ratio and depth, to some degree the flow, inlet and outlet locations, vegetation and topography. Kjellin et al. (2007) found from a simulation of a wetland receiving treated sewage in Sweden that heterogeneity in vegetation had a significant impact, and dominated the wetland residence time distribution and flow patterns, with other influencing factors including the wetland bottom topography and water exchange with stagnant zones and dispersion characteristics.

Therefore further discussions will show how these different RTD shapes can be precisely measured, by means of a tracer flow modelling approach, in an effort to account for the flow pattern across the systems. The flow behaviour within wetlands and lagoons will be represented by the computed hydraulic characteristics and performance measures, which in turn will enable a comparison of the hydraulic performance of wetlands and lagoons. Such an approach will also enable a more detailed assessment of the significance of the possible influences on tracer RTD already suggested in this section.

4.4 TRACER FLOW-PATTERN MODELLING

4.4.1 Introduction

Further to the previous discussion on wetland and lagoon RTDs, this section details the modelling approach performed on the system RTDs to account for the different flow pattern within each treatment scheme. These differences in RTD shapes are represented by the computed hydraulic characteristics and performance metrics from a tanks-in-series (TIS) model. This enables further assessment and precise comparison between wetland and lagoon hydraulic performance, in order to evaluate how these hydraulic performance metrics may be affected by the several possible influences on such performance, as discussed in the previous section.

4.4.2 Evaluation of tracer test results from tanks-in-series (TIS) model

The theoretical background for using a tracer flow pattern modelling approach, and in particular the tank-in-series (TIS) model, are detailed in section 2.6 Chapter 2. The TIS model was adopted for further analysis of the tracer RTDs to yield the mean tracer residence time and other hydraulic characteristics for evaluation of the hydraulic performance of the investigated treatment systems. Based on the TIS model, the tracer RTD shape is characterised by the number of continuously-stirred tanks in series, n, which corresponds to the distribution of residence time within the system. The extent of the distribution of time is essentially governed by the degree of system deviation or dispersion from the plug-flow (ideal flow condition), which in turn results in the variations of flow distribution leading to non-ideal flow movement across the system. Theoretically, a large n TIS will result in a system with limited dispersion, indicated by a small system dimensionless variance (hydraulically more efficient system). Conversely, greater dispersion, and larger dimensionless variance, will result in a smaller n TIS (hydraulically less efficient system). The theoretical relationship between system dimensionless variance, σ_θ^2 and n TIS has been shown in section *2.6.3.1* Chapter 2.

4.4.2.1 TIS model calibration

As noted earlier, the TIS model for tracer RTDs is represented by the gamma distribution function, a two-parameter probability density function, which comprised of the number of tanks-in-series, n and the residence time, τ_i. For verification, the TIS model was first calibrated against several n and τ_i values using data from the trial tracer test at Lambley wetland in July 2008. Accordingly, the model calibration was performed by different approaches until the best fit to actual data was obtained. These approaches were: (i) n and τ_i calculated from moment analysis (ii) n and τ_i simultaneously solved to produce the least squares (LSQ) error between the TIS model and the observed data (iii) n and τ_i from the least squares error for the modified gamma distribution function to account for the delay in tracer detection (Kadlec and Wallace, 2009). By these means, the resulting parameters (e.g. mean residence time, n TIS, dimensionless variance and dispersion number) were compared and the best method was chosen based on the least root mean squares (RMS) error, which corresponds to the best fit of the TIS model and actual tracer test data. These resulting parameters were then used for comparison of system hydraulic performance within the investigated mine water treatment wetlands and lagoons.

In most cases, the TIS from moment analysis exhibited a reasonably poor fit to the tracer RTDs, as it failed to capture a significant portion of most RTD peaks and occasionally missed the RTD tails. This resulted in a greater magnitude of error as indicated by the root mean squares error between the TIS model and tracer RTD data. Minimising the error between the actual and modelled data using the least squares (LSQ) method showed a lesser magnitude of error between the model and actual tracer RTDs. Nevertheless, in cases where there was a delay in tracer detection adoption of this method minimised the extent of system dispersion, characterised by a notably low dimensionless variance (and thus dispersion number). This in turn led to n being large, which seemed unrealistic compared to values of n for typical constructed wetlands (as summarised by Kadlec and Wallace, 2009). Taking into account the delay in tracer detection, by correcting for the shifting time of breakthrough by using the delayed TIS from least squares method, yielded the best fit to actual tracer RTDs in all cases as it takes into account the delay in tracer detection and gave realistic values of n and degree of dispersion. The results of this TIS model calibration are presented in the following section.

4.4.3 TIS model calibration results

Adoption of the TIS model for the 2008 tracer RTDs in Lambley wetland shows the greatest differences between the three modelling approaches (Table 4.8 and Figure

4.11). These differences in the accuracy of the model fit are given by the root mean squares (RMS) error between the observed data and the model fit. As noted earlier, the tracer RTDs from the different tracers employed during the 2008 trial tracer test indicated essentially identical RTD shapes. Modelling these RTDs according to the TIS model also demonstrated fairly similar results of the model fit despite using the different tracers. Here, comparison of the resulting parameters from the TIS fit using the three different methods are shown in Table 4.8. This is undertaken to determine which of these methods is most representative of the actual field data. The modelling data are shown in Appendix E.

Table 4.8 Comparison of TIS model fit to actual data using data from the Lambley wetland (2008). Mean and data range are presented from the different methods; TIS from moment, TIS from least squares (LSQ) and delayed TIS from LSQ (after Kadlec and Wallace, 2009)

	Moment		**LSQ**		**Delayed TIS**	
	Mean	Range	Mean	Range	Mean	Range
Mean residence time, τ_m (d)	0.486	0.435-0.522	0.473	0.449-0.492	0.486	0.461-0.507
Number of TIS, *n*	10.2	7.9-14.6	11.5[c]	10.4-13.2	5.0[c]	4.8-5.2
Variance, σ^2	0.031	0.013-0.035	0.021	0.015-0.023	0.024	0.017-0.026
Mode, τ_p (d)	0.434	0.405-0.456	0.431	0.415-0.445	0.419	0.403-0.432
RMS error	0.277	0.233-0.321	0.226	0.212-0.262	0.190	0.169-0.234
[e]Dimensionless variance, σ_θ^2	0.105[b]	0.068-0.126	0.088[c]	0.076-0.096	0.202[bc]	0.199-0.210
Dispersion number, *D*	0.056[c]	0.035-0.068	0.046[b]	0.040-0.051	0.114[bc]	0.111-0.119
[f]RTD efficiency, e_{RTD}	0.895[b]	0.932-0.874	0.912[c]	0.924-0.904	0.798[bc]	0.801-0.790
[g]Volumetric efficiency, e_v	1.135	1.015-1.221	1.103	1.048-1.150	1.134	1.077-1.185
[h]Hydraulic efficiency, e_λ	1.013	0.946-1.066	1.006[a]	0.968-1.040	0.904[a]	0.863-0.936

All parameters are unitless unless otherwise stated (units in brackets)

Same letters indicate significant difference at [a]differences are significant (*$p<0.05$*), [b]differences are highly significant (*$p<0.01$*), and [c]differences are very highly significant (*$p<0.005$*)

[e]Defined as the variance divided by the square of the tracer mean residence time

[f]Computed as $1-(\sigma_\theta^2)$

[g]Defined as the tracer mean residence time divided by the nominal residence time

[h]Defined as the RTD efficiency multiplied by the volumetric efficiency

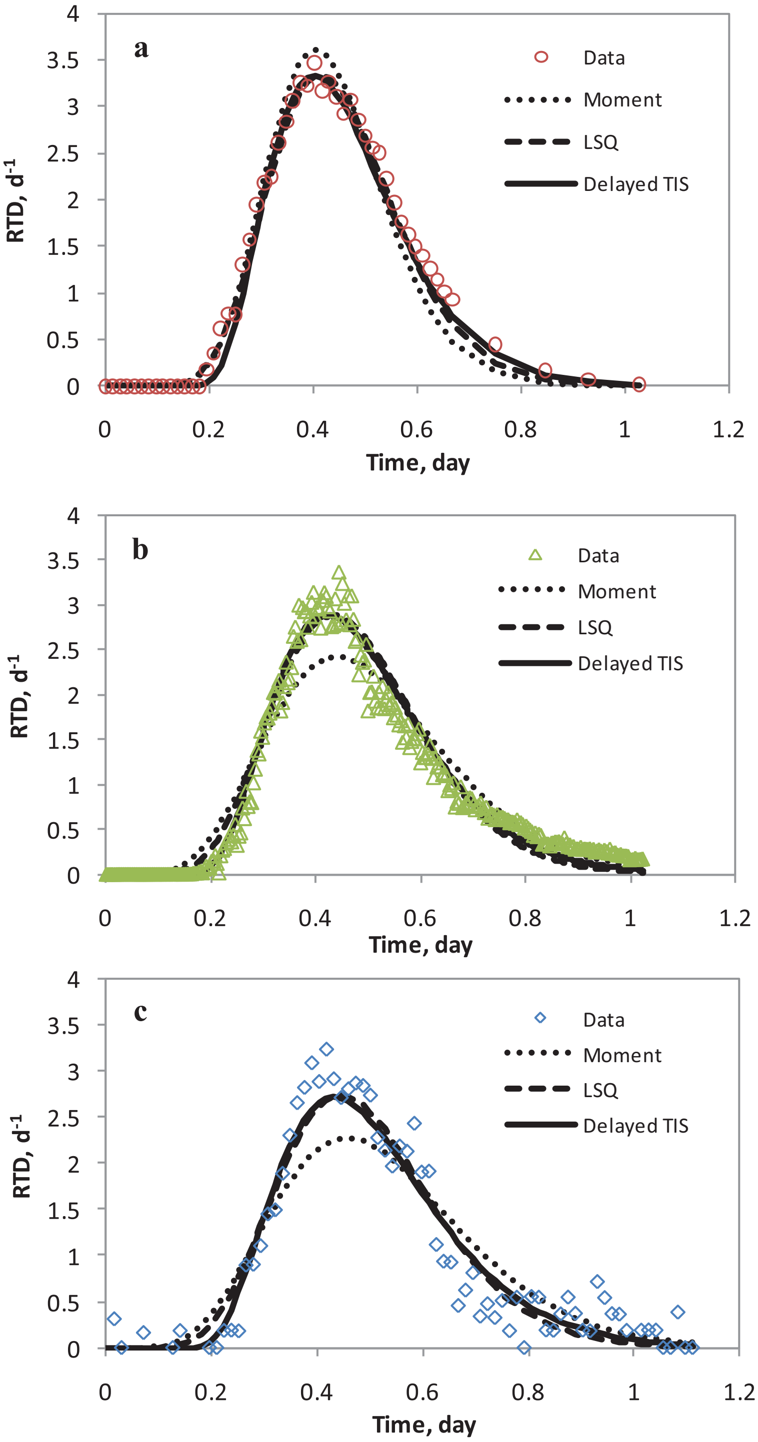


Figure 4.11 TIS fit for Lambley wetland data using TIS from moment, TIS from LSQ and delayed TIS from LSQ to determine the best TIS fit for (a) bromide (b) Na-fluorescein (c) NaCl RTD. Delayed TIS from LSQ yielded the best fit to RTD data

As noted from Table 4.8, the delayed TIS from LSQ method gives the best accuracy of the TIS fit and the RTD data which is based on the lowest RMS error, as shown in Table 4.8. The corresponding *n* TIS from the best fit is 5.0, 5.1 and 4.8 for bromide, Na-fluorescein and NaCl, respectively, showing the consistency of the RTD shape irrespective of tracer, and therefore best representing actual wetland performance. The value of *n* as given from the LSQ is between 10-13 TIS, while the moment gives the *n* of between 8-14 TIS. These differences in *n* TIS between the LSQ and delayed TIS are significant (*p=0.0017*). These distinct ranges of system *n* TIS can be characterised by the extent of wetland dispersive behaviour as indicated by the wetland dispersion number, *D*. The delayed TIS gives *D* between 0.111-0.119 while the LSQ yields a comparatively smaller degree of dispersion in the range of 0.040-0.051 (differences are significant, *p=0.0057*). The moment produces *D* of between 0.035-0.068 (also significantly different from the delayed TIS, *p=0.00008*).

It can clearly be seen that significantly different results are produced from the different TIS approaches, for larger *n* TIS apparently results from a relatively low extent of system dispersion. This relationship is to be anticipated given Eqn. 2.30, which results in an inverse relationship between system dimensionless variance (corresponding to dispersion number) and the *n* TIS i.e. the larger the dimensionless variance (and dispersion number), the smaller the *n*. On the other hand, the tracer mean residence times are within the range of 0.46-0.51, 0.45-0.49 and 0.44-0.52 days using the delayed TIS, TIS from LSQ and TIS from moment approaches, respectively. These differences are not significant (*p=0.8421*). Similarly, the mode (peak of tracer) are not significantly different from one method to another (*p=0.6323*). Therefore, the conclusion of this is that mean residence time and peak tracer alone do not tell the full story of hydraulic performance.

As can be seen in Figure 4.11, the moment fit missed a significant portion of the RTD peak for Na-fluorescein and NaCl, and the tail of bromide RTD, and thus resulted in a relatively high RMS error (23-32%) compared to the other two methods (LSQ yields an RMS error of 17-26%, delayed TIS from LSQ yields 16-23% RMS error, as shown in Table 4.8). This phenomenon has also been observed by Kadlec and Wallace (2009) for free water surface (FWS) and horizontal sub-surface flow (HSSF) wetland systems in many instances in the United States. Graphically, the LSQ and delayed TIS from LSQ illustrate a fairly close fit to one another. However, the resultant parameters e.g. the *n* and dimensionless variance (which are important parameters to determine the RTD shape) may vary significantly as noted earlier. Consequently, due to these significant differences in the computation of *n* TIS and the dimensionless variance (or dispersion number), the overall system hydraulic efficiency may be significantly affected. Significant differences are noticeable between the LSQ and delayed TIS.

On the other hand, the high value of *n* obtained from the LSQ is possibly the result of the relatively low dimensionless variance, which characterises the spread of the tracer from the mean. Neglecting the delay in tracer detection while using the LSQ method has resulted in the spread, or dispersion, of tracer being substantially reduced while in fact, a greater extent of flow dispersion occurs during the actual tracer movements. This is therefore the likely cause of *n* being substantially larger when produced from the LSQ method, which is not desirable. The use of delayed LSQ gives a more representative and reliable degree of dispersion which compensates for the drawback of the LSQ method. Most importantly, the delayed TIS gives the lowest RMS error, which suggests that approximation using this model is the closest to the actual data.

4.4.3.1 Comparison of TIS from moment, TIS from LSQ and delayed TIS from LSQ

Overall, it can be seen that the TIS model using the different modelling approaches indicated significant differences in the resulting hydraulic parameters. In most cases, the TIS from moment exhibited a reasonably poor fit to the tracer RTDs, as it failed to capture a significant portion of most RTD peaks, and occasionally missed the RTD tails. This resulted in a significantly greater magnitude of errors as indicated by the greater RMS error from the moment compared to the other two methods. Additionally, the moment method may result in a large range of system *n* TIS and dispersion characteristics from the different tracers employed. For instance, during the trial tracer test, *n* varied greatly i.e. 8 compared to 14 TIS between NaCl and bromide tracer RTDs when using the moment method, while only a slight difference resulted from the delayed TIS method i.e. 4.8 compared to 5.0 TIS (the 0.2 difference was considered negligible because *n* is typically taken as an integer number of tanks). This suggests that the delayed TIS method is useful to ensure consistency of results when using different tracers and, conversely, the moment method is inappropriate in such circumstances.

The TIS fit from the LSQ method showed a lesser magnitude of errors between the model and actual tracer RTDs compared to the moment method. Adoption of this LSQ method, however, minimised the extent of system dispersion, as characterised by the low dimensionless variance (hence the dispersion number). This in turn has led to n being large, which seemed unrealistically large for such a wetland system (Kadlec and Wallace, 2009). The delayed TIS from LSQ yielded the best fit (as indicated by the lowest RMS error) to actual RTDs, since in most cases it takes into account the delay in tracer detection and gives realistic values of n and degree of dispersion. With respect to a systems' residence time, in most cases the LSQ method computed the lowest mean residence times compared to the moment and delayed TIS methods. This erroneous result could possibly be due to the fact that the LSQ method does not account for the significant plug-flow fraction of water (presumably during the delay), such that this may result in an apparently longer retention of flow in the system (Kadlec and Wallace, 2009).

On the evidence of the tracer test results (all other tracer tests) on which the TIS model were applied, the TIS from least squares gave a better approximation between the observed and predicted residence time distribution curve compared to the moment method. In cases where there was delay in tracer detection, delayed TIS from least squares model demonstrated even better model fit to observed field data. TIS from moment, even though it exhibited larger magnitude of errors between observed data and predicted values, the moment parameters can provide early essential estimation for anticipated shape and scaling parameterisation for tracer RTD curve. The calculated moment parameters could be used as an early prediction value for shape and scaling parameters, which are simultaneously solved by the SOLVER application in Microsoft Excel (solving for alpha α, shape parameter corresponding to n, number of TIS and beta β, scaling parameter resulting in the mean residence time), as described earlier. These early estimations could significantly aid in minimising the errors between the observed and predicted results. Despite the minimal errors it shows, the TIS model was still insufficient to give good fits to tracer test data with multiple peaks, as experienced in a few cases in this study. In such cases, TIS parallel path model was attempted to model the observed flow pattern (Kadlec and Wallace, 2009). However, if the parallel path model is warranted, there is something seriously wrong with system that needs improvement (Kadlec and Wallace, 2009).

4.4.4 Tracer flow-pattern modelling results for wetland systems

The tracer modelling results for the investigated wetland systems are presented in this section. This includes discussion of the variations of system hydraulic characteristics resulting from the tracer modelling approach, typically obtained from the delayed TIS from least squares method, which best fitted to most RTDs observed. This will later allow for comparisons of system hydraulic performance within the different wetland and lagoon systems. An example of tracer modelling results to show year-to-year changes in system hydraulic performance of a wetland system, Lambley, is presented here. Comparisons of system hydraulic performance of other wetland and lagoon systems are also presented in the following discussion.

4.4.4.1 Comparison of TIS model results for the Lambley wetland over a 4 year period

The RTDs from the tracer tests conducted at Lambley each year from 2007 – 2010 were each modelled using the TIS model to evaluate the distribution of the residence time (i.e. flow behaviour) and to assess the hydraulic performance of the wetland during the 4 years of operation since commissioning. This is based on the best fit of the TIS model to actual tracer RTDs according to the delayed TIS from LSQ method (after Kadlec and Wallace, 2009).

Table 4.9 RTD characteristics and performance metrics for the Lambley wetland over the 4 year period since commissioning

Tracer test	Nominal residence time τ_{an} (day)	Mean residence time τ_m (day)	Mode τ_p(day)	Dimensionless Variance σ_θ^2	Dispersion number D	No. of TIS n	RTD efficiency e_{RTD}	Volumetric efficiency e_v	Hydraulic efficiency e_λ
2007[a]	[†]0.299	0.248	0.208	0.324	0.203	3.1	0.676	0.830	0.562
2008[b]	[†]0.321	0.461	0.403	0.199	0.112	5.0	0.801	1.438	1.152
	[‡]0.321	0.507	0.433	0.210	0.119	4.8	0.790	1.580	1.250
	[*]0.318	0.490	0.423	0.198	0.111	5.1	0.802	1.543	1.238
2009[c]	[*]0.323	0.382	0.329	0.236	0.137	4.2	0.764	1.183	0.904
	[†]0.324	0.363	0.315	0.244	0.142	4.1	0.756	1.122	0.849
2010[d]	[*]0.323	0.436	0.372	0.222	0.127	4.5	0.778	1.35	1.05
	[†]0.323	0.440	0.377	0.232	0.134	4.4	0.768	1.361	1.045

All parameters are unitless unless otherwise stated (units in brackets)

[†]Tracer test using sodium bromide (NaBr), [‡]Tracer test using sodium chloride (NaCl), [*]Tracer test using sodium-fluorescein (Na-fluorescein)

[a] Tracer recovery of 84%, [b] Mean tracer recovery of 94%, [c] Mean tracer recovery of 85%, [d] Mean tracer recovery of 95%

Figure 4.12 illustrates the result of the TIS model fitted to actual tracer RTDs from 2007-2010. For consistency note that only bromide RTD data are presented in Figure 4.12 to represent each years' residence time distribution (comparison using the same tracer is more appropriate). It is worth referring back to section *4.3.2.1* when reading this section, since section *4.3.2.1* presents the year-to-year changes in Lambley wetland. Tabulated RTD characteristics and performance metrics for the Lambley wetland are as shown in Table 4.9.

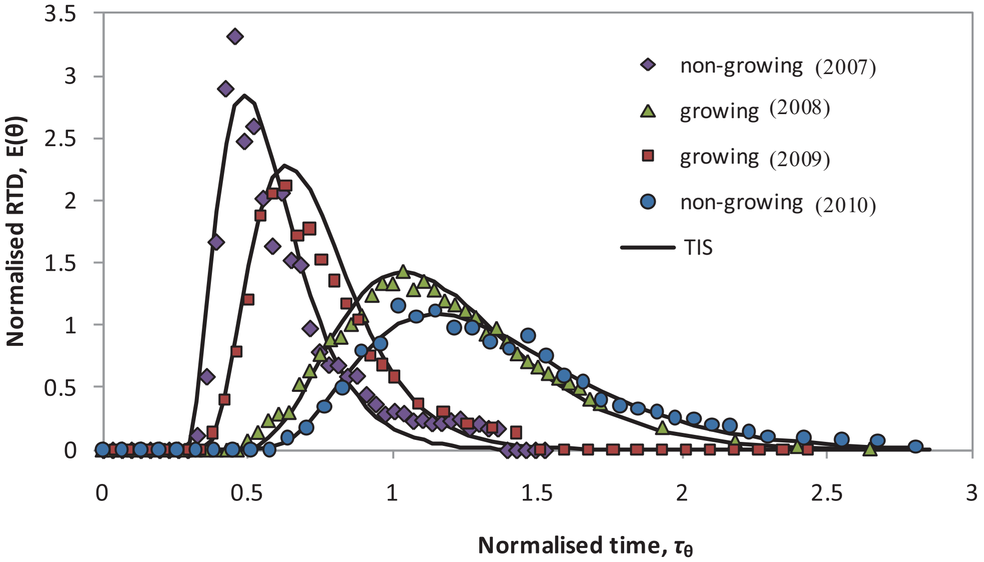


Figure 4.12 TIS fit of actual tracer RTDs for Lambley wetland to illustrate the changes in distribution of system residence time from 2007-2010. Only bromide RTD data are presented in the figure for consistency. TIS are the delayed TIS model from LSQ, which is the best fit to actual RTD data

Note that in Figure 4.12 the TIS fit obtained from the delayed TIS from least squares method produces the best TIS fit to actual tracer data (after Kadlec and Wallace, 2009). In 2007, a mean residence time of 0.25 days was found to correspond to about three TIS (*n*=3.1), illustrated by a slightly high and narrow curve with a long tail (see Table 4.9 and Figure 4.12). This corresponds to system dispersion number, *D* of 0.203. Monitoring of the wetland system in 2008 indicated considerable changes in RTDs (from 3 different tracers with essentially identical shapes; not shown in Figure 4.12), which correspond to about five TIS (*n* ranged between 4.8-5.1). The resulting mean residence time is longer at 0.46-0.51 days. The changes of TIS shapes in 2008 were a result of the relatively smaller extent of flow dispersion compared to 2007, as shown by *D*, which was 0.111-0.119 in 2008, compared to 0.203 in 2007. The TIS curve in 2008 was considerably wider, with a relatively shorter tail, approximating an ideal tracer flow curve compared to system performance in 2007 (see Thackston et al., 1987; Persson et al., 1999 for discussion of ideal tracer flow curves, for example). Further monitoring of the wetland in 2009 revealed a rapid change of *n* from about five to four TIS (*n* between 4.1 and 4.2), which corresponds to a tracer mean residence time of 0.36-0.38 days. The TIS curve was illustrated by a narrower and higher peak curve than that observed in 2008. A greater extent of dispersion was seen during this year, with *D* of 0.137-0.142, thus resulting in a lower *n* TIS. In 2010, the *n* had increased to 4.3-4.5, with a longer mean residence time of 0.44 days, as *D* had decreased to 0.127-0.134. This is reflected in a slightly wider and lower peak TIS curve than observed in the year before (Figure 4.12).

Overall, the wetland was found to be significantly dispersed from ideal plug-flow, indicated by the large extent of system dispersion: *D* ranged from 0.111-0.203 and *n* ranged from 3-5 TIS (Table 4.9). $D<0.01$ is the dispersion limit for a system considered to represent ideal plug-flow (Levenspiel, 1972) which corresponds to about 50 TIS (this author's computation) or 20 TIS if taking an intermediate boundary of $D<0.025$ (Kadlec and Wallace, 2009). Therefore, the results here seem to suggest that adoption of a TIS model is preferable to a plug-flow with dispersion (PFD) model (another commonly applied model for tracer flow studies) for such wetland system. However, results from the TIS model can in fact be compared to those of the PFD model by comparing its Peclet number, *Pe* (a dimensionless parameter which characterises mixing behaviour according to a PFD model, and is simply the inverse of the dispersion number, *D*). The wetland dispersion number computed from this wetland corresponds to *Pe* from 4.9 and 8.9, which indicates the Lambley wetland to be substantially dispersed compared to a plug-flow system (e.g. Kadlec, 1994).

4.4.4.2 Performance of Lambley wetland over a 4 year period from commissioning

Overall, it can clearly be seen that the wetland mean residence time had significantly increased during the second year of wetland operation compared to its early operation. This possibly means that the maturity of the wetland system had greatly improved the residence time i.e. the densely-populated reeds ensured a better distribution of flow across the system without the presence of apparent flow short-circuiting effects as seen during the early wetland operation. However, after three years wetland operation, the residence time seemed to be considerably shorter than the year before, presumably due to the re-occurence of flow streaming effects. In contrast, a relatively longer mean residence time compared to the third year was seen during the fourth year of wetland operation. These changes in mean residence time appear to be due to the effects of short-circuting across such shallow wetland basins (e.g. Thackston et al., 1987; Holland et al., 2004). A study by Holland et al. (2004) indicated that the mean residence time of a wetland (stormwater treatment wetland) represents the fraction of the wetland that is not short-circuited. Therefore the concept of short-circuting can be used to show the wetland volume effectively being used during treatment.

The changes in the Lambley wetland volumetric efficiency, e_v which represents the fraction of water involved during the flow through the system can be seen in Table 4.9. The e_v seems to correspond to the mean residence time, and is reflected by the shape of RTD during the year-to-year wetland performance. For instance, the lowest e_v was found during the system's first year of operation, during which much of the volume was not being optimally utilised, possibly due to short-circuiting as a consequence of the very sparsely-vegetated reeds. Thus, the mean residence time was very short (hence the peak time) and was reflected by the relatively dispersed RTD curve (small *n* TIS) compared to other years. In contrast, improvement in system effective volume during the second year of wetland operation was reflected in the increased mean residence time and a more distributed flow pattern (hence large *n* TIS). This trend was consistent during the 4 years of monitoring (showing the consistency of the TIS model), since the flow-rate was fairly consistent and there were only minor changes in system nominal volume (due to minor changes of ~3% between the highest and lowest wetland water level). Holland et al. (2004) reported that such a minor change in water level may not affect the RTD in a surface flow wetland.

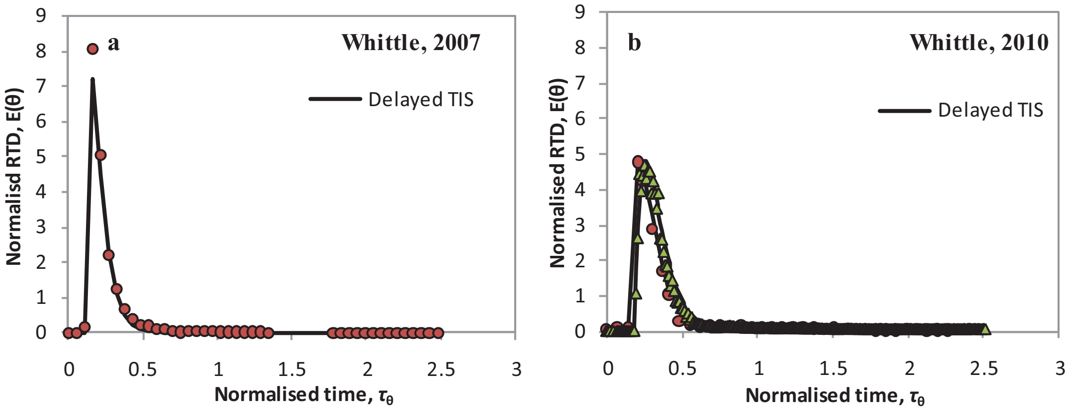
Also notable from Table 4.9, is the wetland RTD efficiency, e_{RTD} which characterises the mixing behaviour of water in the system, and reflects the extent of flow deviation from ideal plug-flow. Note that this performance metric is an approximation of a system's mixing characteristics (relative to ideal plug-flow) (Persson et al., 1999; Kadlec and Wallace, 2009). Improvement of system e_{RTD} was found during the second year of wetland operation whereby this improved wetland mixing behaviour had resulted in a more distributed flow pattern and a lesser degree of dispersion (larger *n* TIS). Lower e_{RTD} was found to correspond with small *n* TIS. This trend was also consistent during the 4 years monitoring. This indication of the effect of flow deviation from an ideal plug-flow could possibly due to flow streaming effects, mainly associated with reeds growth. Kjellin et al. (2007) found that heterogenity in vegetation distribution had the potential to explain a great variation in residence time in a sewage treatment wetland in Sweden.

These variations in wetland e_v and e_{RTD} are ultimately reflected in the variation of system hydraulic efficiency. The wetland hydraulic efficiency, e_λ has improved from 0.56 to 1.15-1.25 between 2007-2008, which then decreased to 0.85-0.90 in 2009. Thus, the system appears to have become more efficient as reeds have developed since commissioning. However, the data from 2009 suggest that this improvement may in fact be short-lived, since further growth of reeds may impart a return to short-circuiting effects due to channelisation. In 2010, e_λ was seen to increase compared to 2009 suggesting that the effect of ongoing reed growth on overall system hydraulic performance is unpredictable. Note that values of e_λ were high in 2008 and 2010 (> 1.0), and this is a reflection of high e_v in each of these years. e_v greater than 1.0 was also seen in 2009 (though not the e_λ). These high volumetric efficiencies (in excess of 100%; $e_v > 1.0$) were likely attributable to the wetland vegetation distribution as discussed earlier, but effect of seasons complicates interpretation.

In essence, despite a consistent flow into the system, the hydraulic performance of this wetland system appears to vary year-on-year, and between seasons. This has been shown by the changes of the wetland hydraulic characteristics and performance metrics, which were noticeably variable since site commissioning. The role of wetland vegetation seems to be a significant influence on the variation in wetland RTD, and thus the hydraulic efficiency of such a wetland system. Clearly, maturely-developed reeds in a wetland system may assist in ensuring a better flow pattern across the system, due to a more uniform flow distribution effects, as indicated by greater n TIS (approching an ideal plug-flow). This on the other hand, is associated with a lower system dispersion number, because the greater the n TIS the less the system deviates from an ideal plug-flow system. Thus, a low system dispersion number would indicate that the system is approaching an ideal system, and should be hydraulically more efficient. Conversely, whenever there is apparent preferential flow paths (i.e. portions of water exiting the system fast and also portions that retained in the system longer as indicated by a long RTD tail), the dispersion number will increase (indicative of a more dispersed flow deviating from an ideal plug-flow pattern) and hence, reducing the number of TIS (less mixing because the flow takes preferential paths across the system). Therefore, the TIS model has shown its reliable application for characterising a wetland system hydraulic performance such as Lambley. This has been achieved by means of assessment of the wetland hydraulic characteristics which appear to reflect the presence of the wetland vegetation itself. Likewise, seasonal effect is also inevitably important for such a change in vegetation growth and flow movement over time as discussed in section *4.3.2.1*. It should also be noted that both the vegetation and seasonal influences are likely working simultaneously, and therefore difficult to distinguish between them in terms of their role in governing hydraulic efficiency.

4.4.4.3 Tracer flow-pattern modelling results for other wetland systems

With respect to the previous discussion on wetland RTDs in section *4.3.2.2*, discussion of the results of the TIS modelling approach applied to other wetland systems are presented in this section. Here, only the best TIS fit to actual RTDs are shown, which were used for evaluation of the hydraulic performance characteristics for each of the investigated wetland systems. These are illustrated on the same scale in Figure 4.13 below. The RTD characteristics and performance metrics from the TIS model for wetland systems are shown in Table 4.10.



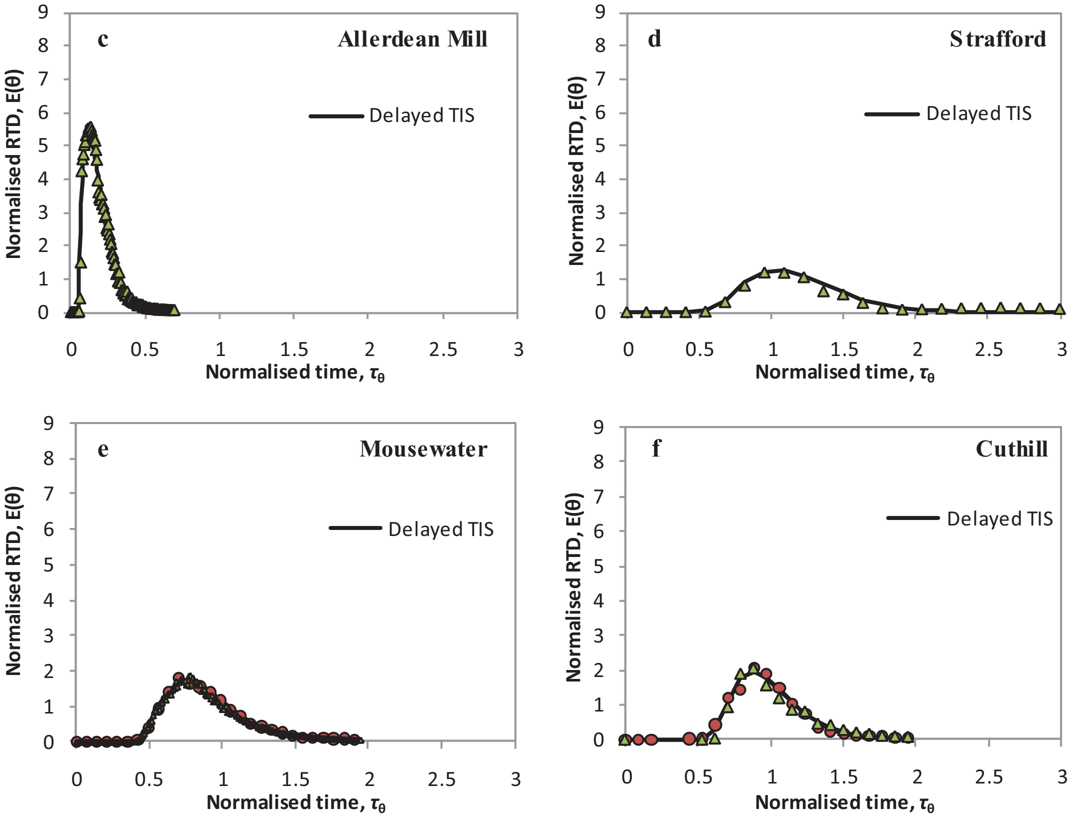


Figure 4.13 Normalised TIS model fitted to tracer RTD data for wetland systems plotted on the same scale for comparison. Red circles denote bromide tracer, green triangle denote Na-fluorescein tracer

Table 4.10 RTD characteristics and performance metrics of wetland systems from the TIS model

Treatment site	**Nominal residence time** τ_{an} **(day)**	**Actual mean residence time** τ_m **(day)**	**Mode** τ_p **(day)**	**Dimensionless Variance** σ_θ^2	**Dispersion number** D	**No of TIS** n	**RTD efficiency** e_{RTD}	**Volumetric efficiency** e_v	**Hydraulic efficiency** e_λ	**Length-to-width ratio L/W**	**System age (during tracer test) (year)**	**Flow rate (L/s)**
Whittle	†0.258	0.053	0.095	0.606	0.577	1.65	0.394	0.204	0.080	5.5	5	25.00
Whittle	†0.237	0.088	0.064	0.511	0.407	1.96	0.489	0.370	0.181	5.5	8	23.07
	*0.240	0.102	0.078	0.506	0.400	1.98	0.494	0.424	0.209	5.5	8	23.07
Allerdean Mill	*0.317	0.107	0.069	0.507	0.401	1.97	0.493	0.338	0.167	2.1	1.5	7.91
Strafford	*0.225	0.362	0.318	0.187	0.104	5.4	0.813	1.605	1.305	5.7	0.8	14.04
Mousewater	†0.742	0.698	0.320	0.238	0.138	4.2	0.762	0.941	0.718	3.5	5.8	31.90
	*0.742	0.699	0.596	0.244	0.142	4.1	0.756	0.942	0.712	3.5	5.8	31.90
Cuthill	†0.771	0.468	0.290	0.240	0.139	4.2	0.760	0.607	0.461	5.3	7.0	10.61
	*0.771	0.468	0.289	0.247	0.144	4.1	0.753	0.607	0.457	5.3	7.0	10.61

†Tracer test using sodium bromide (NaBr), *Tracer test using sodium-fluorescein (Na-fluorescein)
All parameters are unitless unless otherwise stated (units in brackets)

As noted in Figure 4.13, clearly there are distinct TIS shapes between the wetland systems and further to previous discussion in section *4.3.2.2,* there is significant variability between different systems, with several plausible influences on the RTD as discussed earlier. These different RTDs are characterised by the number of TIS, *n*, which ranges from 2-5 TIS (see Table 4.10). These correspond (as an inverse relationship) with system dispersion number, *D*, which ranges from 0.104-0.577. *D*, characterises the dispersion of flow from the mean (mean of the residence time distribution according to an ideal flow pattern). In theory, a greater *n* TIS would indicate a greater amount of complete-mixing, and approximate an ideal plug-flow system (Persson et al., 1999). Therefore there should ideally be a small degree of dispersion from this ideal flow pattern.

Individual assessment of the wetland systems using *n* and *D* showed that the Whittle wetland (during 2007 tracer test) had the highest dispersion number, *D* of 0.577 (corresponding to *n* = 1.7), while the Strafford wetland indicated the lowest system dispersion number of 0.104 (corresponding to *n* = 5.4). The poor flow mixing effect and variation from the ideal flow pattern at Whittle wetland may be attributable to the apparent short-circuiting across the system following its fifth year of operation. Field observation showed that the wetland is a mature system with well-established reeds and a substantial build up of dead plant material (Kruse et al., 2007). This can lead to the development of channels through the wetland, and thus a rapid transit of flow across the system, but also there is portion of water that remained in the system longer (i.e. the long RTD tail). In contrast, the Strafford system is only in its first year of operation, with notably very sparse reed growth, but the flow was well-distributed within the system (i.e. a low dispersion number). Note that this is in contrast to Lambley wetland during its first year operation, during which the flow was very dispersed. Thus, it appears that whilst reeds may result in short-circuiting, neither are they necessarily essential to ensuring good hydraulic performance. The greater flow mixing effect seen at Strafford wetland was probably due to the presence of deep zones and islands created as planting blocks near the inlet and in the middle of the wetland system. This results in a greater mixing and redistribution of flow, and hence a more well-distributed flow across the system. Persson (2000), in a simulation of surface flow wetland shapes of a Scandinavian stormwater treatment wetland, found that an island placed in front of the inlet improves the hydraulic performance with respect to short-circuiting, effective volume and degree of mixing. The study also indicated that an island placed near the side does not lead to lower hydraulic performance. Thus, the flow in the Strafford wetland was found to be much less dispersed than that of Whittle wetland, despite having a fairly similar system length to width ratio. Additionally, a relatively higher flow and water depth in Whittle (hence the volume) compared to the Strafford wetland may encourage flow short-circuiting, resulting in the very narrow early peak of the RTD. Kjellin et al. (2007) found that a high degree of variance on flow movement and early peaks were associated with the wetland water depth / total volume in a simulation of a wetland in Sweden. Furthermore, Holland et al. (2004) reported that a higher wetland water depth may increase the RTD spread (variance) by 57%, reducing its hydraulic efficiency.

The different TIS shapes resulted in the mean residence time for the wetlands ranging from 0.05-0.7 days. However, direct comparison of these mean residence times will not necessarily imply efficiency of the systems e.g. longer residence time does not necessarily mean an efficient system, because such a system would probably have a long nominal residence time (i.e. due to large system volume or a relatively low flow per treatment volume). Instead, an appropriate measure to compare between these system residence times is by assessing the metric of system volumetric efficiency, e_v which is a measure of mean relative to nominal residence time. Generally, the wetland systems have a range of e_v of 0.204-1.605. Again, the lowest was found in the Whittle wetland during the 2007 tracer test, whilst the longest was found in the Strafford wetland in the 2009 tracer test. These, apparently correspond with the systems dispersion characteristics i.e. the n TIS and D, as discussed earlier. The high e_v in the Strafford wetland (mean residence time 60% higher than nominal residence time) shows that the wetland system was capable of retaining a large proportion of water volume during flow passage through the system, whilst enhancing a more distributed flow across the system and thus encourage a long water travel time. Sherman et al. (2009) reported a mean residence time of 50% greater than the nominal residence time in a free water surface wetland treating effluent from a mine's wastewater treatment plant in Australia. However, the reason of this larger mean relative to nominal residence time was not reported. With respect to effective system volume in the Strafford wetland, carefully constructed bottom profiles (e.g. with deep zones and islands) seem to have potential for being a useful tool in enhancing distribution of water in wetlands, which leads to a better utilisation of the volume and longer mean residence time (Kjellin et al., 2007). Kjellin et al. (2007) simulated the bottom topography profiles of a wastewater treatment wetland constructed with several deep zones and four small islands near the inlet which were found to decrease the variance in water residence time. Their simulation of the impact of different factors on water flow pattern concluded, however, that the effect of bottom topography would still be much less than the impact of vegetation distribution.

Both the system dispersion number and system number of TIS are the important parameters to determine a system RTD efficiency, $e_{RTD,}$ which is a hydraulic performance metric of the dispersive flow behaviour (i.e. the extent of a system deviation from an ideal flow pattern). The wetland systems' e_{RTD} ranges from as low as 0.394 to as high as 0.813. The low $e_{RTD,}$ e.g. 0.394 in Whittle wetland, could possibly mean that the flow within the system appears to be dominated by greatly dispersed fractions of flow, given by the large system dimensionless variance of 0.606 (60% of water was attributed to a deviation from its mean). Similarly, high $e_{RTD,}$ (e.g. 0.813 in the Strafford wetland) may be attributable to a lower extent of flow dispersion as given by the relatively low dimensionless variance of 0.187 (only about 18% of the flow was attributed to a deviation from its mean).

Accordingly, these metrics of e_v and e_{RTD} can be used to make an overall assessment of system hydraulic efficiency, e_λ. As noted in Table 4.10, the e_λ ranges between 0.08 and 1.305. Again the lowest and highest values resulted from the Whittle and Strafford wetland respectively. This shows that the TIS model results in consistent hydraulic performance characteristics for these treatment wetlands, e.g. greater e_λ at Strafford wetland resulted from its greater e_v and e_{RTD}, strengthening the conclusion that these inter-related hydraulic parameters (i.e. n TIS, D, σ_θ^2, e_v, and e_{RTD}) are very important for determining the overall system hydraulic efficiency. Of the two parameters e_v and e_{RTD}, the first has a greater impact on the overall system hydraulic efficiency, e_λ. (Figure 4.14, e_v; $R^2 = 0.998$, e_{RTD}; $R^2 = 0.861$ both $p<0.05$). This shows that a hydraulically more efficient system would be achieved if a longer mean relative to nominal residence time could be achieved in a system, thus providing greater potential for pollutant attenuation and degree of treatment received. This relationship between system hydraulic efficiency and iron removal efficiency will be discussed later. Discussion on a site-to-site basis of the other wetland systems are not included here because the reason for the differences in system dispersion characteristics are generally due to the presence of flow short-circuting effects, creating a significant deviation from ideal flow patterns, as characterised by the *n* TIS and *D*. Each of these systems has been discussed in *4.3.2.2*.

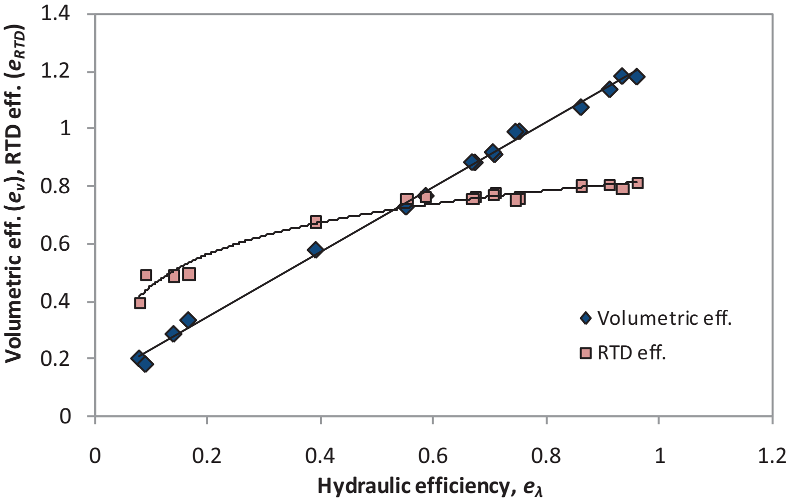


Figure 4.14 System volumetric efficiency (eff.) and RTD efficiency (eff.) in relation to hydraulic efficiency for wetland systems

4.4.4.4 Physical influences on wetland hydraulic performance

Further to discussion in section 4.3.2, it would be interesting to know how the hydraulic characteristics and performance metrics may be affected by the individual possible influencing factors such as length to width ratio, age of system and flow. Therefore, correlation analysis were used to analyse between these factors and the wetland hydraulic characteristics from the TIS model. However, it should be noted that these influences may work simultaneously in each system, therefore it is inappropriate to ignore the effect of others while correlating one to the metric of hydraulic performance. An appropriate analysis to address this issue is to use the partial correlation, a method by which the other variables are 'controlled' whilst correlating one variable to the hydraulic performance metrics. This typically applies when there is a complex relationship between several variables (Field, 2009), such as those found in this study i.e. effect of length-to-width ratio, age and flow on the variation of hydraulic performance (in addition to vegetation and seasonal effects). The correlation coefficients from the partial correlation analysis are shown in Table 4.11 below.

Additionally, the correlation coefficients shown here do not necessarily imply cause and effect between the interacting parameter and hydraulic performance, because of constant engineering design and practice (i.e. length-to-width ratio). For instance, variation in system length to width (L/W) ratio is due to engineered design aspect in different systems that could not be changed over the system operation. Therefore, the correlation presented here is only to show which engineering design aspect is potentially resulting in greater hydraulic efficiency, rather than the effect of varying the length-to-width ratio.

Table 4.11 Partial correlation, *r* between wetlands' hydraulic performance metric and length to width ratio (L/W), flow rate and age of system, $n = 10$

	L/W		**Flow**		**Age**	
Hydraulic parameters	***r***	***p-value***	***r***	***p-value***	***r***	***p-value***
RTD efficiency, e_{RTD}	0.125	0.384	0.369	0.184	-0.177	0.337
Volumetric efficiency, e_v	0.321	0.219	0.489	0.109	-0.464	0.123
Hydraulic efficiency, $e\lambda$	0.328	0.214	0.457	0.457	-0.457	0.457

It is noticeable from table 4.11 that there is no significant correlation found between any factors and the hydraulic performance metrics (all $p>0.05$ significance level). From this partial correlation analysis, it can be seen that there is a great difference when 'controlling' the other variables whilst correlating one to the hydraulic performance metrics. For instance, inclusion of flow and age has greatly increased the amount of variation in hydraulic efficiency attributable to the length to width ratio i.e. from 0.8% to 10.75%, compared to if otherwise the effects of flow and age were ignored (see Appendix N for statistics of wetlands partial correlation; hydraulic efficiency and length-to-width ratio). Similarly, inclusion of length to width ratio and age has reduced the amount of variation in hydraulic efficiency contributed by flow by 3%. However, none of these factors is significantly correlated to the hydraulic performance metric.

This may therefore, suggests that there appears to be other possible influences that might significantly affect the variation in wetland hydraulic performance, which is most potentially the vegetation distribution, coupled with seasonal effects on reed growth. Vegetation is in fact an important factor that affects a wetland flow movement as shown earlier, but it is recognised that this factor may not be the only control.

Rather, there may be multiple influences occurring in the same system. However, there is no single measurement to enable quantification of the individual influence of vegetation except that of the year-to-year changes of wetland RTD in the same system over several years of operation, such as investigated at the Lambley wetland as part of this work. Therefore, a recommendation for future work is to conduct such year-to-year measurements in the same season; a possible weakness of the results presented here. Wetland reeds clearly have a great impact on flow distribution; whereby the reeds' growth may be affected by the age of system. It should also be noted that an increase of wetland age, from its initial commissioning to just the second year of operation, may be important, since the greatest hydraulic efficiency has been observed between these years (at Lambley and Strafford wetlands). This suggests that after the wetland has achieved its optimum hydraulic performance (e.g. following the second year of operation given the evidence here) wetland maintenance or thinning of reeds is important to ensure efficient hydraulic performance over the longer term.

Therefore, as the results here seem to suggest, effects of L/W ratio, flow and age of system do not significantly correlate with the hydraulic performance metrics, suggesting the primary role of vegetation in determining the wetland hydraulic performance (though there are multiple factors interacting in the same time). This relative importance of vegetation effect (in the presence of other factors) in wetlands has also been shown in other studies e.g. Worman and Kronnas (2005); Kjellin et al. (2007). As has been shown by the partial correlation analysis, there is an impact of other factors on one another, indicating the complex relationships among these possible influences in affecting hydraulic performance. Although it is still not certain which of these has the greatest impact, at least other variables are being addressed in some form when identifying an impact of one (Field, 2009). Illustration of the variation in wetlands RTD, volumetric and hydraulic efficiency in relation to L/W, flow and age are shown in Figure 4.15, Figure 4.16 and Figure 4.17, respectively. Note that for each of these factors, there are contributions of other factors that simultaneously affect the variation of hydraulic performance.

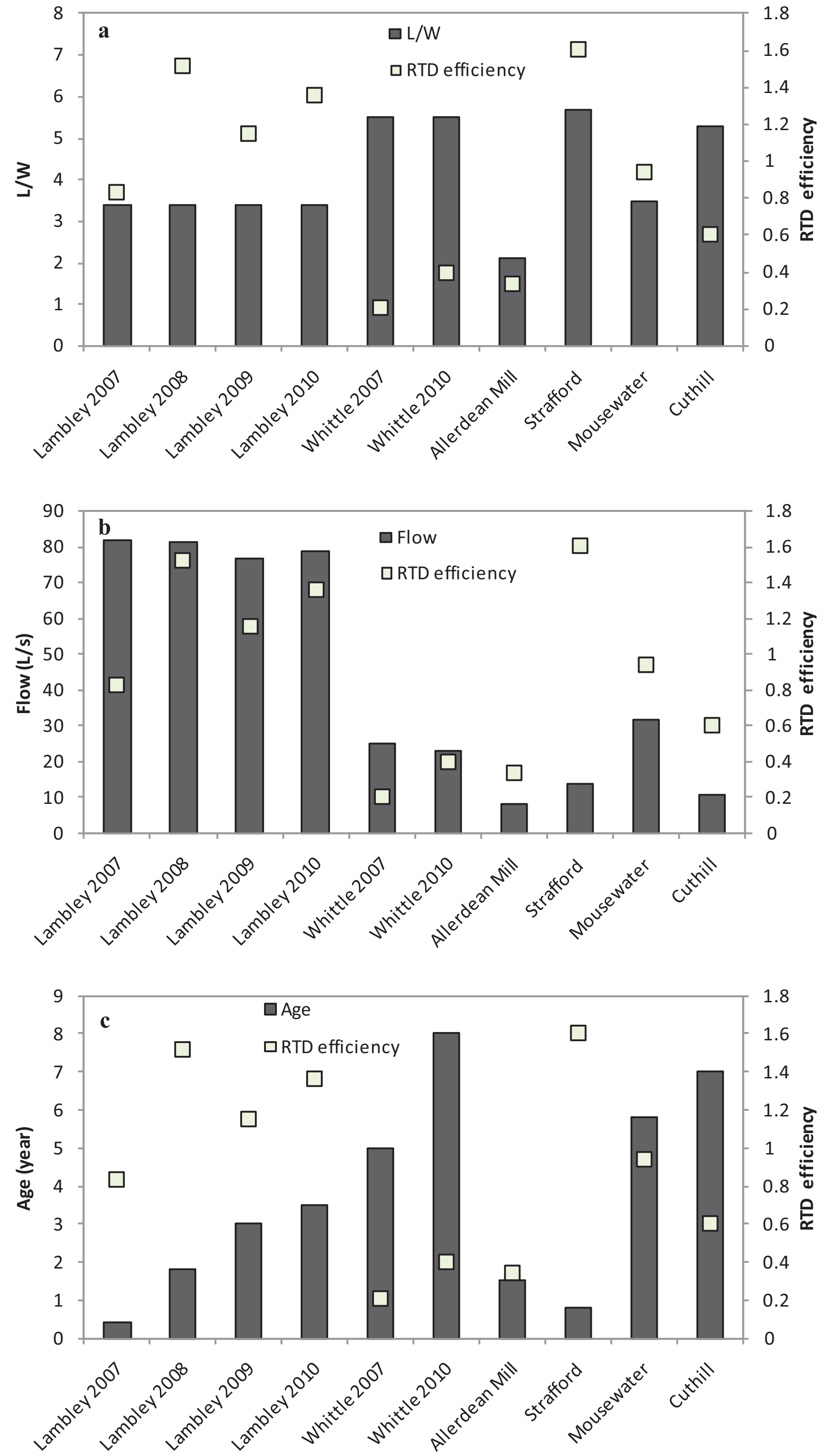


Figure 4.15 Variation in RTD efficiency in relation to (a) length to width ratio (L/W) (b) flow and (c) age for wetland systems

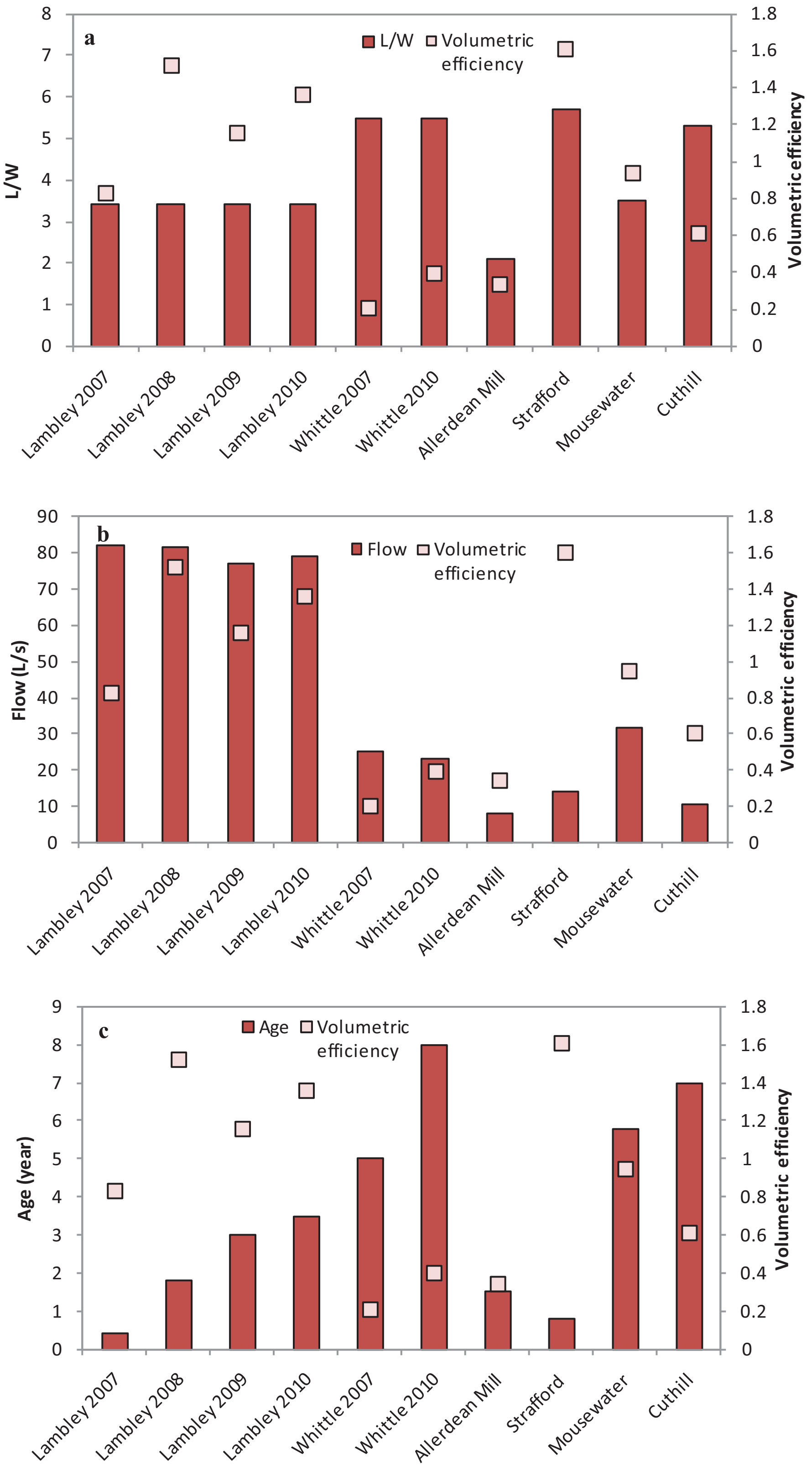


Figure 4.16 Variation in volumetric efficiency in relation to (a) length to width ratio ratio (L/W) (b) flow and (c) age for wetland systems

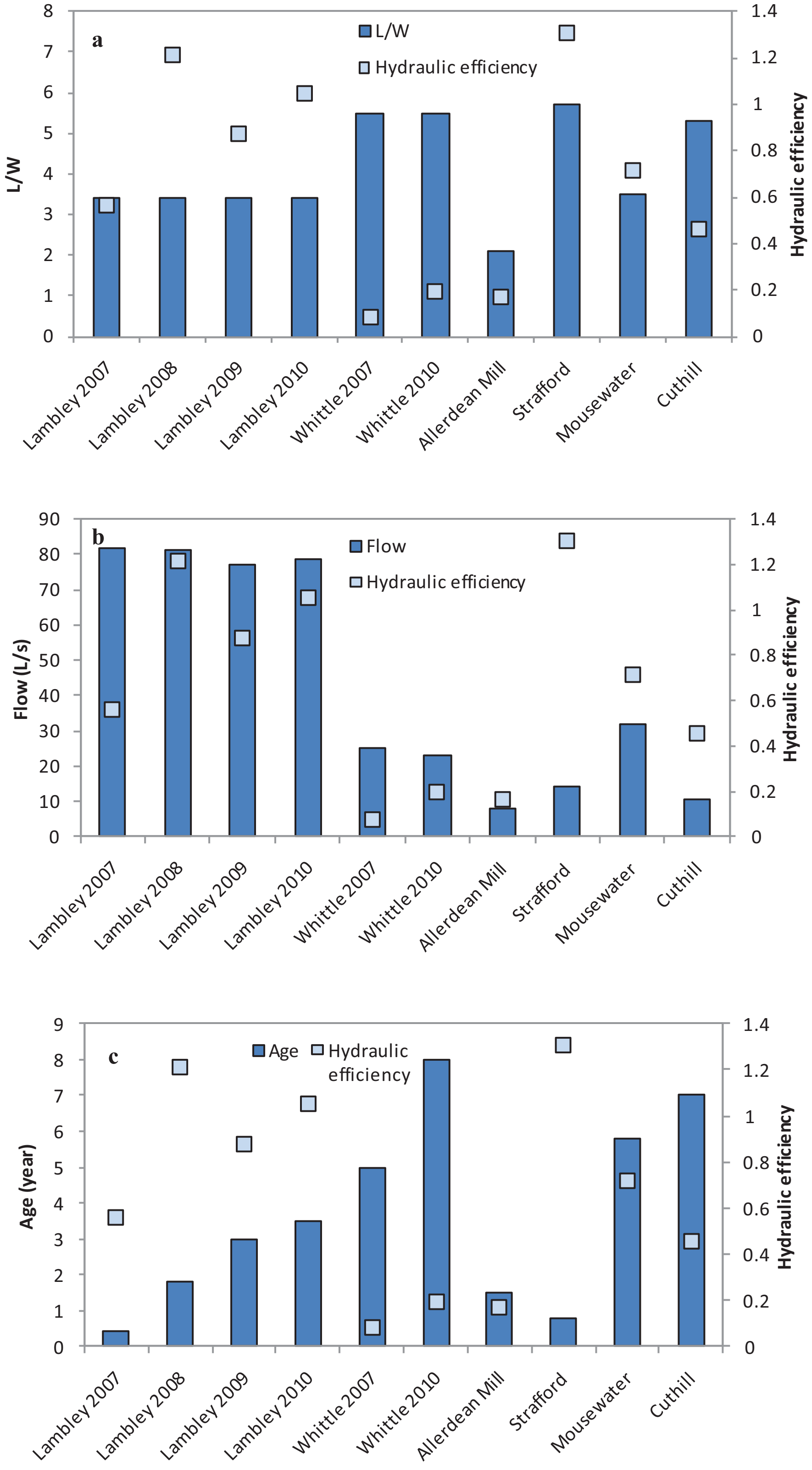
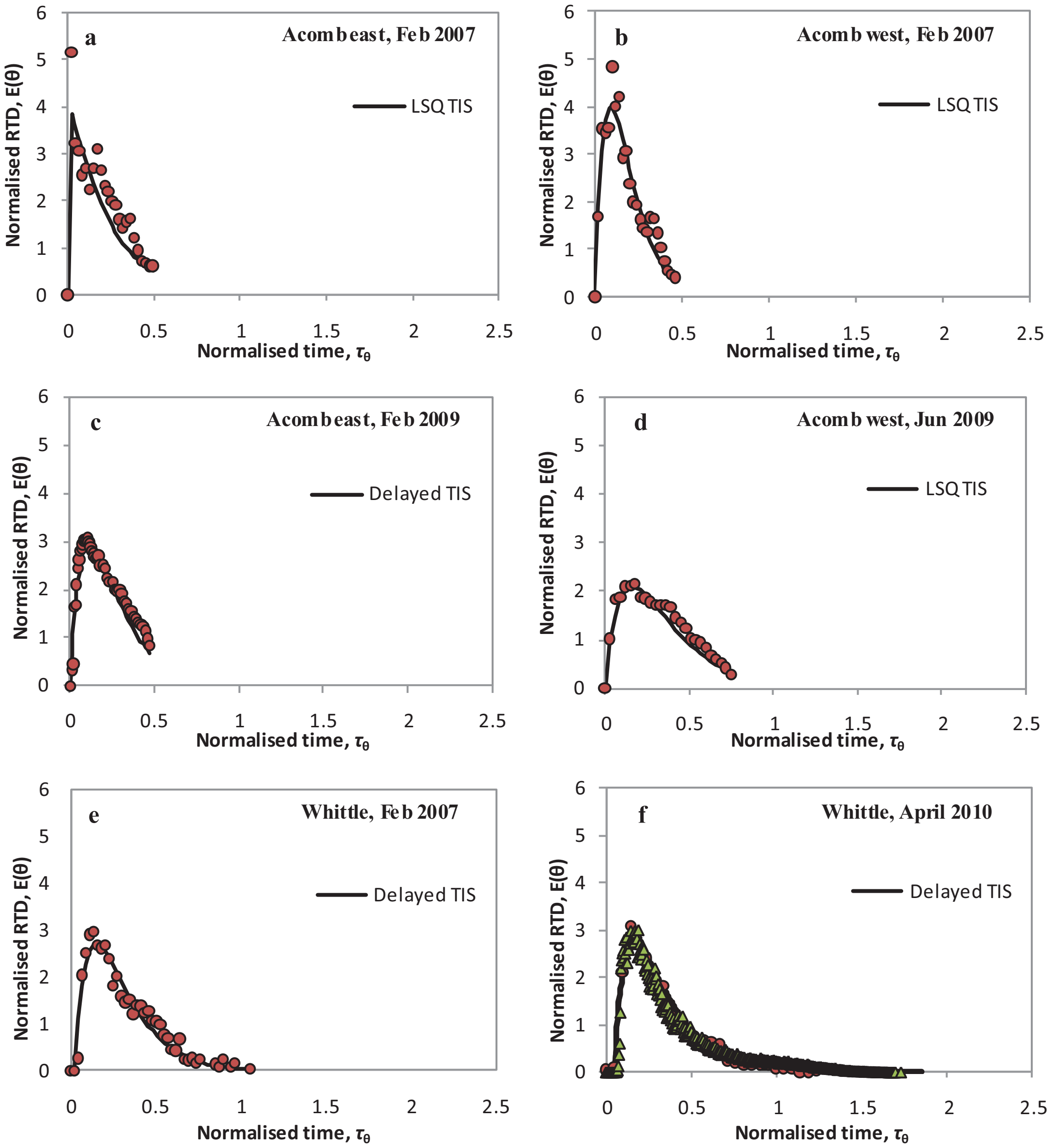


Figure 4.17 Variation in hydraulic efficiency in relation to (a) length to width ratio (L/W) (b) flow and (c) age for wetland systems

4.4.5 Tracer flow-pattern modelling results for lagoon systems

As with the wetland systems, tracer modelling results for lagoon systems are presented in this section. The TIS model fitted to actual tracer RTD data are shown in Figure 4.18 in the normalised forms, and are illustrated on the same scale for comparison between the different lagoon systems. As before, only the best TIS fit are displayed for each RTD from the treatment lagoons.



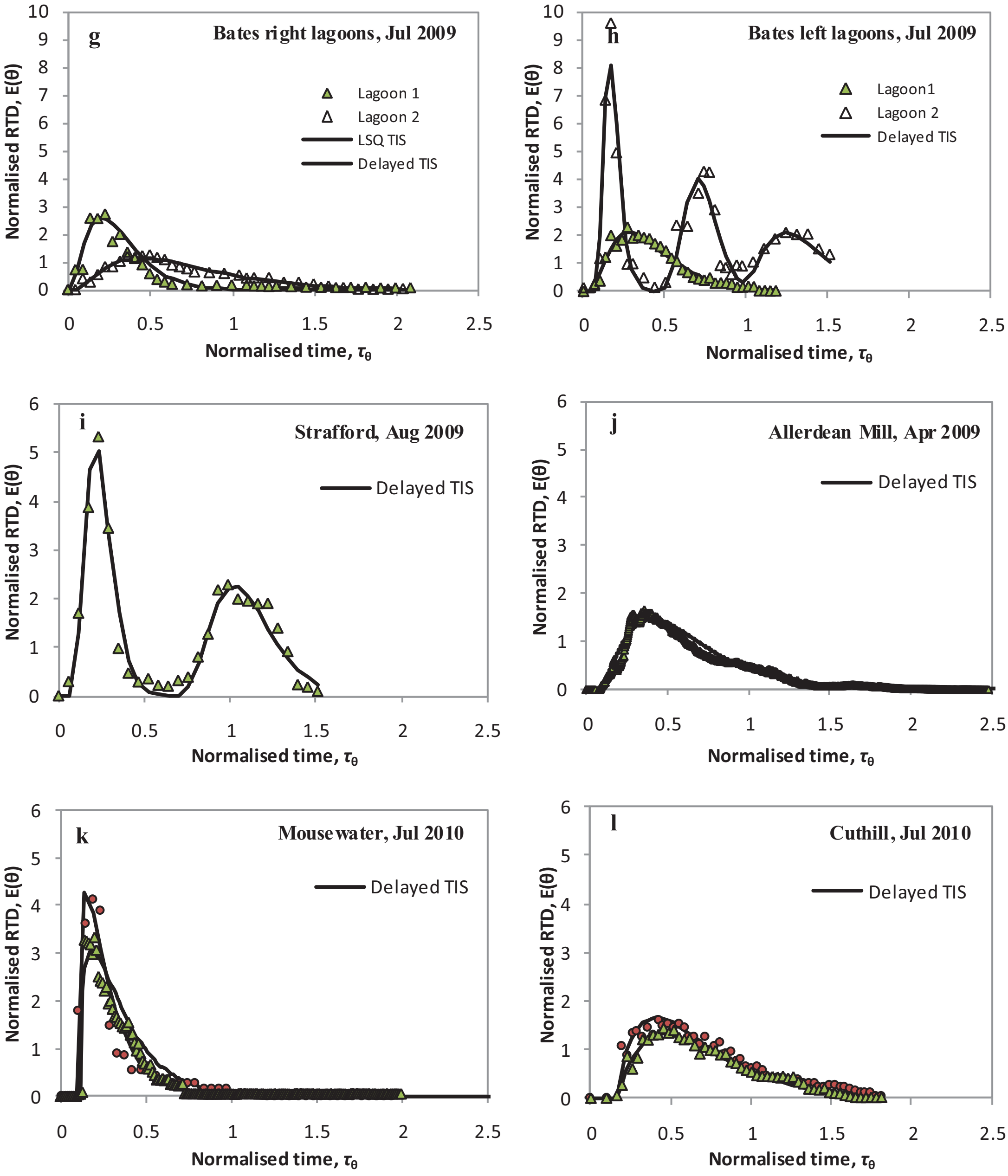


Figure 4.18 Normalised TIS model fitted to tracer RTD data for comparison in wetland systems. Red circles denote bromide tracer, green triangle denote Na-fluorescein tracer

Table 4.12 RTD characteristics and performance metrics of lagoon systems from the TIS model

Treatment site	Nominal residence time τ_{an} (day)	Actual mean residence time τ_m (day)	Mode τ_p (day)	Dimensionless Variance σ_θ^2	Dispersion number D	No of TIS n	RTD efficiency e_{RTD}	Volumetric efficiency e_v	Hydraulic efficiency e_λ	Length-to-width ratio L/W	Design Depth (m)	System age (during tracer test) (year)	Flow rate (L/s)
Acomb(E) 2007	*1.944	0.433	0.027	0.735	0.976	1.36	0.265	0.285	0.075	1.5	2.8	5	6.25
Acomb (W) 2007	*2.082	0.382	0.192	0.498	0.388	2.00	0.502	0.183	0.092	1.5	2.8	5	5.8
Acomb(E) 2009	*1.981	0.505	0.235	0.549	0.467	1.82	0.451	0.255	0.115	1.5	2.8	7	6.25
Acomb (W) 2009	*2.082	0.734	0.347	0.528	0.433	1.90	0.472	0.353	0.167	1.5	2.8	7	6.5
Whittle 2007	*0.605	0.179	0.095	0.510	0.405	1.96	0.490	0.295	0.145	3.0	1.65	5	23
Whittle 2009	†0.642	0.269	0.138	0.575	0.514	1.74	0.425	0.419	0.178	3.0	1.65	8	23
	*0.642	0.278	0.145	0.570	0.504	1.75	0.430	0.433	0.186	3.0	1.65	8	23
Bates (R) 1	†0.918	0.281	0.184	0.346	0.222	2.89	0.654	0.306	0.200	2.0	3.0	5.8	78.69
Bates (R) 2	†0.881	0.656	0.404	0.411	0.284	2.43	0.589	0.745	0.439	2.0	3.0	5.8	78.69
Bates (L) 1	†1.237	0.516	0.355	0.286	0.173	2.95	0.714	0.417	0.297	2.0	3.0	5.8	58.55
Bates (L) 2	$^{\dagger p}$*0.108*	*0.227*	*0.208*	*0.208*	*0.118*	*4.8*	*0.792*	*2.098*	*1.661*	*2.0*	*3.0*	*5.8*	*58.55*
	^{p}*0.409*	*0.448*	*0.496*	*0.079*	*0.041*	*12.6*	*0.921*	*1.095*	*1.008*	*2.0*	*3.0*	*5.8*	*58.55*
	^{p}*0.547*	*0.545*	*0.504*	*0.228*	*0.131*	*4.4*	*0.772*	*0.997*	*0.769*	*2.0*	*3.0*	*5.8*	*58.55*
	^{M}*1.234*	*1.144*	*0.953*	*0.168*	*0.093*	*5.9*	*0.832*	*0.928*	*0.772*	*2.0*	*3.0*	*5.8*	*58.55*
Strafford	$^{\dagger p}$*0.891*	*0.352*	*0.216*	*0.195*	*0.109*	*5.1*	*0.805*	*0.395*	*0.318*	*3.3*	*3.0*	*0.8*	*15.1*
	^{p}*0.672*	*0.663*	*0.551*	*0.170*	*0.094*	*5.9*	*0.830*	*0.987*	*0.820*	*3.3*	*3.0*	*0.8*	*15.1*
	^{M}*1.564*	*0.795*	*0.322*	*0.594*	*0.552*	*1.7*	*0.406*	*0.508*	*0.206*	*3.3*	*3.0*	*0.8*	*15.1*
Allerdean Mill	†1.554	0.952	0.610	0.385	0.257	2.6	0.615	0.612	0.377	4.7	1.6	1.5	6.53
Mousewater	†2.285	0.159	0.083	0.730	0.973	1.4	0.270	0.070	0.019	1.2	2.8	5.8	31.9

	[*]2.285	0.211	0.108	0.727	0.959	1.4	0.273	0.093	0.025	1.2	2.8	5.8	31.9
Cuthill	[†]1.185	0.552	0.296	0.519	0.419	1.9	0.481	0.466	0.224	3.2	2.0	7.1	10.61
	[*]1.185	0.622	0.259	0.465	0.345	2.2	0.535	0.525	0.281	3.2	2.0	7.1	10.61

[†] Tracer test using sodium bromide (NaBr), [*] Tracer test using sodium-fluorescein (Na-fluorescein)

[P] Resulting parameters from parallel TIS model (two-paths modelling approch (Chazarenc et al., 2003))

[M] Resulting parameters from moment analysis

Italicise values are excluded from the comparison of system hydraulic performance (not valid for TIS model comparison)

All parameters are unitless unless otherwise stated (units in brackets)

The lagoons show a relatively greater extent of system dispersion compared to wetland systems as characterised by the greater dispersion number, *D*, and the lower number of TIS, *n*. Overall, the lagoon systems have *D* in the range 0.173 – 0.976, which corresponds (as an inverse relation) with *n* TIS of between 2-3 TIS (Table 4.12). Note that the resulting parameters from the parallel TIS model are not accounted for in this comparison. Two-path flow pattern is apparently seen from Bates (Left) lagoon 2 and Strafford lagoon; when a parallel path model is warranted, this suggests that there is something seriously wrong with the system that needs improvement (Kadlec and Wallace, 2009). Therefore, for consistency these systems were excluded for comparison of system hydraulic characteristics and performance metrics resulting from the TIS model. The highest *D* of 0.976 (the system with greatest dispersion from ideal plug-flow) was observed in the Acomb east lagoon (2007), which corresponds with *n* = 1.4, while the lowest *D* of 0.173 was found in Bates (first lagoon on the left side) which corresponds with *n* = 2.95. These probably reflect the apparent short-circuiting of flow as seen from the very sharp and quick peak of RTD from the Acomb east lagoon, in contrast to a more distributed flow in the Bates lagoon (although lagoons generally have narrower RTDs than seen in most wetlands).

The resulting mean residence times for the lagoons were found to be in the range of 0.159-0.952 days. The system volumetric efficiency, e_v, which is used to compare between the mean relative to nominal residence times ranged from 0.07-0.745. The lowest e_v was found in the Mousewater lagoon, while the highest was found in the Bates lagoon (the second lagoon to the right side). The comparatively low e_v found in the Mousewater lagoon was due to a relatively low mean residence time compared to the nominal residence time due to the large volume of the system. Such a narrow RTD, with *n* = 1.4, suggests that the effect of flow short-circuiting was also pronounced within this system and a large fraction of water was rapidly transmitted across the surface due to reduced lagoon depth.

The greater dispersion characteristics of the lagoons has resulted in a relatively lower range of system RTD efficiency, e_{RTD} (0.265-0.714), compared to wetland systems. These correspond (as an inverse relationship) to a system dimensionless variance, σ_θ^2, of 0.286-0.735. The greatest estimated dispersion in a lagoon system, $\sigma_\theta^2 = 0.735$ and

e_{RTD} = 0.265, was found in the Acomb east lagoon during the 2007 tracer test. The reason for this was probably the fact that this lagoon system received a very high influent iron concentration (approximately 40 mg/L). This is coupled with hydrogen peroxide dosing into the lagoon system to provide greater oxidation and hence precipitation of the iron, which ultimately settles as iron hydroxides, which largely accumulate at the bottom of the lagoon. This appeared to favour development of significant preferential flow paths across the surface of the lagoon, which resulted in a very quick, narrow RTD peak of the tracer. This effect was reduced during the 2009 test, following sludge removal in 2008, when a lower dimensionless variance, σ_θ^2 (0.549), and a greater mixing efficiency, e_{RTD} (0.451), was evident. Therefore the Acomb east lagoon volumetric efficiency improved during 2009, with more volume being involved during flow-through, and an overall improvement in system hydraulic efficiency, i.e. e_λ from 0.075 to 0.115. Therefore regular ochre sludge removal/dredging is important to maintain or improve hydraulic performance, and the discussion above quantifies the level of this improvement.

Overall, the lagoon systems have values of e_λ from as low as 0.019 to as high as only 0.439. The lowest value was found at the Mousewater lagoon, while the highest was found in Bates (the second lagoon to the right side). Clearly, this was reflected by the metric of e_v for both systems, rather than the e_{RTD}. For instance, the Mousewater lagoon had the lowest e_λ (0.019) because of its lowest e_v despite having a slightly higher e_{RTD} than the Acomb east lagoon (2007). Similarly the Acomb east lagoon, despite having the lowest e_{RTD}, still had a greater e_λ than the Mousewater lagoon. The Bates lagoon has both the highest e_λ (0.439) (the second lagoon to the right side) and the highest e_v of 0.745, despite its slightly lower e_{RTD} than the other Bates lagoon (first lagoon on the left side). Therefore, as in the wetland systems, system volumetric efficiency is of substantial importance to the overall system hydraulic efficiency (e_v; $R^2 = 0.953$, e_{RTD}; $R^2 = 0.849$ both $p<0.05$).

4.4.5.1 Physical influences on lagoon hydraulic performance

As for wetland systems, the partial correlation between the lagoon hydraulic characteristics and performance metrics, and the factors influencing them, such as length-to-width ratio, age of system, flow and depth, were determined. These partial correlation coefficients are shown in Table 4.13.

Table 4.13 Partial correlation, r between lagoons' hydraulic performance metrics and length-to-width ratio (L/W), depth, flow and age of system, $n = 12$

Hydraulic parameters	**L/W**		**Depth**		**Flow**		**Age**	
	r	*p-value*	*r*	*p-value*	*r*	*p-value*	*r*	*p-value*
RTD efficiency, e_{RTD}	0.727*	0.013	0.665*	0.025	0.262	0.248	0.171	0.330
Volumetric efficiency, e_v	0.741*	0.011	0.560	0.058	0.134	0.365	0.462	0.105
Hydraulic efficiency, e_λ	0.814**	0.004	0.695*	0.019	0.299	0.217	0.375	0.160

Correlations are *significant ($p<0.05$); **highly significant ($p<0.01$)

As noted in Table 4.13, there are significant correlations between RTD, volumetric and hydraulic efficiency to the length-to-width ratio (L/W), and RTD and hydraulic efficiency to the depth. This agrees with the findings by Persson and Wittgren (2003) that effective volume is primarily determined by the length-to-width ratio, and dispersion (RTD efficiency) is primarily determined by the length-to-width ratio and to some degree by the depth. Persson and Wittgren (2003) found from a simulation of wetland shapes (wetland treating water from agricultural areas) that effective volume increased with increasing L/W, but depth is also identified as an important influence. Thackston et al. (1987) also found that a high length-to-width ratio in shallow ponds correlated to greater hydraulic efficiency up to a L/W ratio of 10. Above a L/W ratio of 10, no improvement in hydraulic efficiency was seen.

Here, a greater depth is seen to have influence on a greater lagoon e_{RTD} and e_λ. As the results here seem to suggest, it is likely that the greater depth of a lagoon may result in increase in the n TIS (greater n means a lesser degree of dispersion, the more it approaches ideal plug-flow, hence greater e_{RTD}); n TIS and depth are significantly correlated ($p<0.05$, see Appendix N for statistics of lagoon partial correlation; n TIS and depth). This is expected because a greater depth would help to minimise apparent streaming effects typically associated with shallow water or reduced effective depth (Kruse et al., 2009). This is in contrast to findings from research by Holland et al.

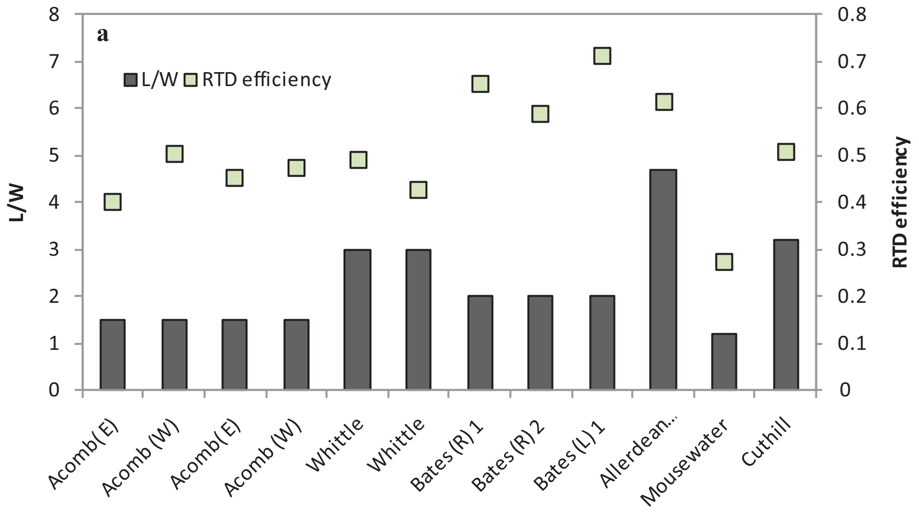
(2007), which suggested that an increased depth would encourage a reduction in volumetric efficiency (hence the hydraulic efficiency) as the effect of short-circuited flow and larger mixing characteristics would be pronounced. As suggested earlier in section 4.3.4, apparent short-circuiting effect seen in most lagoons is associated with a greater volume/depth of the lagoon. However, statistics here suggest a contrary result that a greater depth would enhance greater hydraulic efficiency. A conclusion here is therefore, the role of lagoon depth is two-fold:

- Greater depth may result in apparent short-circuiting effect when there appear to be large amount of dead zones due to ochre build-ups and debris in the deeper part of lagoon
- Lagoon with a greater depth is also useful because such a configuration may retain a greater proportion of effective volume, increasing its efficiency, despite presence of dead zones (compared to a shallow lagoon)

Based on the partial correlation analysis and from the evidence of the results, clearly, both the greater L/W (up to ratio 4.7) and depth (up to 3 m) have a significant influence on the greater lagoon hydraulic efficiency, as observed from this study. Greater L/W was found to significantly correlate to greater depth, although this may imply a coincidence of engineering design rather than any sort of cause and effect. Therefore in such lagoon systems it appears that the length-to-width ratio and depth are the two important factors that need to be considered when addressing lagoon hydraulic performance. Lagoons typically associated with short-circuiting effects with respect to depth often appear to do so due to the presence of large build ups of ochre in the base of the lagoons. Therefore regular ochre sludge removal is important to ensure efficient hydraulic performance. Other researchers have also found that system dispersion (i.e. dispersion number or its inverse, the Peclet number, which both characterise system hydraulic efficiency) is related to the length-to-width ratio and depth (e.g. Fischer, 1967; Nameche and Vasel, 1998) for water bodies similar to ponds e.g. for systems with large width-to-depth ratio, aerated lagoons and waste stabilisation ponds.

The partial correlation analysis also shows that inclusion of other factors whilst correlating one factor to the hydraulic performance metric does gives a great difference when otherwise other factors are excluded. For instance, inclusion of depth, flow and age effects has increased the amount of variation in hydraulic efficiency due to L/W by more than 50%. This again, suggests that there appears to be complex relationship between these factors that influence the lagoon hydraulic performance; e.g. the effect of L/W may not stand alone, but there are effects of depth, flow and age to reflect its significant influence of hydraulic performance. Similarly, the significant effect of depth on hydraulic efficiency is also reflected in the contribution of other factors such as L/W, flow and age, e.g. depth effect increased from only 2% to 48% when other factors are included in the correlation analysis (see Appendix N for statistics of lagoon partial correlation; hydraulic efficiency and L/W and depth). Illustration of the variation in lagoons RTD, volumetric and hydraulic efficiency in relation to L/W, depth, flow and age are shown in Figure 4.20 - Figure 4.22. As before, for each of these factors, there are contributions of other factors that simultaneously affect the variation of hydraulic performance.

Certainly, there appear to be complexities in lagoons' and wetlands' hydraulic behaviour. This has also been reported by other researchers (e.g. Fischer, 1967; Nameche and Vasel, 1998; Goulet and Pick, 2001; Persson, 2000; Persson and Wittgren, 2003; Worman and Kronnas, 2005; Kjellin et al., 2007). Effects of length-to-width ratio, depth, flow, vegetation, seasons, inlet and outlet locations, and topography are typically invoked to explain the complex relationships observed in wetlands and ponds.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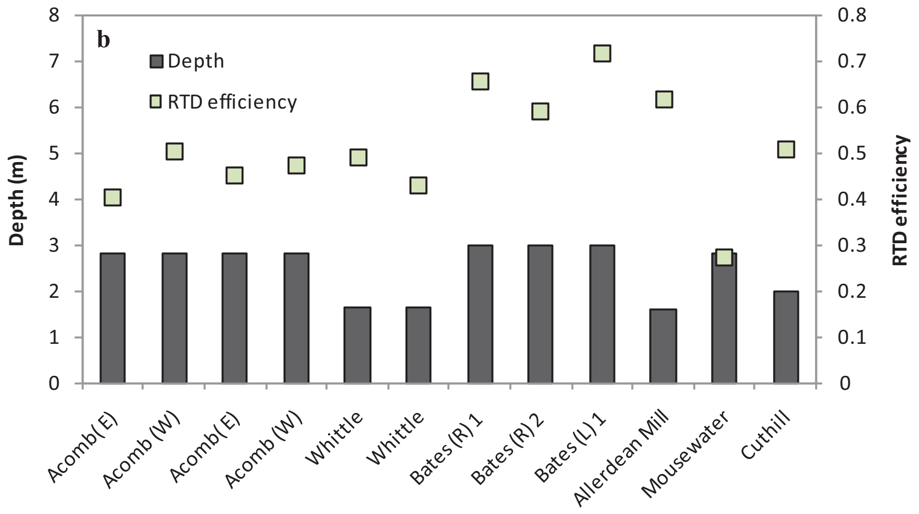
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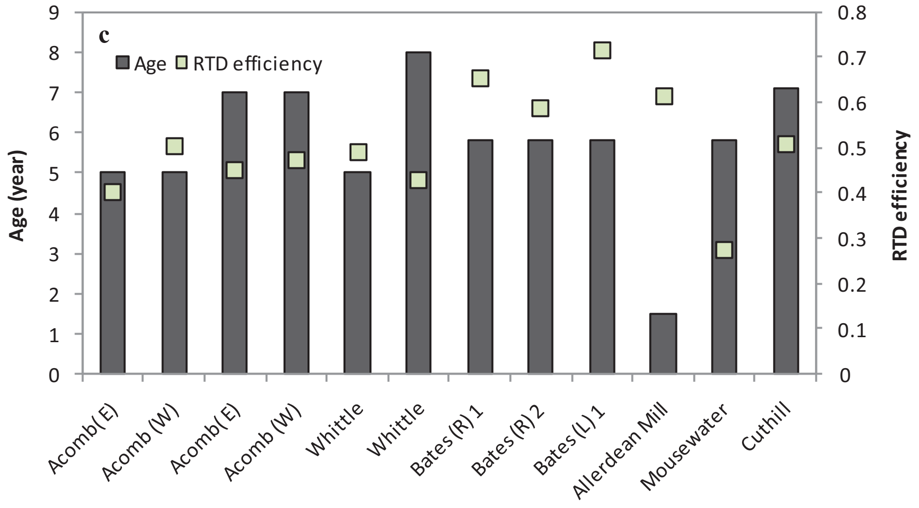
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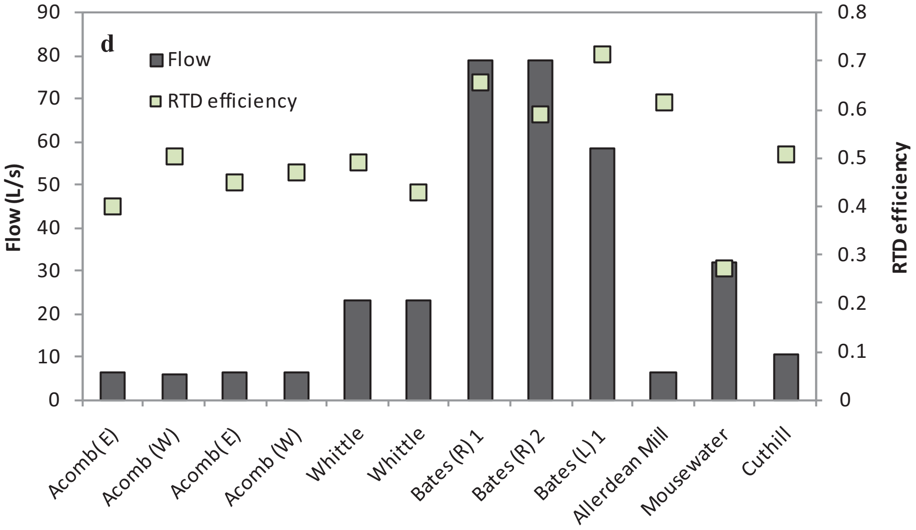
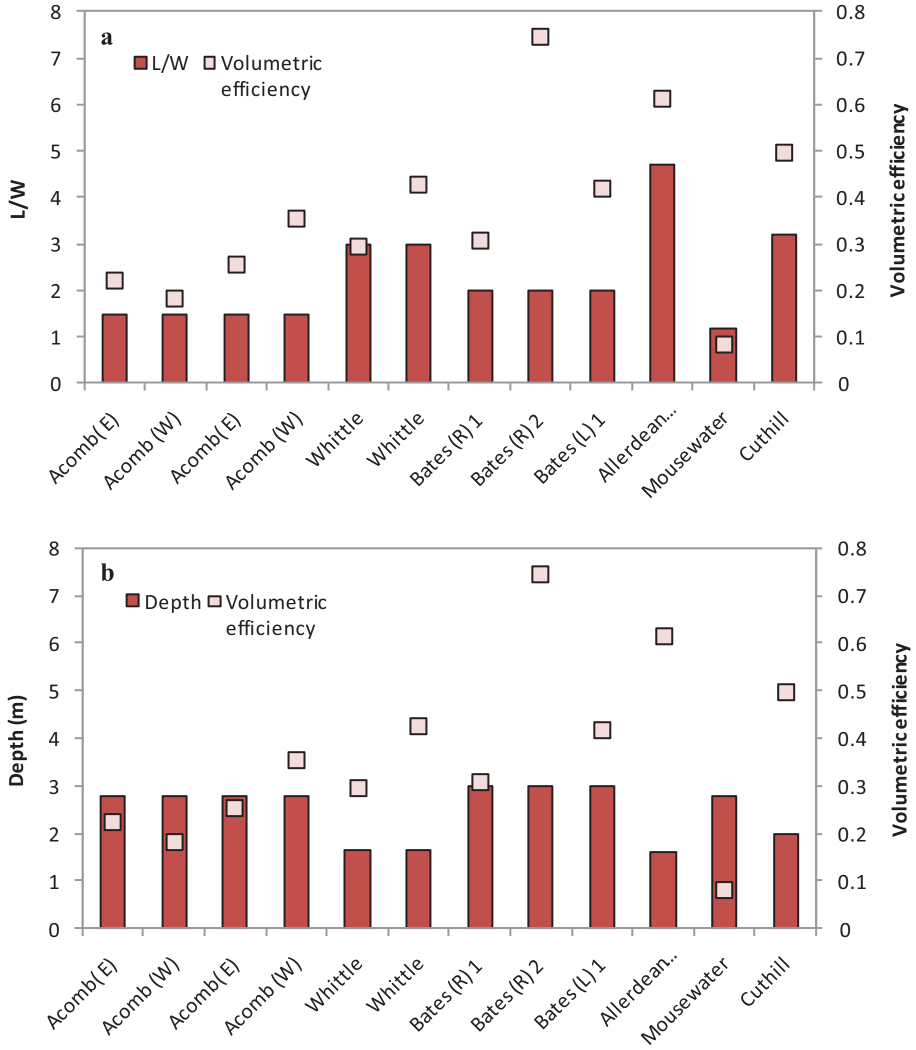


Figure 4.20 Variation in RTD efficiency in relation to (a) length-to-width ratio (b) depth (c) age and (d) flow for lagoon systems



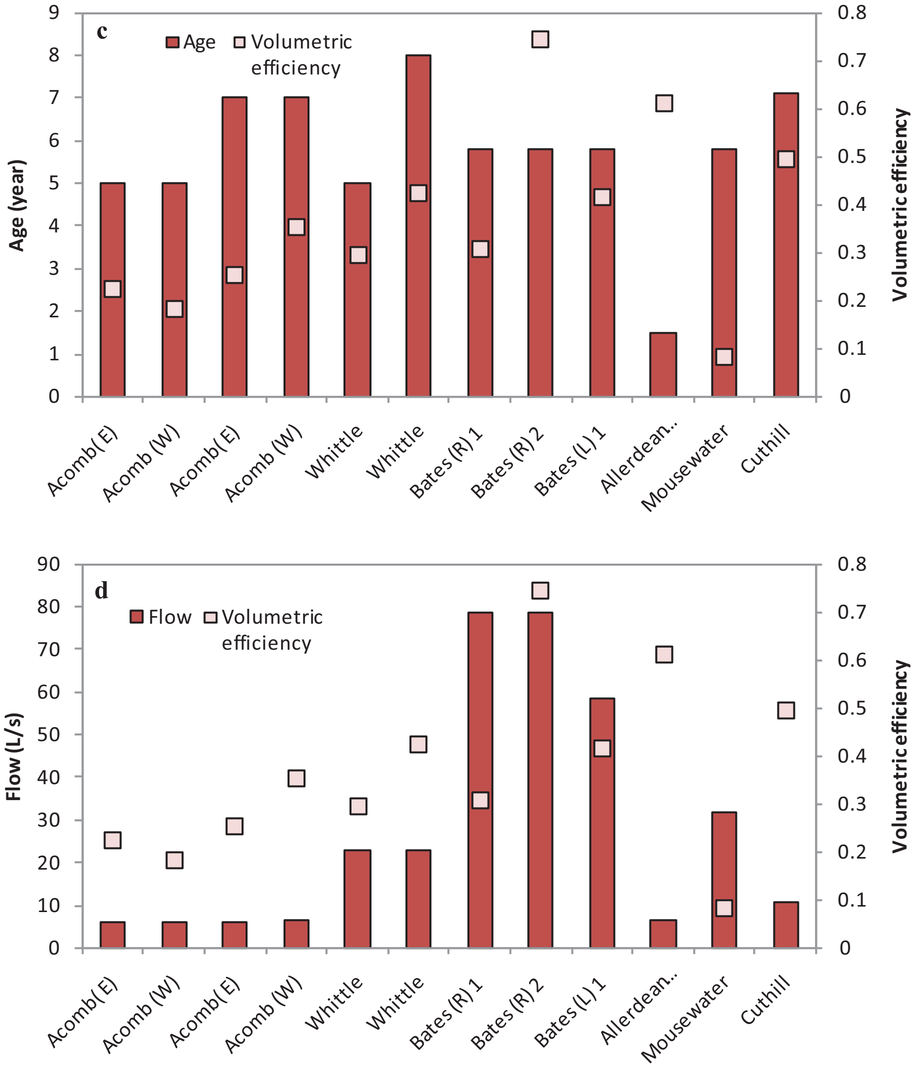
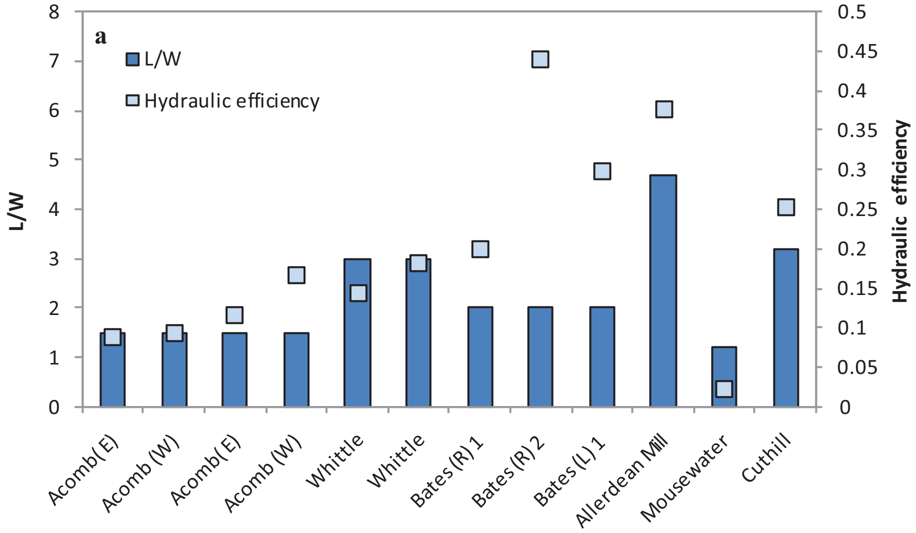


Figure 4.21 Variation in volumetric efficiency in relation to (a) length-to-width ratio (b) depth (c) age and (d) flow for lagoon systems



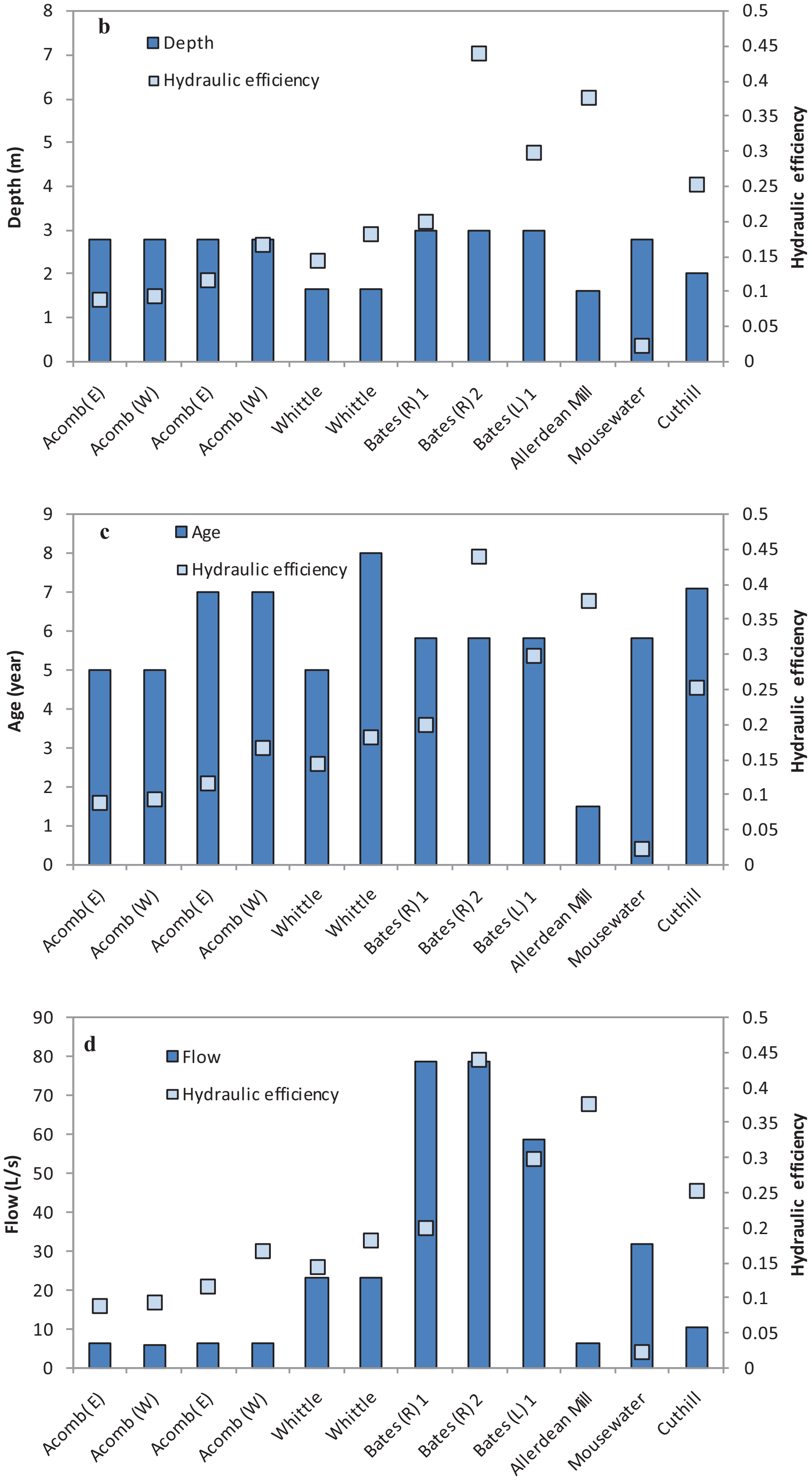


Figure 4.22 Variation in hydraulic efficiency in relation to (a) length-to-width ratio (b) depth (c) age and (d) flow for lagoon systems

4.4.6 Comparison of hydraulic characteristics and performance metrics of mine water treatment lagoons and wetlands

Comparison of the hydraulic characteristics and performance metrics for lagoons and wetlands are made using parametric and non-parametric independent t-test statistical analysis to compare the significance of difference between lagoons and wetlands based on the hydraulic parameters from the TIS model (Field, 2009). The statistical comparisons are made using the mean value of each parameter to compare between lagoon and wetland system. Statistics for parametric and non-parametric t-test are shown in Appendix N. Tabulated mean, standard error, median, minimum and maximum values for each parameter are shown in Table 4.14.

Table 4.14 Summary of statistics for hydraulic characteristics and performance metrics of mine water treatment lagoons and wetlands

	Lagoon			**Wetland**		
Parameter	**Mean (S.E)**	**Median**	**Min/Max**	**Mean (S.E)**	**Median**	**Min/Max**
Nominal residence time, τ_{an} (d)	1.450 (0.177)	1.396	0.61/2.29	0.378 (0.064)	0.319	0.23/0.77
Mean residence time, τ_m (d)	0.474 (0.068)	0.469	0.18/0.95	0.333 (0.065)	0.368	0.05/0.70
Mode, τ_p (d)	0.247 (0.047)	0.214	0.03/0.61	0.263 (0.046)	0.304	0.07/0.46
Dimensionless variance, σ_θ^2	0.492 (0.035)	0.504	0.29/0.73	0.329 (0.048)	0.243	0.19/0.61
Dispersion number , D	0.421 (0.060)	0.397	0.17/0.97	0.236 (0.052)	0.141	0.10/0.58
Number of TIS, n	2.12 (0.14)	1.98	1.4/2.95	3.61 (0.424)	4.2	1.65/5.4
RTD efficiency, e_{RTD}	0.508 (0.035)	0.496	0.27/0.71	0.672 (0.048)	0.758	0.39/0.81
Volumetric efficiency, e_v	0.366 (0.054)	0.330	0.08/0.75	0.896 (0.160)	0.886	0.20/1.61
Hydraulic efficiency, e_λ	0.198 (0.036)	0.175	0.02/0.44	0.662 (0.140)	0.639	0.08/1.31

All parameters are unitless unless otherwise stated
n = 12 for lagoon and 10 for wetland

Typically, nominal residence times for lagoons are high compared to wetland systems because generally lagoons have a larger volume than wetlands, albeit lower flow rates to the lagoons may sometimes contribute to this difference. The nominal residence time averaged 1.450 days for lagoons and 0.378 days for wetlands. These differences are highly significant ($p<0.001$). Accordingly, greater mean residence time is seen for lagoons, although this does not necessarily imply good hydraulic performance given the different system volumes and flow rates between the lagoons and wetlands. Clearly, longer mean residence times were seen in the lagoons compared to wetlands because lagoons typically have greater nominal volumes than most wetlands, and therefore retention would ideally be longer in lagoons. The average mean residence time is 0.474 days for lagoons and 0.333 days for wetlands. However, there was no significant difference of mean residence time between these lagoons and wetlands (*$p=0.154$*). The reason is possibly because the mean residence time for lagoons is substantially less than the nominal residence time, suggesting lower system effective volume. The mode (peak time for RTD) averaged 0.247 days for lagoons and 0.263 days for wetlands. Differences are not significant (*$p=0.817$*). Differences in the nominal and mean residence time and the time to peak between lagoons and wetlands are shown in Figure 4.23 below.

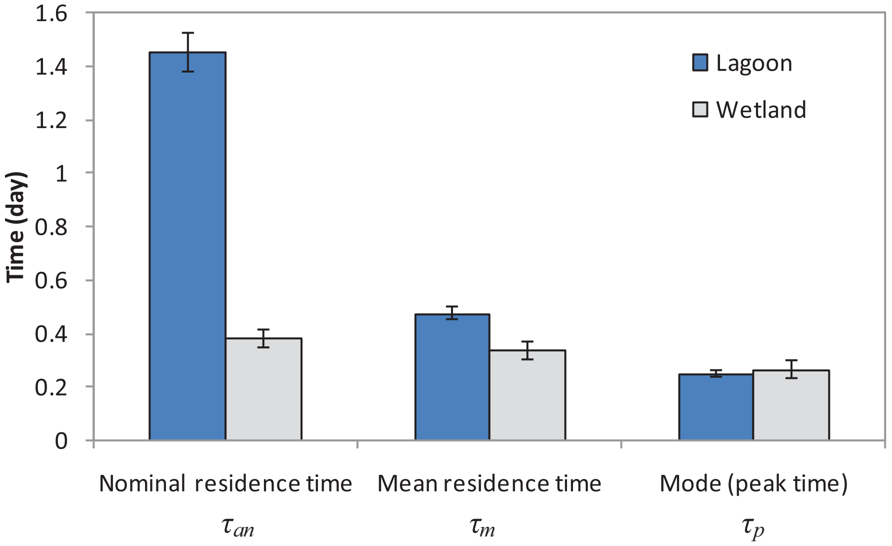


Figure 4.23 Comparisons of mean values of nominal residence time, mean residence time and the time to peak between lagoon and wetland (error bars: 95% confidence interval)

The dispersive characteristics of water movement across the systems can be represented by the dimensionless variance, dispersion number and the number of TIS. The mean dimensionless variance (which corresponds to the spread of the RTD) is 0.492 for lagoons and 0.329 for wetlands. Differences are significant for *$p<0.05$*. This shows that lagoons are dispersed from an ideal flow pattern to a greater degree than wetlands. This is also reflected in the lower *n* TIS and greater dispersion number, *D*, of lagoons. Lagoons have an average *n* TIS of 2.1 while the wetlands have an average *n* TIS of 3.6. These differences are significant (*$p<0.01$*). The system dispersion number for lagoon averaged 0.421 and for wetland, 0.236 (differences are also significant, $p<0.05$). Clearly, the lagoons have significantly different flow dispersive characteristics, such that the apparent short-circuiting or streaming of flow seems to be an important factor that needs to be considered in ensuring efficient hydraulic performance. These differences are graphically shown in Figure 4.24. The reason for the greater dispersion characteristics in the lagoons is mainly due to the greater flow short-circuiting effect typically associated with stagnant dead zones in deeper parts of lagoons, which favours development of flow short-circuiting across the surface due to reduction in depth.

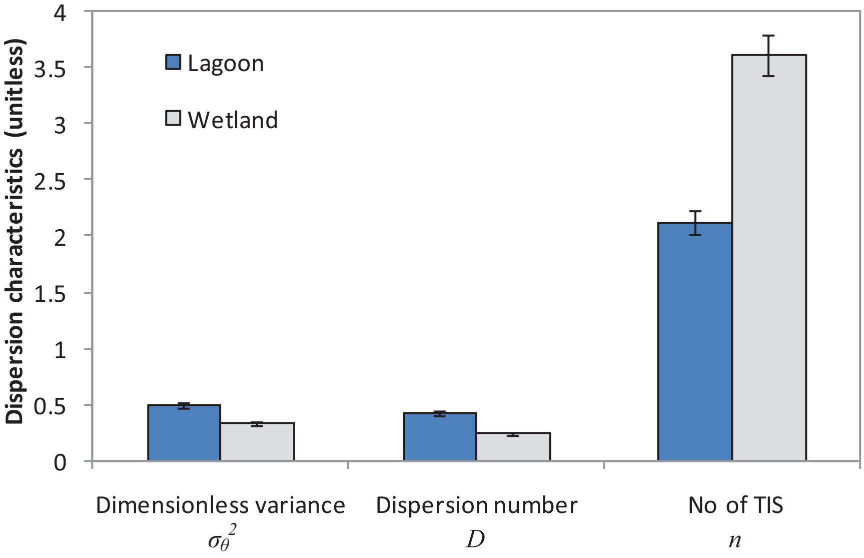


Figure 4.24 Comparisons of mean values of system dimensionless variance, dispersion number and the number of TIS between lagoon and wetland system (error bars: 95% confidence interval)

Accordingly, system volumetric efficiency, e_v, is an appropriate hydraulic performance metric to assess the significance of mean relative to nominal residence time, since it indicates the effectiveness of system volume. It can be seen that the mean wetland volumetric efficiency is comparatively greater than that for lagoons (0.896 for wetlands compared to 0.366 for lagoons), showing that a greater proportion of the total volume of the wetland system is being involved in the passage of water through such units compared to lagoons. These differences are significant ($p<0.01$), suggesting that much of the lagoon volume is not being optimally used during the flow through them. Again, this is likely because some of the lagoon volume was being occupied by the dead zones, most likely created by the accumulated ochre, reducing the effective depth in the systems. It is worth noting that the lower volumetric efficiency of lagoons also indicates that they have a relatively shorter retention time than wetlands. The system RTD also suggest greater efficiency for wetlands compared to lagoons, which indicates a better flow distribution/mixing i.e. approaching plug-flow across the wetland systems. The mean RTD efficiency for wetlands is 0.672, compared to 0.508 for lagoons. These differences are also significant ($p<0.05$), showing that the lagoons exhibit a significantly lower degree of mixing than wetlands. Consequently, the overall system hydraulic efficiency for wetlands is much greater than lagoons; a mean of 0.662 in wetlands compared to a mean of 0.198 in lagoons. These differences are very significant ($p<0.01$). It is therefore clear that system hydraulic efficiency is much lower in lagoon systems. This probably reflects the more dispersed flow patterns within lagoon systems (i.e portions of water that exit the systems fast and also portions that leave the systems more slowly (the long RTD tails)). Additionally, the presence of dead zones with large ochre sludge has significantly reduced much of the lagoon's effective volume (and hence residence time). These differences in RTD, volumetric and hydraulic efficiency are shown in Figure 4.25.

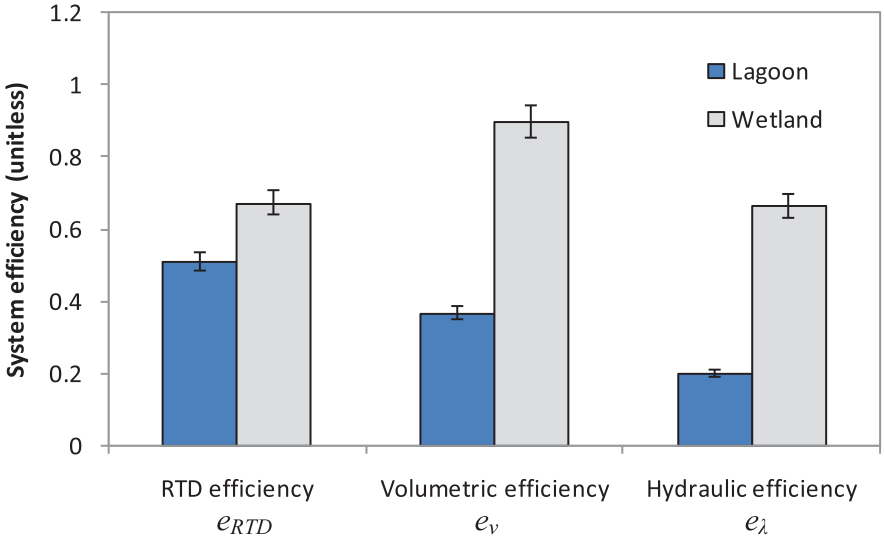


Figure 4.25 Comparisons of mean values of system RTD, volumetric and hydraulic efficiency between lagoon and wetland (error bars: 95% confidence interval)

4.4.7 Comparison to other passive treatment systems

As illustrated in Table 4.14, the actual mean residence time for wetlands averaged 0.474 days and for lagoons 0.333 days. These are significantly lower than the measured mean retention time of 3.5 days in several passive treatment systems for coal mine drainage in the United States (Hedin, 1994). The systems in the US receive a flow rate varying from 0.17-16.67 L/s, with surface areas of 0.1-10 ha (comparatively large system areas, with relatively lower flow, compared to the passive systems investigated in this study), which explains the longer retention time in those systems.

In terms of the hydraulic performance, regardless of wetland or lagoon, the flow pattern across the studied systems are characterised by the number of TIS of 1.4-5.4 TIS, which corresponds to dispersion number, D, of 0.10-0.97. These can be compared to a number of wetlands in the United States, for which n is 0.3-10.7 for free water surface (FWS) wetlands and 2.5-34.4 for horizontal sub-surface (HSSF) wetlands (Kadlec and Wallace, 2009). Therefore, the mine water treatment wetlands and lagoons studied here fall within the range of n TIS for FWS wetlands. Interestingly, none of the FWS observed in the US (as summarised by Kadlec and Wallace, 2009) receive polluted mine water. Thus, the results from this study have successfully situated the mine water treatment systems in the UK within the range of typical wetlands (for wastewater, stormwater and agricultural treatment) based on the hydraulic characterisation from the TIS model.

The FWS wetlands systems in the US are characterised by a large amount of dispersion of $0.07<D<0.35$ (Kadlec, 1994). Bavor et al. (1988) reported $D = 0.27$ for an open water surface-flow wetland, and Simi and Mitchell (1999) reported $D = 0.28$ for a constructed wetland treating oil refinery wastewater, both are examples in Australia. Generally, the mine water treatment systems studied fall within this range of dispersion, with exceptions in a few cases. It was found from the studied systems that significantly high D were observed mostly in lagoons where apparent short-circuiting affected the flow pattern across the systems, mainly due to accumulated ochre reducing the effective depth of water. Therefore, regular sludge removal is important if efficient lagoon performance is to be maintained.

The systems' volumetric efficiency, e_v, found in this study are within the range of 0.08-0.75 for lagoons, and between 0.2-1.61 for wetlands. This is comparable to performance of 65 wetlands in the United States; e_v ranging between 0.2-0.9 for basins devoid of vegetation, and between 0.7-2.56 for wetlands (Kadlec and Wallace, 2009). Certainly, as was found in this study, lagoons have a lower range of e_v compared to wetlands, and that the very low e_v in lagoons is typically associated with reduced depth due to accumulation of ochre and debris as stated above. The systems in the US have mean residence times of 0.70-35 days. These include a wide range of wetland areas, from as small as 4 m^2 to as large as 5 780 000 m^2 (Kadlec and Wallace, 2009), whilst in this study, the treatment systems range between 600-8400 m^2.

4.5 CHAPTER SUMMARY

This chapter has investigated the factors governing the hydraulic performance of both mine water treatment lagoons and wetlands. The key findings from this investigation of system residence time distribution, following the tracer tests, can be summarised as follows:

Residence time distribution (RTD) analysis

- Generally, RTD shapes appear to be greatly affected by the vegetation distribution across the wetland systems; those sparsely-populated with reeds, such as during early colonisation, may result in flow channelling effects, whilst mature reeds tend to favour a more well-distributed flow. However within such maturely-developed reed colonies the presence of accumulated dead or living plant materials, and the build-up of settled ochre, may also result in the creation of preferential flow paths, and hence short-circuiting effects.
- Evaluation of residence time distribution in the Lambley wetland shows a variation in the distribution of residence time in the wetland over 4 years of operation since commissioning. Vegetation effects seem to be an important factor influencing the variation in RTDs, although seasonal effects cannot be ruled out since individual tracer tests were undertaken in different seasons. This is a possible weakness of this study; in order to investigate the effect of vegetation, several measurements should be performed within the same season.

- Evaluation of RTDs in other wetland systems show how residence time may behave differently in different systems, due to design configurations, seasonal effects and age of operation, in addition to the role of vegetation.
- Assessment of lagoon RTDs indicates - flow patterns which are generally more dispersed than seen in wetlands, suggesting the presence of more pronounced short-circuiting effect (fast moving water) but also large amount of slow moving water that leaves the systems in the absence of vegetation. Depth effect and the presence of large amount of ochre identified as a key issue.
- There appear to be multiple influences that possibly affect the RTDs in lagoons and wetlands i.e. vegetation and seasonal variation (growing or non-growing season), system age, flow and geometry (length-to-width ratio and depth).

Further to this discussion on wetland and lagoon RTDs, a modelling approach was adopted to precisely analyse and characterise the RTDs, in an effort to account for the different flow patterns, which significantly influence the shape of the RTDs. This would therefore assist in ascertaining in more detail the possible influences on the hydraulic characteristics of wetlands and lagoons, initially assessed through RTD analysis (as discussed above).

Tracer flow analytical modelling approach

- The tracer flow modelling was performed using a tanks-in-series (TIS) model calibrated using three different approaches whichever best fitted the actual data. Delayed TIS from least squares method yielded the best fit (as indicated by the lowest root mean squares error) to actual RTDs, since in most cases it takes into account the delay in tracer detection and gives realistic values of n and degree of dispersion. This approach was used in the following RTD analysis and for computing system hydraulic efficiency for wetlands and lagoons studied.
- Differences in RTD shapes are represented by the computed hydraulic characteristics and performance metrics from the TIS model. This enables further assessment and precise comparison between wetland and lagoon hydraulic performance, in order to assess how these hydraulic performance

metrics may be affected by the several possible influences as previously suggested.

- TIS modelling at the Lambley wetland shows that despite a consistent flow into the system, the hydraulic performance of this wetland system appears to vary year-on-year and between seasons. The role of wetland vegetation seems to be significant, and to be reflected in the variation in wetland RTD, and therefore the hydraulic efficiency of such wetland systems.
- For wetland systems, effects of L/W ratio, flow and age of system do not significantly correlate with the hydraulic performance metrics, suggesting the primary role of vegetation in determining the wetland hydraulic performance (though there are multiple factors interacting in the same time). The partial correlation analysis shows that there are complex relationships among these possible influences; each factor does have influence on another in affecting the hydraulic efficiency, therefore it is difficult to identify with certainty which of these factors has the greatest influence on hydraulic performance. There is also difficulty of establishing cause and effect relationships between the possible influences and hydraulic performance because some of these influences are constant engineered design aspects (i.e. design configuration).
- For lagoon systems, both the greater L/W (up to a ratio of 4.7) and depth (up to 3.0 m) have a significant influence on the greater lagoon hydraulic efficiency, e_{λ}. Specifically, greater e_{v} is determined by greater L/W and greater e_{RTD} is determined by greater L/W and to some extent by depth. Partial correlation analysis also shows that there are complex relationships among those factors affecting hydraulic efficiency, and again it is difficult to identify which of these factors has the greatest impact on hydraulic performance.
- Overall, mean lagoon volumetric efficiency is comparatively lower than the wetlands, showing that a greater proportion of the total volume of the lagoon system is not being involved in the flow of water through lagoons. Thus, there is a relatively shorter retention time in the system. Lower RTD efficiency was also seen in lagoons, which indicates a greater flow dispersion compared to wetlands. This is evident from the greater extent of flow dispersive behaviour (i.e. higher D and lower n TIS). Consequently, the overall system hydraulic efficiency for lagoons is much lower ($e_{\lambda} = 0.20$) than wetlands ($e_{\lambda} = 0.66$).

- In light of the findings from this study, the highest hydraulic efficiency is seen in Strafford wetland (e_λ = 1.31; n TIS = 5.4). This system appears to be efficient in terms of its RTD and volumetric efficiency (e_{RTD} = 0.81 and e_v = 1.61). This is possibly due to the presence of deep zones and the constructed islands (planting blocks) in the wetland system, which appears to enhance distribution of water, and thus encourage a long water residence time. For lagoon systems, one of the Bates lagoons shows the highest hydraulic efficiency (e_λ = 0.44; n TIS = 2.4, although these values do not indicate an efficient hydraulic performance compared to wetlands). The lagoon seems to be rather efficient in terms of its volumetric efficiency (e_v = 0.75) but still less efficient than wetlands for ensuring a more well distributed flow (e_{RTD} = 0.59), reflecting the fact that most lagoons studied deviate greatly from the ideal flow pattern, which is typically due to greater short-circuiting effects, compared to wetland systems.

CHAPTER 5

RESULTS AND DISCUSSION:

GEOCHEMICAL PERFORMANCE OF MINE WATER TREATMENT SYSTEMS, AND RELATIONSHIPS TO HYDRAULIC PERFORMANCE

5.0 RESULTS AND DISCUSSION: GEOCHEMICAL PERFORMANCE OF MINE WATER TREATMENT SYSTEMS, AND RELATIONSHIPS TO HYDRAULIC PERFORMANCE

5.1 INTRODUCTION

This chapter discusses the geochemical factors that influence treatment performance of the mine water treatment lagoons and wetlands investigated. Particular discussion is focused on the removal of iron, which is the primary pollutant of concern in all the systems studied. The geochemical processes that are critical to the removal of iron in treatment systems are discussed. Central to the current investigation is the relationship between system hydraulic factors and system performance in terms of iron removal, and this is discussed in detail in light of the results. The implications for design and maintenance of such systems conclude the results and discussion of this chapter.

5.2 MINE WATER HYDROCHEMISTRY

Summary hydrochemical statistics (mean, median, minimum and maximum of physicochemical parameters and chemical constituents) for the lagoon and wetland systems are shown in Table 5.1 and Table 5.2 respectively. Of the 8 treatment sites investigated, regardless of settlement lagoons or wetlands, pH was in the circum-neutral range (6.4-8.1), temperature between 4.3-19.4 ^{o}C, specific conductivity between 1199-13960 µS/cm, Eh between -117-224 mV and alkalinity between 84-1224 mg/L as $CaCO_3$. The greatest conductivity and alkalinity were seen from Bates treatment scheme, which mine water is very saline. As noted in Table 5.1 and Table 5.2, iron is the primary metal of concern, with manganese a lesser concern, and other metals below the detection limit. Fe concentration was clearly removed in both the lagoons and wetlands and is discussed in detail in the following section.

Table 5.1 Hydrochemical composition of influent and effluent of seven mine water treatment lagoons investigated ($n = 14$). Hydrochemistry data for each system are shown in Appendix C.

	Influent		Effluent	
Parameter/constituent	Mean/Median	Min/Max	Mean/Median	Min/Max
Physical parameter				
pH	6.80/6.81	(5.81/7.40)	7.15/7.22	(6.92/7.44)
Temperature (ºC)	12.3/11.4	(4.3/16.7)	13.3/12.3	(10.3/18.1)
Spec. cond (µS/cm)	3336/1482	(936/13960*)	4022/1473	(1199/13900*)
Eh (mV)	17/-32	(-120/257)	14/8	(-188/149)
Alkalinity (mg/l CaCO$_3$)	365/265	(178/852)	394/240	(136/1224)
Major constituent[†]				
Ca	240.78/228.91	(65.47/448.56)	241.93/229.60	(65.49/417.28)
Mg	128.29/57.74	(40.24/519.55)	149.37/58.22	(40.45/503.04)
Na	401.63/43.39	(10.18/2281.71)	508.97/43.26	(16.86/2250.01)
K	28.29/13.45	(6.10/117.78)	32.99/12.47	(6.09/114.21)
Cl	441.62/47.95	(17.22/3184.49)	630.11/48.58	(28.49/3150.53)
SO$_4$	1046.27/578.81	(295.68/3055.81)	1119.13/559.82	(399.96/3012.04)
Metal constituent[†]				
Al	<LOD	<LOD	<LOD	<LOD
Fe	18.27/18.12	(4.36/34.1)	8.85/6.45	(1.30/24.88)
Mn	1.21/0.69	(0.57/4.11)	1.31/0.62	(0.54/3.97)
Si	6.12/5.08	(4.14/9.86)	5.46/4.49	(4.11/7.50)
Zn	<LOD	<LOD	<LOD	<LOD

Table 5.2 Hydrochemical composition of influent and effluent of six mine water treatment wetlands investigated ($n = 13$). Hydrochemistry data for each system are shown in Appendix C.

	Influent		Effluent	
Parameter/constituent	Mean/Median	Min/Max	Mean/Median	Min/Max
Physical parameter				
pH	7.21/7.27	(6.09/7.76)	7.28/7.41	(6.40/8.11)
Temperature (ºC)	12.9/11.7	(8.7/18.1)	12.7/11.9	(6.8/19.4)
Spec. cond (µS/cm)	2587/1208	(441/13900*)	2162/1147	(423/13890*)
Eh (mV)	11/-8	(-83/88)	64/51	(-59/224)
Alkalinity (mg/l CaCO$_3$)	284/196	(84/834)	266/196	(98/663)
Major constituent[†]				
Ca	167.98/149	(47.73/417.28)	153.85/139.8	(47.50/367.99)
Mg	99.00/45.69	(20.29/503.04)	86.15/46.79	(20.22/526.46)
Na	299.74/7.64	(4.36/2250.01)	247.18 /7.49	(3.99/2887.75)
K	26.37/6.27	(4.85/114.21)	16.58/6.30	(4.81/112.93)
Cl	358.43/48.93	(11.57/3150.53)	287.45/47.5	(11.11/3520.61)
SO$_4$	757.35/409.76	(43.37/3012.04)	688.68/366.31	(35.45/3320.61)
Metal constituent[†]				
Al	<LOD	<LOD	<LOD	<LOD
Fe	7.59/6.70	(3.01/20.8)	0.88/1.01	(0.11/1.7)
Mn	1.08/0.79	(0.45/3.70)	0.49/0.45	(0.07/0.85)
Si	4.84/4.49	(3.62/9.47)	4.36/4.11	(3.42/7.13)
Zn	<LOD	<LOD	<LOD	<LOD

[†] Chemical constituents in unit mg/L. Data present mean, median, minimum and maximum of each parameter/constituent

*High salinity water of Bates treatment scheme

In both lagoons and wetlands, as water flowed through the system, pH increased while concentration of alkalinity and Fe decreased (Table 5.1 and Table 5.2). Increased pH is a common feature in passive systems containing sufficient bicarbonate alkalinity (i.e. net-alkaline water), and may be attributable to degassing of the dissolved CO_2 (Younger et al., 2002; Cravotta, 2007), which is often above atmospheric partial pressure of CO_2 upon first emergence of mine waters to the surface.

$$HCO_3^- = CO_{2\ (gas)} + OH^- \qquad [5.1]$$

As shown in the above equation, degassing may decrease pCO_2 via dissolution of HCO_3^-, releasing $CO_2(g)$, but also producing OH^- ions, and therefore increasing pH. The decrease in alkalinity is due to neutralisation of acidity produced by iron oxidation and hydrolysis (Hedin, 1994).

$$Fe^{2+} + 2HCO_3^- + 1/4O_2 \longrightarrow FeOOH + 3/2H_2O + 2CO_2 \qquad [5.2]$$

Additionally, as in alkaline waters, high partial pressure of CO_2 in wetland waters and substrates, produced from both aerobic and anaerobic microbial respiration, may enhance calcite precipitation, a process which consumes alkalinity (Younger, 2007). In the waters investigated here the calcite saturation index (SI calcite) indicates mine water which is nearly saturated or supersaturated with respect to calcite at the effluent point of the treatment units. Thus a lower alkalinity in the effluent of most systems may be observed as a consequence of this calcite precipitation, in addition to the acidity neutralisation noted above (see Appendix M for SI index).

The comparatively high specific conductivity within the lagoons is due to the greater total solute content of these waters, as demonstrated in Figure 5.1 for both lagoons and wetlands (conductivity correlated strongly with total of meq/L cations or anions, $R>0.97$, $p<0.05$). As seen in Figure 5.1, sulphate and calcium constitute the greatest proportion of anions and cations respectively, in both lagoons and wetlands.

Despite the differences in the total meq/L cations and anions in the lagoons and wetlands (Figure 5.1) the charge balance calculation indicates electroneutrality in all treatment sites within the acceptable range of ± 5-10% (Younger, 2007). It should be noted that a very high total ion concentration in one treatment site (Bates) is due to the fact that the system receives highly saline water. This skews the mean data shown in Tables 5.1 and 5.2, which is why median data are also shown.

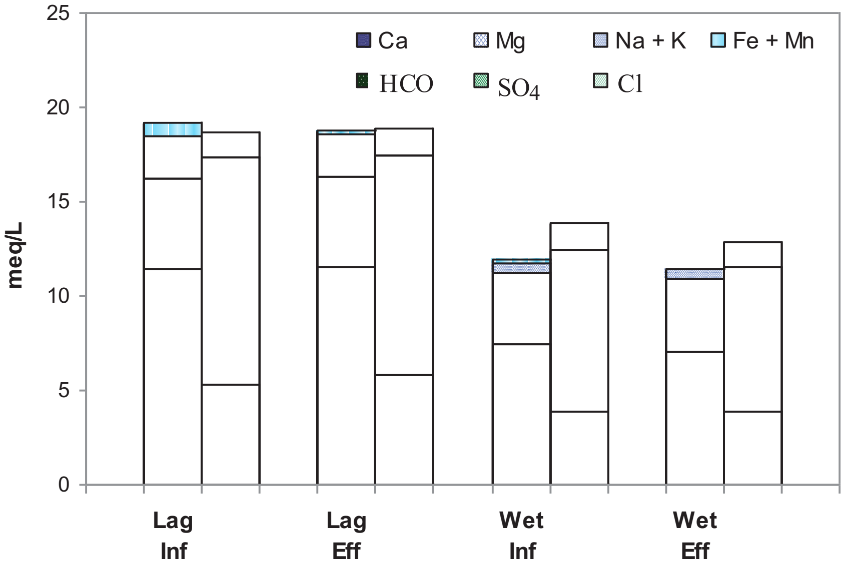


Figure 5.1 Cluster stacked columns for major cation (left column) and anion (right column) compositions of influent and effluent of lagoons and wetlands. Data are medians for samples collected from all treatment sites (*n* = 17, 21, 19 and 15 for lagoon influent and effluent and wetland influent and effluent, respectively)

5.3 IRON REMOVAL IN MINE WATER TREATMENT SYSTEMS

5.3.1 Comparison of iron removal in lagoons and wetlands receiving ferruginous mine waters

Distribution of the influent and effluent iron concentrations of the investigated mine water treatment lagoons and wetlands are graphically shown in Figure 5.2 (average values from treatment systems studied). This variability in iron concentrations show that iron is generally removed from the treatment systems (the diagonal line on Figure 5.2 represents no Fe removal, influent = effluent concentration). Clearly, significant removal of iron occurs in wetland systems. There is lower removal of iron seen from the lagoons. Note that for these systems investigated, lagoons receive relatively higher iron concentrations than wetlands by design (i.e. lagoons typically designed as primary treatment unit(s), while wetlands serve as the secondary treatment unit(s)). Summary iron removal for the investigated lagoons and wetlands are presented in Table 5.3. Full performance data are included in Appendix C and are summarised in Appendix K (Table K1 and Table K2).

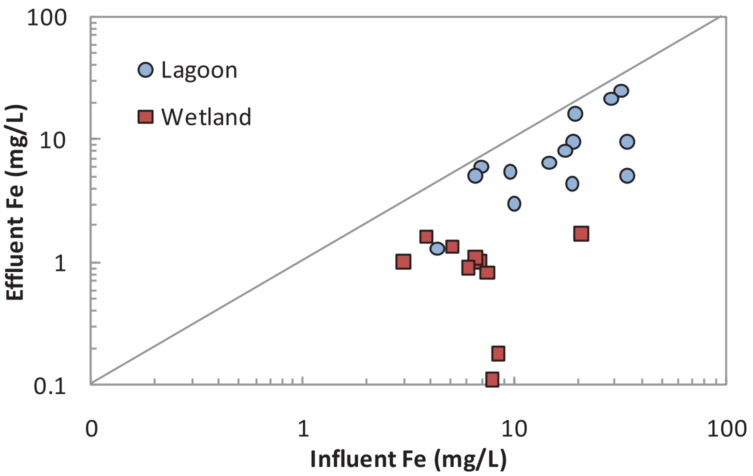


Figure 5.2 Influent and effluent Fe concentrations of the investigated mine water treatment systems

Table 5.3 Summary iron removal for coal mine water treatment lagoons and wetlands (*n* = 14 for lagoon and 10 for wetland)

	Lagoon			**Wetland**		
	Mean (S.E)	**Median**	**Min/Max**	**Mean (S.E)**	**Median**	**Min/Max**
Fe in (mg/L)	18.27 (2.79)	18.12	4.36/34.1	7.59 (1.56)	6.70	3.01/20.8
Fe out (mg/L)	8.85 (1.46)	6.45	1.30/24.88	0.88 (0.12)	1.01	0.11/1.7
Flow in (L/s)	33.30 (9.01)	17.95	5.85/83.32	34.40 (7.96)	24.04	7.91/84.83
[a]Fe loading rate (kg/d)	35.39 (7.66)	18.41	3.77/128.95	20.58 (4.71)	14.82	2.06/47.92
[b]Fe removal efficiency (%)	44.50 (5.42)	49.36	13.88/85.19	85.42 (2.71)	85.11	57.66/98.60
[c]Fe load removal (%)	45.36 (5.11)	46.38	13.88/85.19	83.86 (3.55)	85.45	47.69/99.01
[d]Area-adjusted removal ($g/m^2/d$)	12.40 (2.50)	8.49	1.40/39.15	4.93 (0.86)	5.14	1.28/17.19
[e]Residence time adjusted removal (g/m^2)	33.11 (6.99)	23.96	2.59/102.50	33.91 (18.6)	11.79	3.86/324.34
[f]First-order removal (m/d)	1.06 (0.17)	0.85	0.22/2.60	1.58 (0.11)	1.74	0.70/2.25
[g]TIS first-order removal (m/d)	1.37 (0.27)	1.16	0.22/4.31	2.38 (0.24)	2.36	0.93/5.29

Data present mean data and standard error of mean (S.E) in parenthesis, median, and minimum (min) and maximum (max) values of performance data for lagoons and wetlands.
[a]Calculated as Q x Inf Fe; where Q = flow rate (L/s)
[b]Calculated as (Inf Fe – Eff Fe)/Inf Fe x 100
[c]Calculated as Q(Inf Fe – Eff Fe)/Q*Inf Fe x 100
[d]Calculated as Q(Inf Fe – Eff Fe)/A; where A = system area (m^2)
[e]Calculated as area-adjusted removal/actual residence time (d)
[f]Calculated as Q(ln[Inf Fe – Eff Fe])/A
[g]Calculated as $Qn([\text{Inf Fe} / \text{Eff Fe}]^{1/n})/A$; where *n* = number of tanks-in-series

As shown in Table 5.3, influent waters are relatively high in iron concentration, with means of 18.27 mg/L and 7.59 mg/L for lagoons and wetlands respectively. These differences in influent iron are significant ($p<0.005$), such that the lagoons receive significantly higher iron concentration by design as stated earlier. Iron concentrations are reduced to a mean concentration of 8.85 mg/L in lagoons and 0.88 mg/L in wetlands. Differences are also significant (*p<0.0001*), the wetlands are capable of removing iron to a significantly low mean effluent concentration (i.e. less than 1 mg/L). As noted from Table 5.3, lagoons receive a higher iron loading rate (mean of 35.39 kg/d) than wetlands (mean of 20.58 kg/d). This is not surprising, because lagoons are designed as the primary treatment unit and wetlands are used as the subsequent treatment unit for final polishing of pollutant (refer to section 5.3.2 that discusses this in detail). However, differences in iron loading rate for lagoons and wetlands are not significant (*p>0.05*). These differences in influent and effluent iron concentrations and iron loading rate between lagoons and wetlands are illustrated in Figure 5.3. The rates of iron removal can be compared using commonly applied treatment system performance measures i.e. iron removal efficiency (%), load removal (%), area-adjusted removal (g/m^2/d) and first-order removal (m/d). Also included in this study is the TIS removal rate (m/d) (Table 5.3).

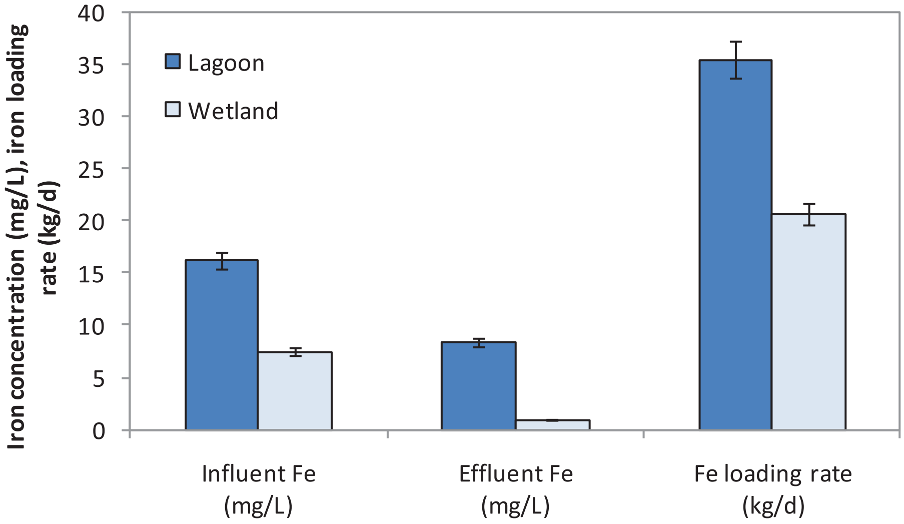
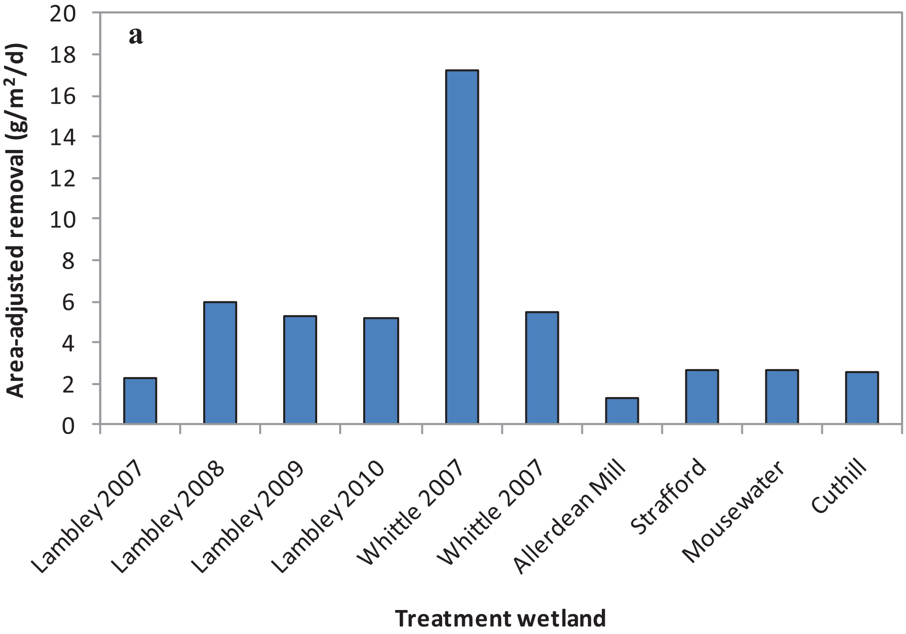


Figure 5.3 Comparisons of mean values of influent Fe concentration, effluent Fe concentration and Fe loading rate between lagoon and wetland (error bars: 95% confidence interval)

The mean iron removal efficiency for lagoons is 44.50%, which is significantly lower than wetlands (mean of 85.42%). Differences are significant (*p<0.0001*). On average, 45.36% and 83.86% of iron load is removed from the treatment lagoons and wetlands respectively. The rate of iron load removal is significantly greater in wetlands (*p<0.0001*). These differences in iron removal efficiency and load removal are shown in Figure 5.5 below. In mine water treatment systems, it is common to report iron removal in terms of the load removal per unit area (the area-adjusted removal rate) (following Hedin et al., 1994). Calculation of area-adjusted removal rate reveals large deviations of actual removal rate for wetlands from the design criteria rate used i.e. mean of 4.93 g/m^2/d (median of 5.14 g/m^2/d) compared to the recommended design criteria of 10 g/m^2/d (see Figure 5.4a for individual area-adjusted removal rate in wetlands). Note that the apparently high area-adjusted removal rate is seen from Whittle wetland (cell 1); this is likely because this wetland cell receives a comparatively high influent iron i.e. 20 mg/L compared to other wetlands. The deviation of area-adjusted removal rate from the design criteria rate has been suspected by practitioners previously, since the rate of iron removal is, to some extent at least, dependent on the influent concentration of iron (e.g. Tarutis et al., 1999; Hedin, 2008). Therefore reliance on a zero-order removal rate (independent of pollutant concentration) has the potential to result in under-performing systems. Even though lagoons are not originally designed on the basis of 10g Fe/m^2/d criteria, comparison using the metric of area-adjusted removal exhibit a greater removal rate on this basis in lagoons compared to wetlands i.e. mean of 12.40 g/m^2/d (median of 8.49 g/m^2/d) (see Figure 5.4b for individual area-adjusted removal rate in lagoons). However, it is also noticeable that there is a wide range of area-adjusted removal rates in the lagoons (minimum of 1.40 to a maximum of 39.41 g/m^2/d) i.e. performance is variable. While the lagoons demonstrate a closer median area-adjusted removal rate to the design metric i.e. 8.49 g/m^2/d, this does not directly imply that iron removal in the lagoons is zero-order, not least because many of the lagoons were designed based on estimated retention time i.e. 48 hours retention. Differences in area-adjusted removal between lagoons and wetlands are significant ($p<0.01$).



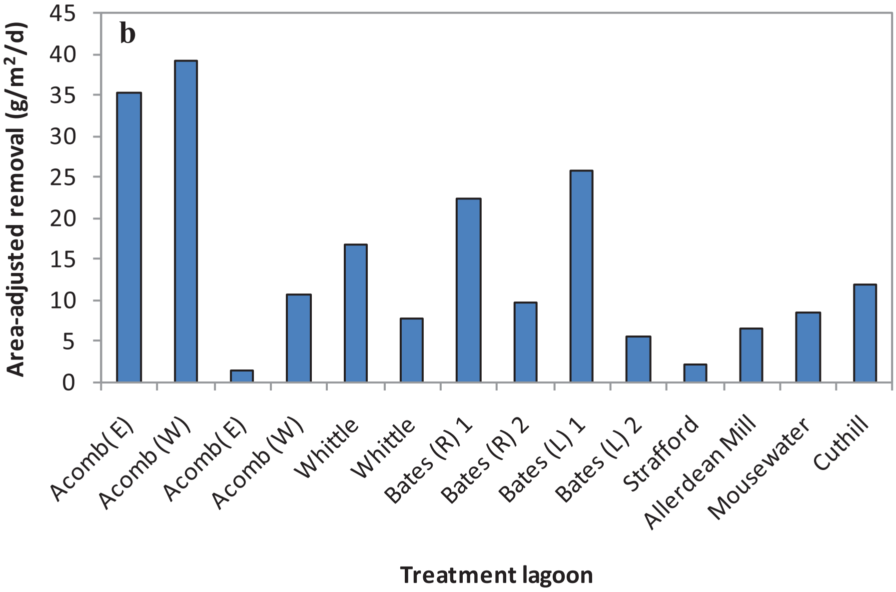


Figure 5.4 Variation in area-adjusted removal rates for individual (a) wetland and (b) lagoon

Furthermore, it is difficult to directly compare the area-adjusted removal rates between lagoons and wetlands because the performance of wetlands is invariably based on area removal rates, while retention time seems to be a more robust approach to the design of lagoons. Therefore, taking into account the actual residence time within the system, the removal rate can be given in unit of g/m^2 by dividing the area-adjusted removal rate (g/m^2/d) by the residence time (d). The mean removal rates calculated in this manner is 33.11 g/m^2 (median of 23.96 g/m^2) for lagoons, compared to a mean of 33.91 g/m^2 (median 11.79 g/m^2) for wetlands. Thus, whilst the lagoons have a greater removal rate than the wetlands based on this metric, the mean values are very similar for lagoons and wetlands. The greatly different median values here is likely reflected in the greatly variable values of removal on this basis in lagoons and wetlands i.e. lagoons typically have lower residence time, thus greater removal in unit g/m^2. Mean differences between lagoons and wetlands for iron removal efficiency, load removal, area-adjusted removal and residence time adjusted removal are illustrated in Figure 5.5.

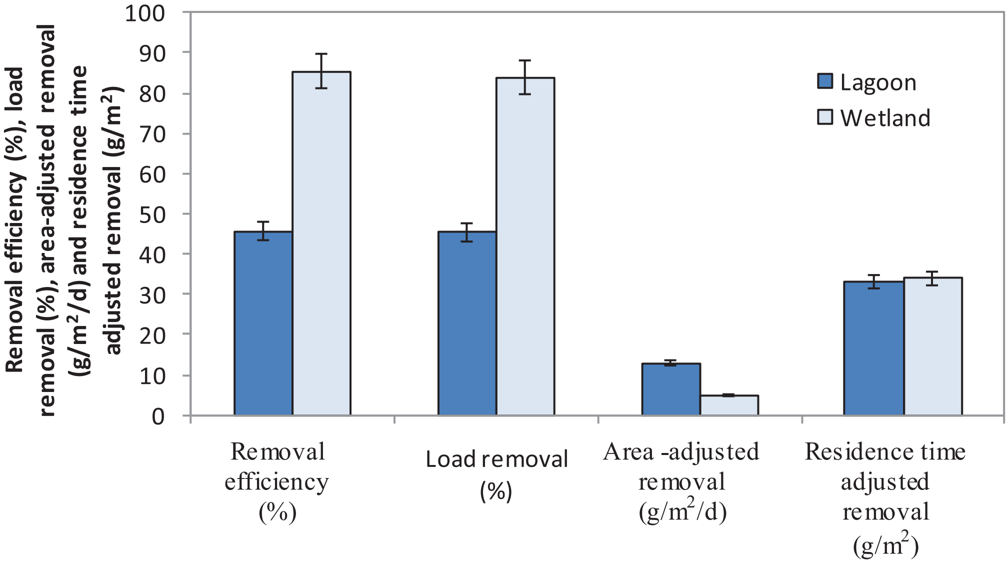


Figure 5.5 Comparisons of mean values of iron removal efficiency, load removal, area-adjusted removal and area removal rate between lagoon and wetland (error bars: 95% confidence interval)

Because first-order kinetics for iron removal has been proposed for treatment lagoons and wetlands, this removal metric is included here. Calculation of the first-order removal rate constant indicates a mean value of 1.06 m/d (median of 0.85 m/d) for lagoons and 1.58 m/d (median of 1.74 m/d) for wetlands, values which are markedly differed from the 0.18 m/d median value by Tarutis et al. (1999) for wetlands treating acid mine drainage in the United States. However, given the different inflow characteristics from which Tarutis et al. (1999) developed their first-order removal rate, it is inappropriate to simply compare this value of rate removal with those of the systems investigated here. Differences between lagoons and wetlands are significant

($p<0.05$). Mean differences between lagoons and wetlands are illustrated in Figure 5.6.

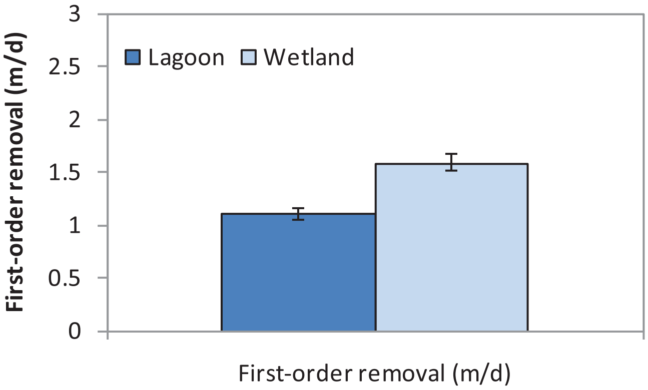


Figure 5.6 Comparisons of mean values of first-order removal between lagoon and wetland (error bars: 95% confidence interval)

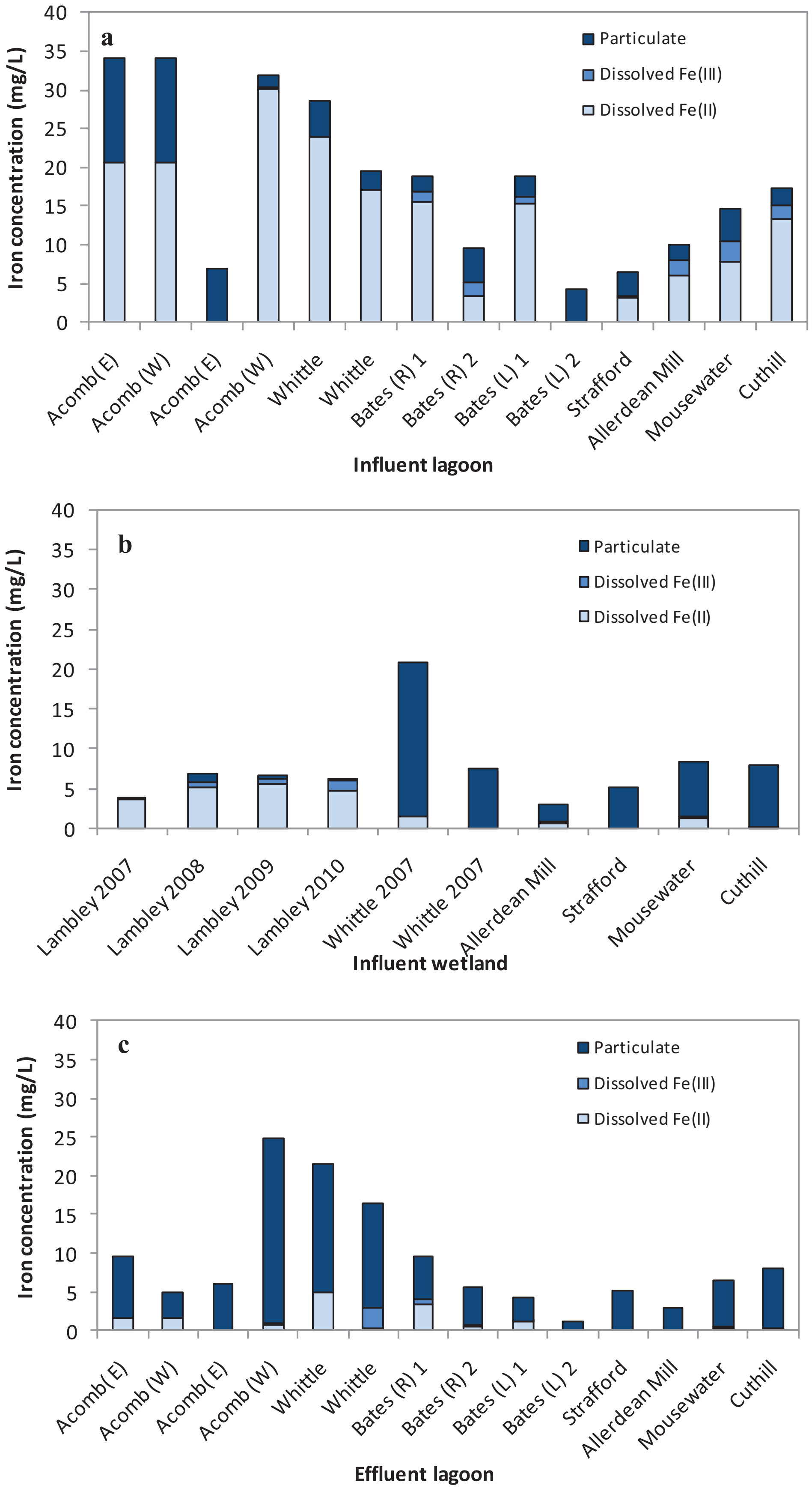
Generally it can be seen that the lagoons show a relatively poorer performance compared to wetlands in terms of iron removal, with the exception of a higher area-adjusted removal rate in lagoons. This may in part be due to the comparative hydraulic efficiency of the lagoons and wetlands i.e. the lower iron removal performance in lagoons shown here may reflect the lower lagoon hydraulic efficiency as discussed in section 4.4.6 of Chapter 4. This is further discussed in section 5.4.2.

Additionally, there are significant correlations found between all iron removal performance metrics in wetlands and influent iron concentration, and first-order removal and iron loading rate (see Appendix K; Figure K.1 and Figure K.2 for scatter plots of iron removal metrics as a function of influent iron and iron loading rate). The greater removal of iron at higher influent iron concentration adds weight to the appropriateness of a first-order kinetic model (concentration-dependent) for iron removal in the wetland systems. However, there are no such correlations found for lagoons, except between area-adjusted removal rate and influent iron concentration. Therefore in lagoons, performance of iron removal appears to be more variable compared to wetlands.

5.3.2 Controlling processes for iron removal

The oxidative removal of iron in alkaline water occurs by means of oxidation of ferrous to ferric iron and hydrolysis to ferric oxyhydroxide, which then settles in the system, and / or accretes to plant material in the case of wetlands (Wieder et al., 1985; Henrot and Wieder, 1990). Under alkaline conditions (pH ~ 6-8), and in an aerobic environment, the rate-limiting processes are oxidation and settling (Hedin, 2008). At pH conditions such as those in the systems investigated here, the reaction rate is first-order with respect to Fe^{2+} and dissolved oxygen and second order with respect to pH (Hedin, 2008). The oxidation rates for the systems investigated were calculated from the change in ferrous iron concentration between inlet and outlet whilst the settling rates were calculated from the change in total iron between inlet and outlet (after Hedin, 2008). To account for the variability in flow rate and system area, removal rates were given in units of $g/m^2/d$. These oxidation and settling rates were compared to the available influent ferrous iron and total particulate iron, respectively.

Samples of the mine water were collected during the tracer tests. Total and dissolved iron concentrations were collected to precisely understand the mechanisms under which iron is removed in the mine water treatment systems (Wieder et al., 1985; Wieder, 1994; Goulet and Pick, 2001). The influent and effluent iron contents, of which the dissolved Fe(II) and Fe(III) and particulate iron for lagoons and wetlands are illustrated in Figure 5.7. In most cases, iron is present in Fe(II) form in the influent of lagoons (Figure 5.7a), in which 83-100% of this Fe(II) is oxidised before leaving the systems (*cf.* Figure 5.7c). The wetlands receive most iron in particulate iron form except for Lambley wetland (Figure 5.7b); the Lambley treatment scheme comprises solely of wetlands in series without primary treatment in lagoon such as for other wetlands investigated, therefore upon emergence to surface environment, iron present in ferrous iron form in the influent. Iron is greatly removed in the wetlands to ≤1 mg/L at most effluents of wetlands (Figure 5.7d). Note: full data for iron oxidation and settlement rates in lagoons and wetlands investigated are provided in Appendix K (Table K3 and Table K4).


a
Iron concentration (mg/L)
40
35
30
25
20
15
10
5
0
Particulate
Dissolved Fe(III)
Dissolved Fe(II)
Acomb(E)
Acomb (W)
Acomb(E)
Acomb (W)
Whittle
Whittle
Bates (R) 1
Bates (R) 2
Bates (L) 1
Bates (L) 2
Strafford
Allerdean Mill
Mousewater
Cuthill
Influent lagoon
b
Iron concentration (mg/L)
40
35
30
25
20
15
10
5
0
Particulate
Dissolved Fe(III)
Dissolved Fe(II)
Lambley 2007
Lambley 2008
Lambley 2009
Lambley 2010
Whittle 2007
Whittle 2007
Allerdean Mill
Strafford
Mousewater
Cuthill
Influent wetland
c
Iron concentration (mg/L)
40
35
30
25
20
15
10
5
0
Particulate
Dissolved Fe(III)
Dissolved Fe(II)
Acomb(E)
Acomb (W)
Acomb(E)
Acomb (W)
Whittle
Whittle
Bates (R) 1
Bates (R) 2
Bates (L) 1
Bates (L) 2
Strafford
Allerdean Mill
Mousewater
Cuthill
Effluent lagoon

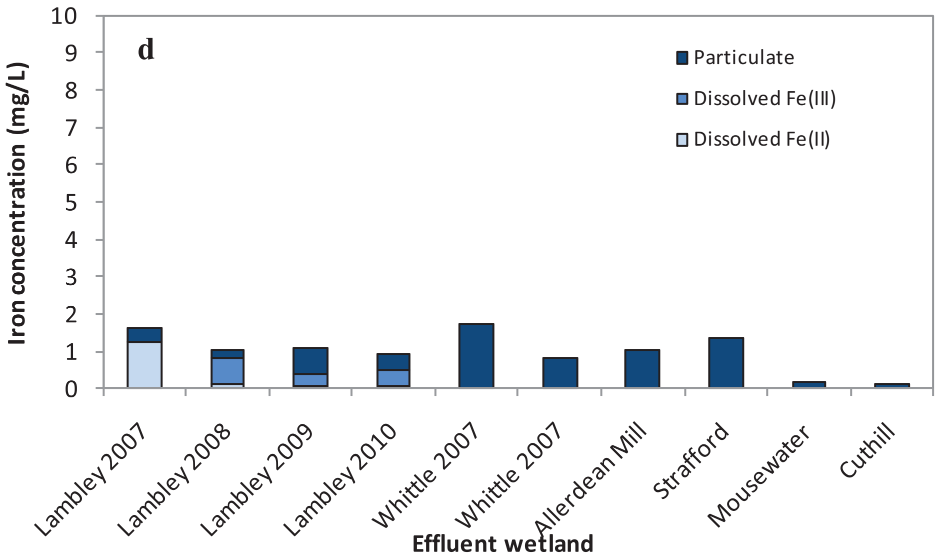


Figure 5.7 Influent and effluent iron contents (total, dissolved (ferrous) and particulate iron concentrations) in (a) influent of lagoons (b) influent of wetlands (c) effluent of lagoons and (d) effluent of wetlands

The concentration-dependence for iron removal processes (i.e. oxidation and settlement) are graphically shown in Figure 5.8 and Figure 5.9. The rates of iron oxidised and settled per unit area in the treatment systems are clearly dependent on the available ferrous iron and total particulate iron, respectively.

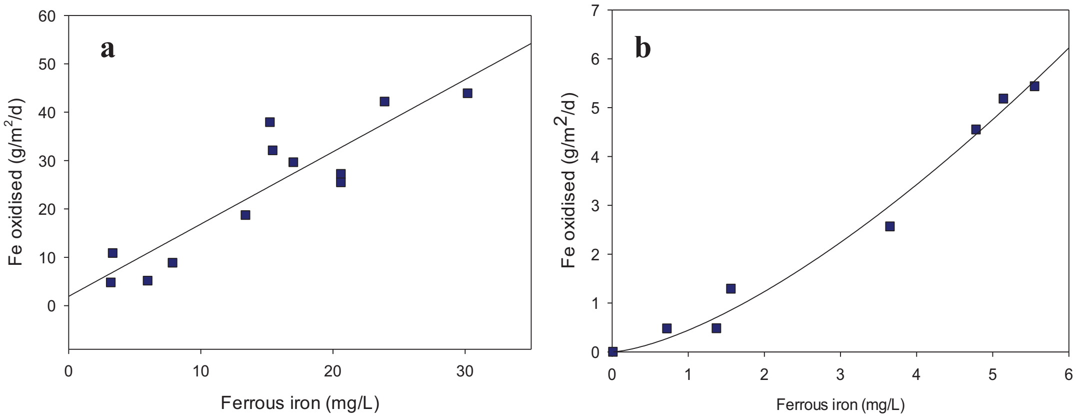


Figure 5.8 Iron oxidised as a function of ferrous iron available in (a) lagoon; $y = -1.9321+1.4936x$, $p<0.0001$, $R^2 = 0.8037$ (b) wetland; $y = 0.4446x^{1.4757}$, $p<0.0001$, $R^2 = 0.9850$ (after Hedin, 2008)

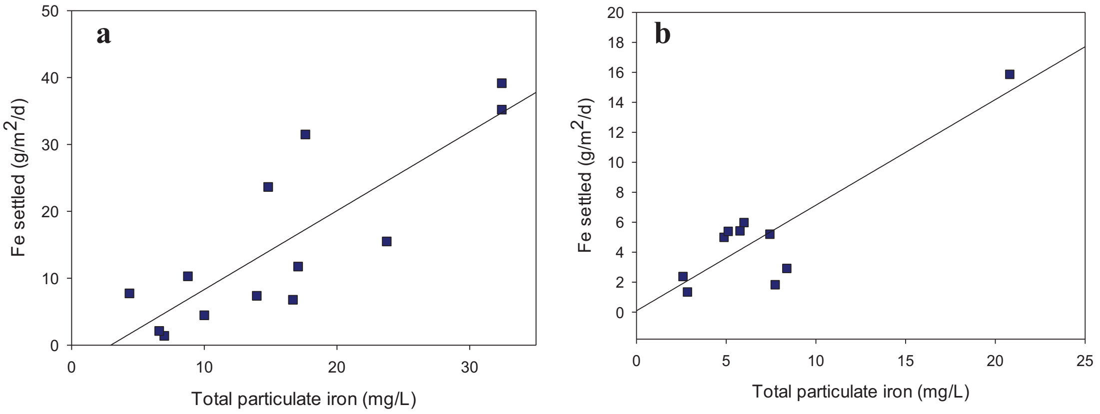


Figure 5.9 Iron settled in the treatment systems as a function of total particulate iron for (a) lagoon; $y = -3.4785+1.1787x$, $p=0.0004$, $R^2 = 0.6921$ (b) wetland; $y = -0.0884+0.7046x$, $p=0.0008$, $R^2 = 0.7749$ (after Hedin, 2008)

In the lagoons, the mean iron oxidation rate is 20.51 g/m^2/d compared to a mean settling rate of 15.19 g/m^2/d. This reflects the relatively higher ferrous iron concentration available in the lagoon systems (see Figure 5.7a). Conversely, in wetlands, the mean iron oxidation rate is only 2.00 g/m^2/d compared to a mean settling rate of 5.13 g/m^2/d. This corresponds with the relatively lower ferrous iron available and that most iron entering the wetland is in particulate form (see Figure 5.7b).

As seen in 5.8 and Figure 5.9, higher oxidation and settlement rate per unit area are seen in lagoons compared to wetlands, simply because there is a comparatively higher available iron for both processes in the lagoons. Thus, this may also explain the relatively higher area-adjusted removal rate in the lagoons. However, as the results here seem to suggest, these higher oxidation and settlement rates in lagoons do not necessarily imply a better iron removal efficiency in the system (*cf.* lower iron removal efficiency found in lagoons compared to wetlands). This may therefore suggest the influence of hydraulics factors on treatment efficiency for iron removal in such systems i.e. poor hydraulic efficiency is reflected in relatively poor performance using this metric of treatment performance. This concentration-dependence of iron removal is consistent with the findings of Hedin (2008) for a passive treatment systems (a series of ponds and wetlands) treating alkaline coal mine drainage in Pennsylvania, United States. Therefore, on the evidence of field data from this study, it seems that the greater iron oxidation is the primary control for iron removal processes in lagoon systems whilst in wetlands, the removal is controlled by the iron settling as evidenced by the greater settling rate within this system (see Figure 5.10 below). Note that these mechanisms for iron removal in lagoons and wetlands studied are further investigated via column experiments in the laboratory, as discussed in detail in the following section.

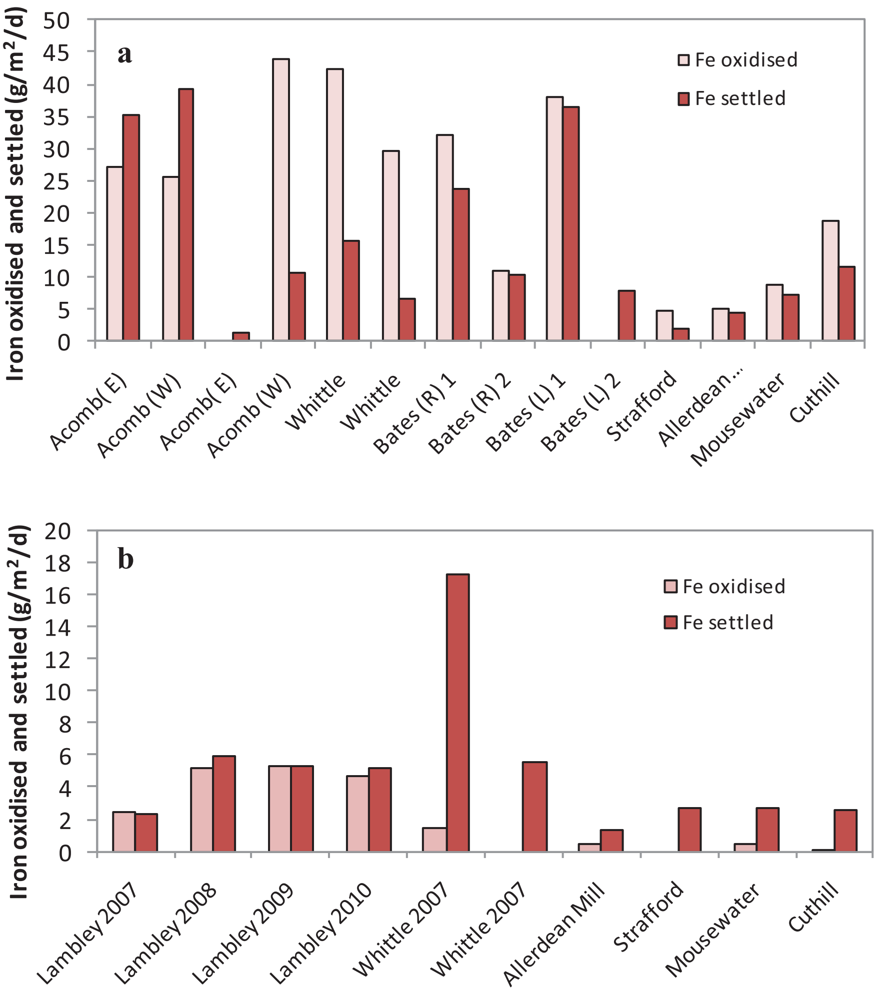


Figure 5.10 Iron oxidation and settling rate as controlling removal processes in (a) lagoons and (b) wetlands

5.3.3 Time- and concentration-dependence of iron removal in mine water treatment lagoons and wetlands

The geochemical and physical processes (oxidation and settlement) that govern removal of iron are concentration-dependent. This concentration-dependence of geochemical processes governs the time-dependence of the overall process of iron removal, such that reduction in iron concentration with time approximates an exponential decrease.

In the absence of acidity (as is the case in the systems investigated here) the most important contaminant in coal mine waters is usually iron, which is typically present at the point of discharge as ferrous iron. The objective of mine water treatment is therefore to encourage the oxidation of ferrous iron to ferric iron, and then the hydrolysis and precipitation of ferric iron within the confines of the treatment systems, as follows:

$$Fe^{2+} + 1/4O_2 + H^+ \leftrightarrow Fe^{3+} + 1/2H_2O \qquad [5.3]$$

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 \downarrow + 3H^+ \qquad [5.4]$$

Under appropriate geochemical conditions (principally elevated pH and an oxic environment), both reactions will proceed in the forwards direction, and therefore the limiting factor to effective treatment becomes time. It should also be noted that the oxidation of iron is generally governed by the first-order kinetics for iron removal i.e. dependent on the initial concentration of ferrous iron, in addition to reasonably high pH and the presence of oxygen (Hedin et al., 1994; Younger et al., 2002). Furthermore, according to first-order removal, longer residence time will result in greater removal of pollutants in general e.g. suspended solids, nutrients and biochemical oxygen demand by the wetland (Persson et al., 1999; Goulet et al., 2001). Therefore, a longer residence time gives more time for sedimentation of particles and reactions to occur and improves the treatment efficiency (Kjellin et al., 2007). It is worth noting that a large system is therefore preferable, but the actual limiting factor to installation of such systems becomes a practical engineering one of identifying an area of land of sufficient size, and also the cost of acquiring such a large land area.

5.3.3.1 Column tests

The time- and concentration-dependence of iron removal in both lagoons and wetlands was investigated via laboratory column tests in this study. The tests were conducted to observe the conditions under which ferrous iron is oxidised and settled in the influent and effluent of treatment systems when dissolved oxygen and pH are not limiting. Semi-continuous measurements (readings every 5 minutes) of turbidity, pH, temperature and dissolved oxygen of supernatant water in each 5 litre vessel were made using a 6-series Multiparameter Water Quality Sonde, suspended in the vessels for 24 hours. Supernatant samples for analysis of iron were collected every 5 to 10 minutes, depending on real-time turbidity measurements. By this means, turbidity measurements were made, with a view to establishing whether it would be possible to use it as a rapid tool for monitoring treatment performance with respect to iron. Detail experimental set up is presented is section 3.4.1 of Chapter 3.

Examples of the changes in total, dissolved and particulate iron concentration and turbidity measurements in the water columns are shown in Figure 5.11 (turbidity shown for the first 12 hours of 24 hours semi-continuous measurement). Note that turbidity readings are fairly constant beyond the first 12 hours and are therefore not shown in Figure 5.11. Supernatant samples were collected on a regular basis during the first 6 hours of experiment. This is when oxidation and settlement are presumably occurring at significant rates due to the higher initial iron concentration. Beyond the first 6 hours further decreases in suspended iron concentrations are assumed to be of relatively minor importance, and this is suggested by the data shown in Figure 5.11 i.e. significantly reduced iron concentration after 6 hours. The column tests were repeated for each of the investigated treatment systems, both for lagoons and wetlands; full experimental data are included in Appendix L.

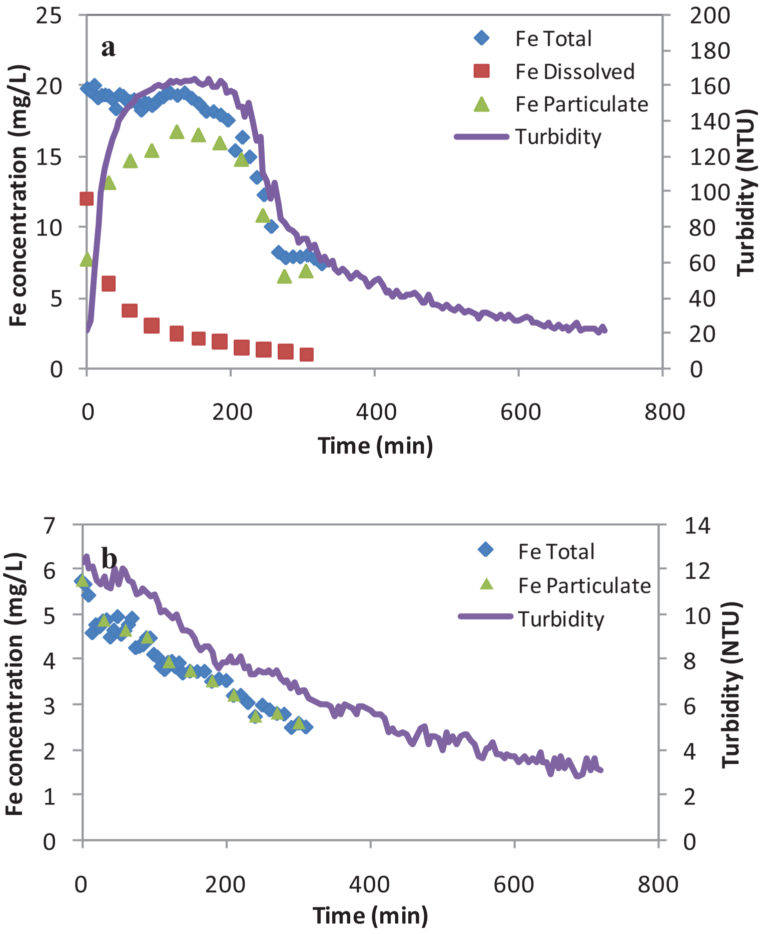
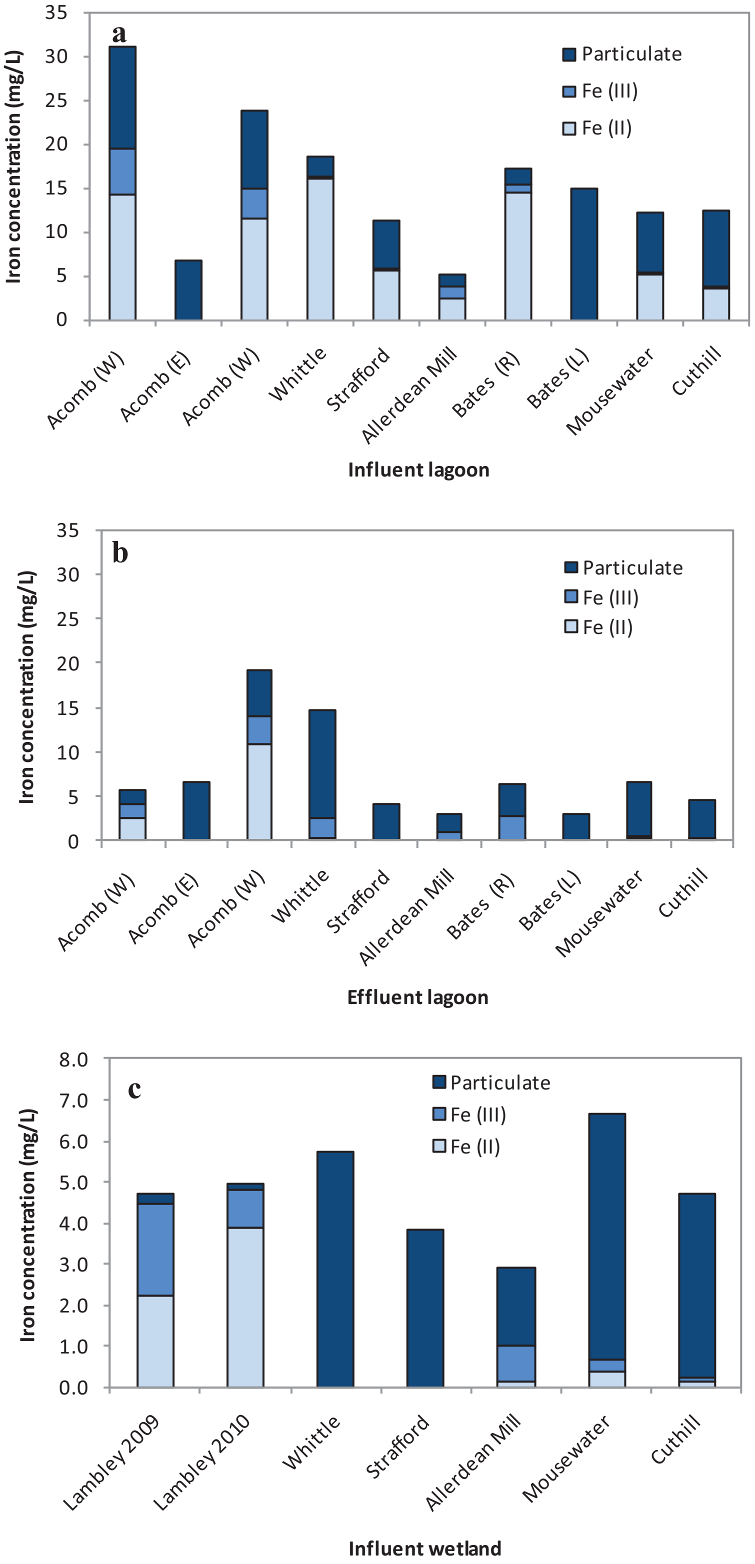


Figure 5.11 Example of changes in total, dissolved and suspended (particulate) iron, and turbidity measurement at Whittle (a) lagoon (b) wetland. Note that dissolved Fe concentrations are < limit of detection (LOD) at Whittle wetland

For lagoons, most iron is generally present in the form of dissolved ferrous iron at the start of the experiment (e.g. Figure 5.11a, see Figure 5.12a for all lagoons results), and the ferrous iron is therefore rapidly oxidised to ferric iron at this stage. This hydrolysed ferric iron then begins to settle (after about 100 minutes in the example in Figure 5.11a), and therefore the particulate iron concentration, and total iron concentration, begins to decrease. This is reflected in a steep decrease in turbidity.

In most wetland cases, however, initial iron concentration is predominantly as suspended (particulate) iron (e.g. Figure 5.11b, see Figure 5.12c for all wetlands results), and the dissolved iron present is in much lower concentrations, or even below the detection limit (0.1 mg/L). Therefore, settlement of these suspended oxyhydroxide iron is seen as the limiting process for iron removal in wetlands under aerobic, net-alkaline pH conditions (Hedin, 2008). Detailed discussions of iron oxidation and settlement rates in lagoons and wetlands are presented below.



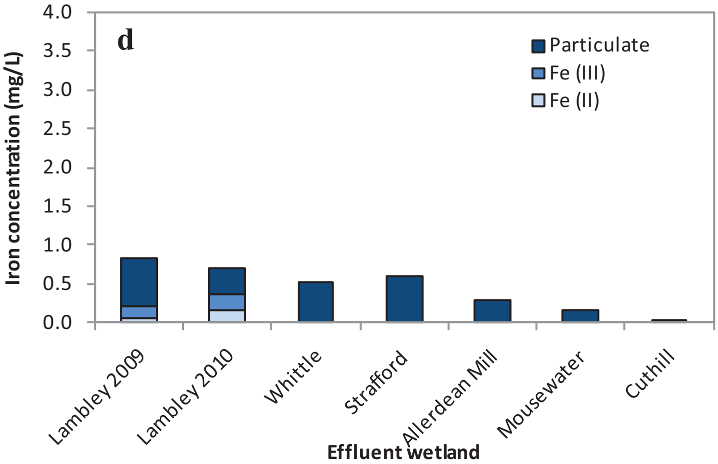


Figure 5.12 Influent and effluent iron contents (dissolved (ferrous and ferric) and particulate iron concentrations) during column experiments for (a) influent of lagoons (b) effluents of lagoons (c) influents of wetlands and (d) effluent of wetlands

5.3.3.2 Reaction rates calculation

The oxidation rates of ferrous to ferric iron were determined by measuring the changes in ferrous iron concentration over time in the column experiment described above. This was obtained by plotting $\log_{10}$ [FeII] versus time, according to a pseudo first-order expression (Davison and Seed, 1983). The oxidation rates were subsequently calculated from the slope of the plot multiplied by -2.3 (Sung and Morgan, 1980; Davison and Seed, 1983). See Appendix I for full illustration of iron oxidation rate determination in each system.

Likewise, the settlement rates of ferric oxyhydroxides were observed by measuring the changes in suspended iron (measured as turbidity) over time, since turbidity is a good measure of the amount of suspended solids contained in a water column. In such a ferruginous mine water column as in the investigated mine water treatment systems, the presence of suspended solids constitute mainly of oxyhydroxide iron (suspended iron hydroxides). This is visually seen as turbid orange water in the water column. Settlement of these oxyhydroxide iron will complete the mechanism under which iron is removed within the treatment systems.

Relationships between suspended (particulate) iron and turbidity can be clearly seen within the investigated treatment systems from the correlation and linear regression analysis, for which the correlation coefficient, R^2 is between 0.80-0.99 (see Table 5.4

and Appendix H). These correlations were calculated for the part of the column experiments during which simultaneous measurements of particulate iron concentration and turbidity were made e.g. Figure 5.11. It can be seen that particulate iron correlates strongly to turbidity, suggesting that the declining pattern of turbidity over time is due predominantly to the decreasing concentration of suspended iron due to settlement. Accordingly, the iron settlement rates were obtained by plotting $\log_{10}$ [$Fe_{particulate}$] versus time, according to pseudo first-order expression. Iron settlement rates were then calculated from the slope of the declining portion of the plot multiplied by -2.3 (Sung and Morgan, 1980; Davison and Seed, 1983). See Appendix J for full illustration of iron settlement rate determination in each system.

Table 5.4 Correlation coefficients, R^2, between suspended (particulate) iron and turbidity measurement in mine water treatment lagoons and wetlands

Lagoon			Wetland		
Site	Inlet	Outlet	Site	Inlet	Outlet
Acomb	[a]0.9697	$0.8699^{\ddagger}$	Lambley	[f]0.8310^{*}	0.8841
	[b]0.9331	0.8993		[g]0.8702^{**}	0.9336
	[c]0.9031	0.8184^{*}	Whittle	0.9435	$0.7975^{\dagger}$
Whittle	0.9603	0.9688	Strafford	0.9622	$0.8090^{\dagger}$
Strafford	0.9607	0.8425	Allerdean Mill	0.9291	0.9836
Allerdean Mill	0.9101	0.9749	Mousewater	0.9351	0.9364
Bates	[d]0.9733	0.9274	Cuthill	0.9388	0.9629
	[e]0.9970	0.8924			
Mousewater	0.9148	0.9351			
Cuthill	0.9859	0.9075			

All p-values are <0.0001 significant level except † $p<0.0005$, ‡$p<0.001$, * $p<0.005$, ** $p<0.01$

[a,b,c] Sampling on December 2008, February 2009 and June 2009, respectively

[d,e] Right and left side lagoon, respectively

[f,g] Sampling on November 2009 and April 2010, respectively

5.3.3.3 Comparison of iron oxidation and settlement rates in mine water treatment lagoons and wetlands

Characteristics of mine water (during column tests) and the corresponding iron oxidation and settlement rates in lagoons and wetlands are summarised in Table 5.5.

Generally, a higher initial iron concentration (up to 5 times higher) is seen in lagoons compared to wetlands. Consequently, the rate of iron oxidation is markedly faster in the lagoons because under aerobic, net-alkaline conditions (approximately neutral pH), this process is governed by the concentration of ferrous iron (note that most of the iron initially entering the lagoon systems is in dissolved ferrous iron form; (refer to Figure 5.12a and Appendix L). In a similar manner, the rate of iron settlement in lagoons is relatively faster than in wetlands (although with a lesser magnitude of difference than the oxidation rate) given the relatively higher concentration of available particulate iron for settlement (once oxidation and hydrolysis has occurred).

Table 5.5 Mine water characteristics of lagoon systems during column tests

	Lagoon‡			**Wetland**†		
	Mean (S.E)	**Median**	**Min/Max**	**Mean (S.E)**	**Median**	**Min/Max**
*Total Fe (mg/L)	11.39 (1.72)	9.01	2.92/31.11	2.62 (0.64)	1.88	0.013/6.68
*Dissolved Fe (mg/L)	6.92 (1.67)	4.01	0/19.66	1.66 (0.78)	0.67	0.21/4.79
*Ferrous Fe (mg/L)	5.86 (1.54)	3.65	0.11/16.12	0.99 (0.56)	0.17	0.07/3.87
*Particulate Fe (mg/L)	5.86 (0.85)	5.26	1.33/15.05	1.79 (0.60)	0.57	0.013/6.01
Fe oxidised (mg/L)	6.56 (1.97)	4.90	0/15.75	1.29 (0.72)	0.36	0.11/3.7
Total particulate Fe (mg/L)	9.53 (1.34)	8.12	2.01/23.19	2.26 (0.59)	1.45	0.013/6.37
Fe oxidation rate (min^{-1})	0.0108 (0.0019)	0.0115	0.0017/0.0220	0.0040 (0.0015)	0.0020	0.001/0.0101
Fe settlement rate (min^{-1})	0.0032 (0.0004)	0.0030	0.0013/0.0062	0.0020 (0.0002)	0.0021	0.0008/0.0029

*Initial concentration at start of experiment
†$n = 14$, ‡$n = 20$

Irrespective of influent or effluent samples, the plots of iron oxidation and settlement rates as a function of available iron for each process in lagoons and wetlands are shown in Figure 5.13. Both the influent and effluent points, each has different chemistry of iron i.e. proportion of dissolve and particulate iron, such that this may have influence on iron removal processes. Therefore, the rates of iron removal (oxidation and settlement) are assessed at each of these points. Accordingly, iron oxidation rates were plotted against available ferrous iron concentration, while iron settlement rates were plotted against available total particulate iron concentration (after Hedin, 2008). Statistical relationships shown in each plot in Figure 5.13 (i.e. power and linear regression, respectively) are for lagoons data only. Note that the wetlands data are inserted for comparison and are shown in detail in Figure 5.14. It is clear that higher iron oxidation rates are seen at higher ferrous iron concentrations. Similarly, iron settlement rates are greater at higher total particulate iron concentrations. Both processes are significantly correlated with available iron present for each process at > 99.99% confidence level, showing that these removal processes in lagoons are strongly governed by initial iron concentration, which agrees with the findings of Tarutis et al. (1999) and Hedin (2008). Graphically, it can be seen that the removal rates in wetlands are much lower compared to lagoons (Figure 5.13), as discussed earlier.

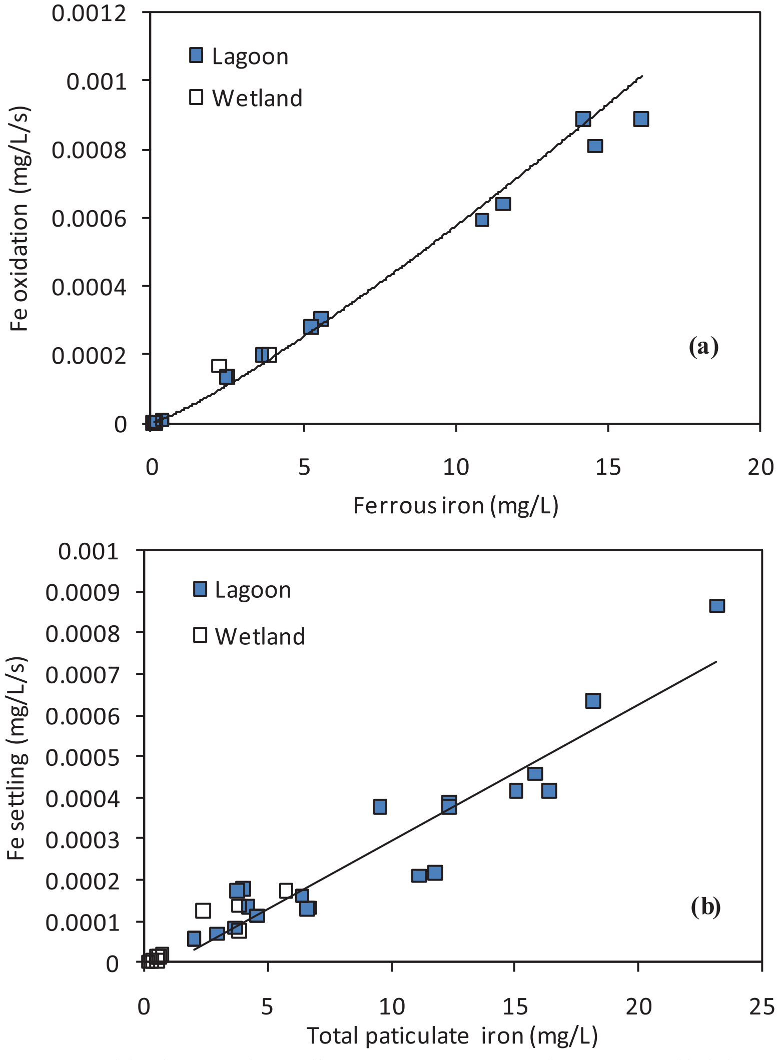


Figure 5.13 Iron oxidation and settling rate as a function of available ferrous iron and total particulate iron, respectively, for mine water treatment lagoon and wetlands (derived using methods of Hedin (2008)). The fitted curve represents the relationship between each data set for lagoon systems only. Data for wetlands inserted for comparison. (a) y = 4E-05$x^{1.191}$, p<0.0001, R^2 = 0.9963 (b) y = 3E-05x-3E-05, p<0.0001, R^2 = 0.8824

Plots of oxidation and settlement rates in wetlands are presented in Figure 5.14. It can be seen that iron settlement rates in wetlands are greatly dependent on the available iron for the process i.e. rates are higher at higher total particulate iron in the systems (Figure 5.14a). The relationship between iron oxidation rates and the available ferrous iron in wetlands can be represented by a power regression relationship, as shown in Figure 5.14b. However, it should be noted that this relationship is greatly influenced by the two higher 'points' (which are the column test data from the Lambley treatment systems). The fact is, the Lambley wetland comprises four wetland cells in series, without pre-treatment in settlement lagoons as in most other cases. This is coupled with the fact that most iron entering the wetland is in the dissolved, ferrous iron form. Therefore, it is not surprising that higher initial concentrations of ferrous iron are seen within this system. In contrast, other wetland systems investigated here are secondary treatment unit(s) following settlement lagoons as the primary system(s). Consequently much lower concentrations of ferrous iron are seen entering these systems, in which most iron is present in the form of particulate ferric hydroxides. At low initial concentrations of ferrous iron the rate of iron oxidation seems to be independent of initial concentration (lower portion of Figure 5.14b), although more data would be required to confirm this.

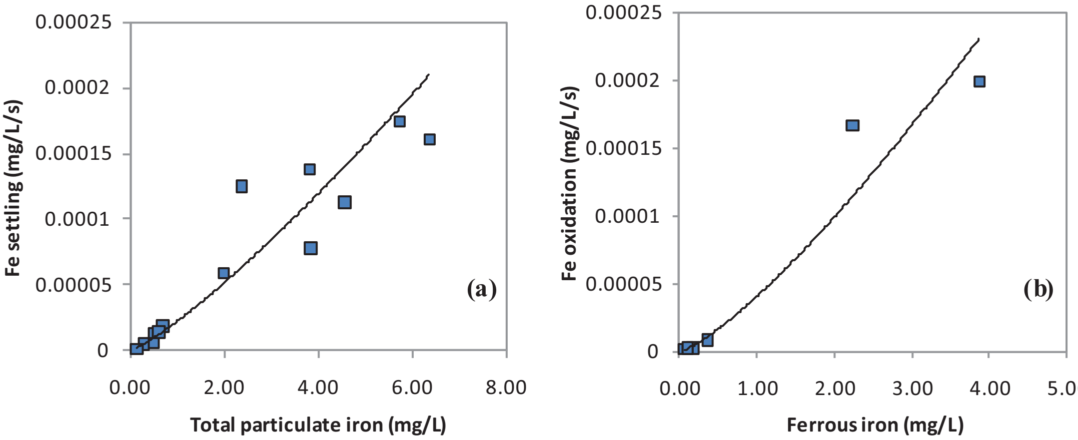


Figure 5.14 Fe oxidation and settling rate in wetland system as a function of available ferrous iron and total particulate iron, respectively (using methods of Hedin(2008)). (a) $y = 2E\text{-}05x^{1.2107}$, $p<0.0001$, $R^2 = 0.9553$ (b) $y = 4E\text{-}05x^{1.2826}$, $p<0.0001$, $R^2 = 0.9799$

It is therefore clear that the rates of iron oxidation and settlement in lagoons are strongly dependent on initial iron concentrations, in particular the ferrous iron and total particulate iron available for the processes of oxidation and settlement. In addition to the above discussion, comparison between the removal rates between influent and effluent water samples of the lagoons and wetlands has also been made, and is discussed below; full data are shown in Appendix L. This assessment was made because influent and effluent waters may have different characteristics, which may have an impact on the removal rates between these points, and thus may suggest the limiting process for iron removal at each point. Furthermore, some of the effluents from treatment lagoons serve as the influent to subsequent wetland systems, such that these inter-related points may have an influence on the overall extent of iron removal.

- ***Lagoon systems***

Individual assessment of the lagoon influent and effluent chemistry generally indicates that iron oxidation and settlement rates are higher in influent waters compared to effluents. The reason for this has been discussed previously i.e. higher concentrations of initial ferrous and particulate iron for each process at influent points. In most cases, the rates of iron oxidation are typically higher than the settlement rates at the influent points (Figure 5.15a). This is because most iron present is in the dissolved ferrous form at the influent points, providing a greater means for the iron oxidation process. There are, however, exceptions to this general trend. For instance, the Acomb lagoon (which is dosed with hydrogen peroxide to enhance the oxidation of ferrous to ferric iron and therefore settlement of ferric hydroxide in the systems).

In contrast, at the effluents most systems exhibit greater iron settlement rates compared to iron oxidation rates (Figure 5.15b). This has been suspected because at these points (effluents), most ferrous iron has been largely oxidised to ferric iron, followed by hydrolysis of these ferric to oxyhydroxide iron, leaving most iron in the form of suspended (particulate) iron, which finally settle out in the systems. However, in the Acomb lagoon (i.e. the west lagoon), iron oxidation is still evident at the effluent point despite settlement rate dominance. On the other hand, the settlement rates also seem to be the dominant process at system effluents in cases where dissolved ferrous iron present in reasonably low concentrations i.e. < LOD, such that initial iron is assumed to be of particulate iron forms. Therefore, in such a case, where initial iron is considerably low, oxidation rates may be limited by the available ferrous iron for the process, hence favouring the settlement rate dominance in the system.

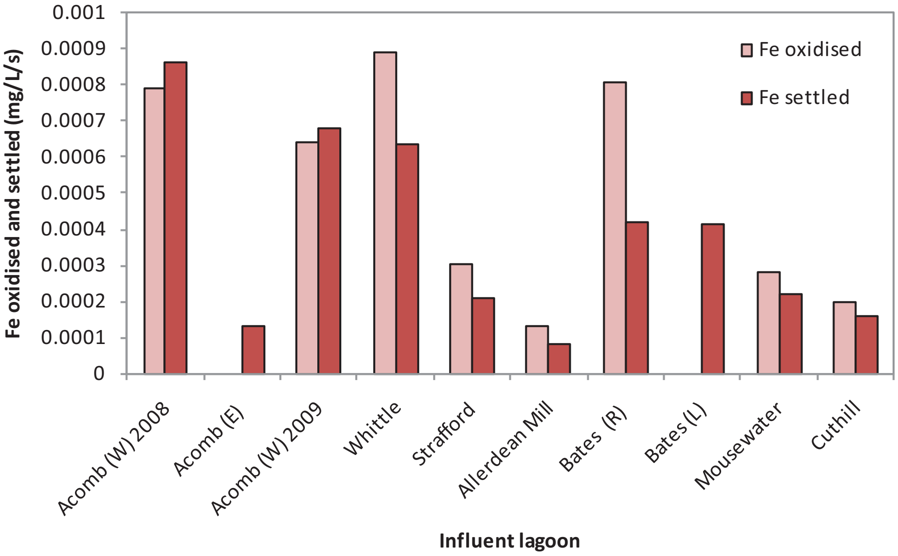


Figure 5.15(a) Iron oxidation and settling rate during column experiments as controlling removal processes in lagoons influent

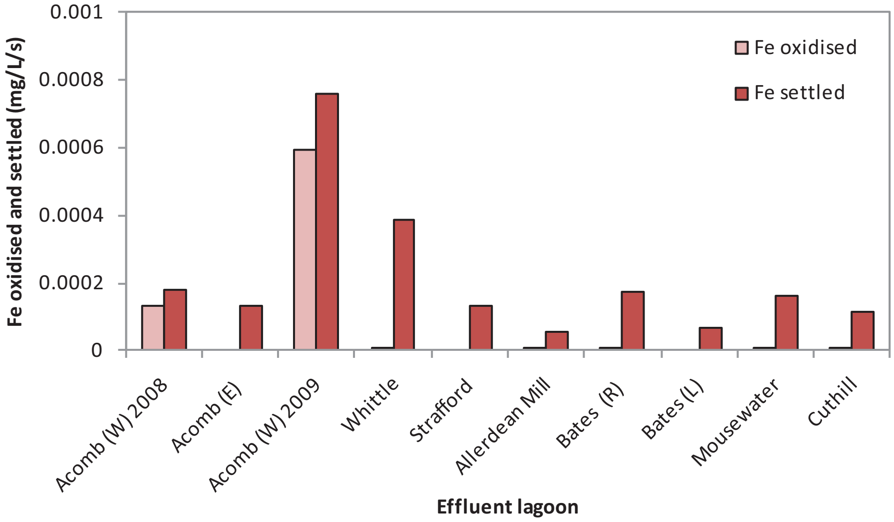


Figure 5.15(b) Iron oxidation and settling rate during column experiments as controlling removal processes in lagoons effluent

- ***Wetland system***

In wetland systems settlement is generally the dominant process compared to oxidation, both at system influent and effluent points (Figure 5.16a and Figure 5.16b), with the exception of Lambley wetland. On the evidence of the investigated wetlands, most systems have an initial iron concentration that is largely in the form of particulate iron. Ferrous iron is present in comparatively low concentrations or below the detection limit. The main reason for this appears to be that a large portion of ferrous iron has already been oxidised in settlement lagoon(s) prior to wetland treatment. Thus, this is likely the reason for relatively greater iron settlement rates compared to oxidation in most wetlands, which also occurs at many of the lagoon effluent points (i.e. oxidation rate becomes limited by the reasonably low ferrous iron available for the process).

Notwithstanding the general dominance of settlement over oxidation in wetlands, settlement rates are clearly greater at influent compared to effluent of the systems, because total particulate iron is present in much higher concentrations at the influent, favouring higher rates of settlement of iron. It has already been noted that these wetland systems appear to be the secondary unit(s) following settlement lagoon(s) as the pre-treatment system. In contrast to this, the Lambley wetland, which is constructed solely to treat a reasonably low influent iron, receives an influent iron which is largely in the dissolved form. In this case, as anticipated, the system exhibits greater oxidation than settlement rates at the system influent, whilst at the effluent of this wetland settlement dominates over the oxidation rates.

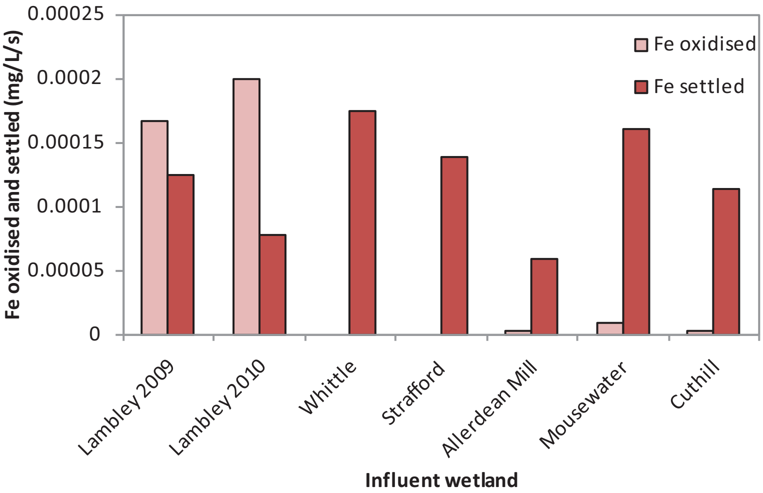


Figure 5.16(a) Iron oxidation and settling rate during column experiments as controlling removal processes in wetlands influent

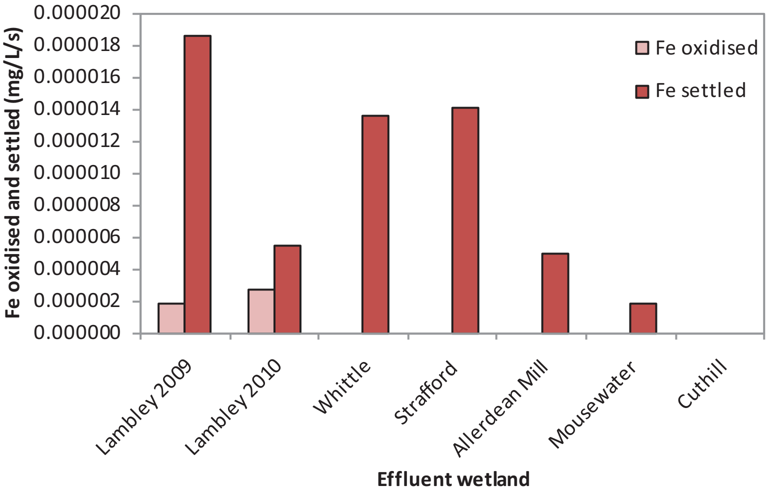


Figure 5.16(b) Iron oxidation and settling rate during column experiments as controlling removal processes in wetlands effluent

Overall, clearly the oxidation and settlement rates are dependent on time. The rates are faster in lagoons compared to wetlands as a consequence of the higher concentration of iron available for the processes. This reflects the first-order kinetics of iron removal i.e. rates are higher at higher initial iron concentrations. Therefore, the higher area-adjusted removal rate in lagoons (based on zero-order kinetics) may be a function of the higher initial iron concentration in the systems. However, as noted earlier, this higher removal per unit area in lagoons does not correspond with the absolute treatment efficiency and other treatment performance metrics i.e. load removal, first-order removal and TIS removal. Therefore, this may suggest that the use of first-order removal model may be appropriate to represent the pollutant removal in the systems. Similarly, a TIS first-order removal model may be a better option for it takes into account the effect of flow pattern on pollutant attenuation.

5.4 RELATIONSHIPS BETWEEN HYDRAULIC AND GEOCHEMICAL FACTORS IN MINE WATER TREATMENT LAGOONS AND WETLANDS

5.4.1 Relationship between hydraulic performance and iron removal at the Lambley wetland over 4 years of operation

According to first-order removal kinetics greater removal of pollutants will be achieved with longer residence time (e.g. Goulet et al., 2001; Kruse et al., 2009). Therefore a greater removal of iron would be anticipated in a more hydraulically efficient system. Figure 5.17 illustrates the iron removal rates and hydraulic performance metrics for the Lambley wetland over its 4 years of operation. As shown in the figure, there is a close relationship between these hydraulic performance characteristics and iron removal in this treatment system. Note that in this wetland the effect of different system geometry (i.e. length-to-width ratio and depth) and flow rates could not be accounted for since they are constant, but such an assessment has been made for other systems (see section *4.4.4.4* of Chapter 4). It has previously been shown (in section *4.4.4.2* of Chapter 4) that vegetation may have a significant influence on hydraulic performance. Given the relationships in Figure 5.17, it appears that vegetation, via its influence on hydraulics, also has an important effect on geochemical performance. Iron removal performance data are shown in Table 5.6.

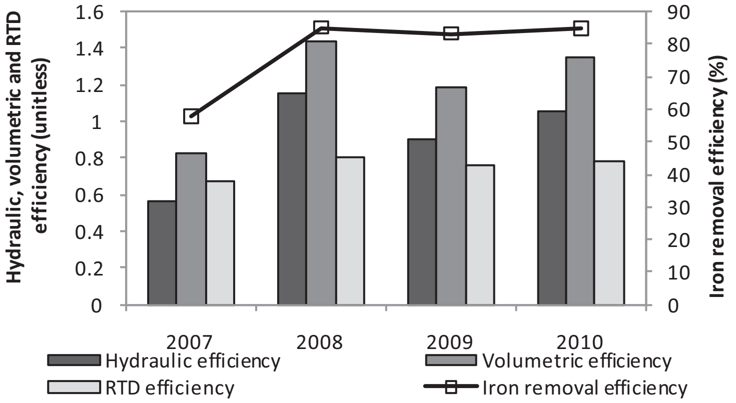


Figure 5.17(a) Hydraulic performance characteristics in relation to iron removal efficiency for Lambley wetland

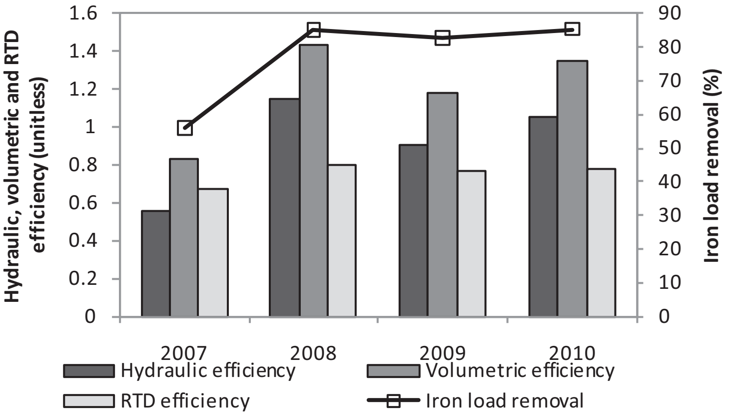


Figure 5.17(b) Hydraulic performance characteristics in relation to iron load removal for Lambley wetland

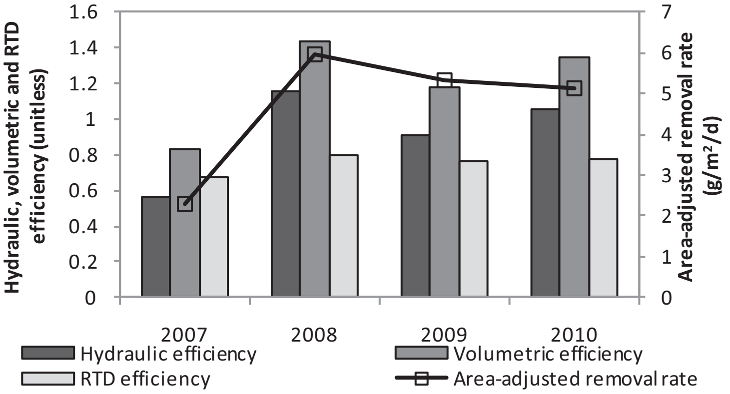


Figure 5.17(c) Hydraulic performance characteristics in relation to area-adjusted removal rate for Lambley wetland

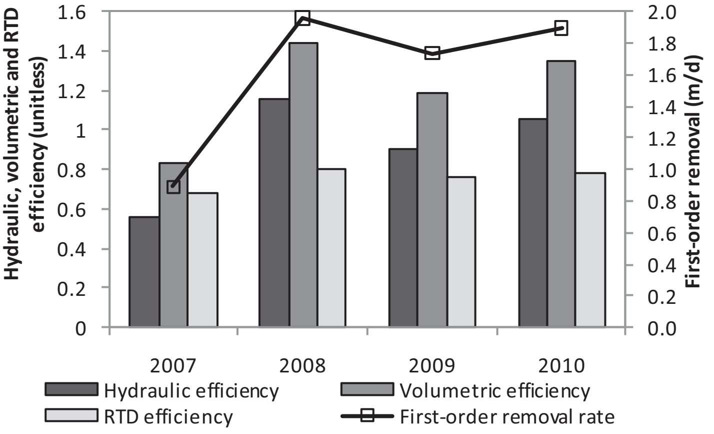


Figure 5.17(d) Hydraulic performance characteristics in relation to first-order removal for Lambley wetland

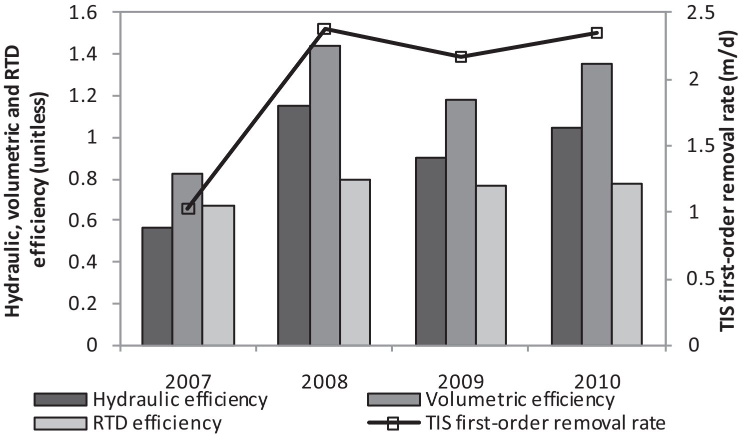


Figure 5.17(e) Hydraulic performance characteristics in relation to TIS first-order removal rate for Lambley wetland

The iron removal efficiency of the Lambley wetland was found to be in the range of 57.67-85.11% from 2007-2010 (see Table 5.6). The iron removal efficiency within the wetland was relatively low during early wetland operation in 2007. A year later significant iron removal was observed, and then it slightly decreased and increased over the next two years. This pattern clearly corresponds to the wetland hydraulic efficiency, most notably the changes in system volumetric efficiency. As discussed earlier, changes in volumetric efficiency largely influence the overall hydraulic efficiency of the wetland. This suggests that effective volume (and hence residence time) has had an important impact on iron removal processes.

In the first year of wetland operation (2007) the relatively shorter residence time (see Table 4.9 of Chapter 4) limited the retention of iron within the wetland, and hence there was only a small degree of treatment received. This was coupled with the immaturity of the wetland system during early colonisation with reeds, apparently limiting the efficiency of iron attenuation processes in the wetland. Notwithstanding this, from 2008-2010 (Figure 5.17a and Figure 5.17b), iron removal efficiency and load removal were found to consistently correspond to hydraulic efficiency as reeds have developed well. These maturely developed reeds may provide a relatively larger surface area for precipitation and adsorption of iron onto plant material, although this succession process depends on the hydrological characteristics of the wetlands, such as water depth, flow rate, water chemistry and seasonal variation (Fennessy et al., 1994; Goulet and Pick, 2001). The wetland vegetation also has an important role in maintaining efficient hydraulic performance i.e. better flow distribution across the system to encourage longer hydraulic residence time and provide a more effective volume to enhance the degree of iron attenuation, as discussed in section *4.4.4.2* of Chapter 4. The slight decrease in iron removal efficiency in 2009 corresponds with the decrease in hydraulic efficiency, possibly due to re-occurrence of flow short-circuiting effect (due to rapid movement of water through the densely-populated reeds, and in particular channelisation created by the dead vegetation within the mature reed colonies that had developed in the 3 years of wetland operation). This has significantly reduced the RTD and volumetric efficiency, and hence lower retention and decreased iron attenuation.

In addition to iron removal efficiency and load removal, it is common convention to report performance of mine water treatment wetlands in terms of area-adjusted removal rate (Younger et al., 2002), which is calculated by dividing iron load removed by the system (in units of g/d) by wetland area (m^2). Using this metric it can be seen that the area-adjusted removal rate increased between 2007 and 2008, whilst a slight reduction in the removal rate was seen in 2009 and 2010 (Figure 5.17c). During the second year of operation the wetland was in fact receiving relatively higher influent iron concentration. Note that in 2008, 2009 and 2010, the area-adjusted removal rates are consistent with the influent iron concentrations (even with minor changes in concentration). This may therefore be an indication of the first-order kinetics of iron attenuation, noted by Hedin et al. (1994) and Tarutis et al. (1999) among others i.e. higher oxidation and settlement rate occurs at higher initial iron concentration. A greater oxidation rate was seen with higher dissolved (ferrous) influent iron load (concentration multiplied by flow), whilst greater settlement rate was found to correspond with higher total particulate iron load. As shown in Figure 5.17d and Figure 5.17e, the metrics of first-order removal and TIS removal rate also consistently correspond to hydraulic performance. Additionally, the TIS removal rate also takes into account the flow pattern within the system in affecting iron removal performance. Thus, the results from this wetland satisfied the first-order kinetics model for iron attenuation i.e. greater iron removal was seen for higher influent iron concentration and longer hydraulic residence time, with the latter appearing to be controlled by the reeds' growth.

Table 5.6 Iron removal in Lambley wetland over the 4 years operation since site commissioning
Fe oxidised and Fe settled calculated after Hedin (2008)

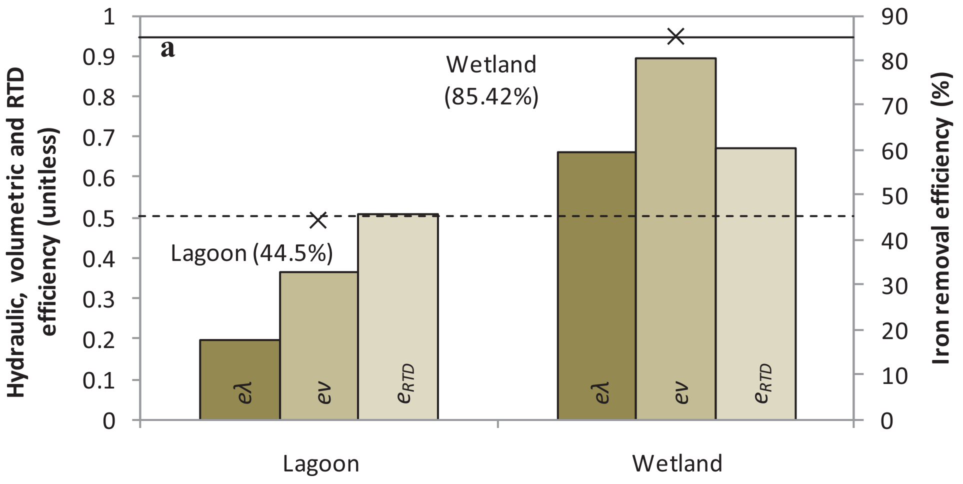
		Fe total (mg/L)	**Fe dissolved (mg/L)**	**Ferrous Fe (mg/L)**	**Fe particulate (mg/L)**	**Total particulate Fe (mg/L)**	**Fe oxidised ($g/m^2/d$)**	**Fe settled ($g/m^2/d$)**	**Influent Fe loading (kg/d)**	**Fe removal efficiency (%)**	**Fe load removal (%)**	**Area-adjusted removal ($g/m^2/d$)**	**First-order removal (m/d)**	**TIS removal rate (m/d)**
Lambley 2007	In	3.841	3.65	3.65	0.19	2.59	2.48	2.29	27.17	57.67	56.13	2.29	0.89	1.02
	Out	1.626	1.25	1.25	0.38									
Lambley 2008	In	6.810	5.85	5.14	0.96	5.99	5.17	5.96	47.92	85.11	85.07	5.96	1.96	2.38
	Out	1.014	0.82	0.11	0.19									
Lambley 2009	In	6.580	6.31	5.55	0.27	5.77	5.34	5.32	43.71	83.28	82.97	5.32	1.74	2.16
	Out	1.1	0.38	0.05	0.72									
Lambley 2010	In	6.070	5.90	4.78	0.17	4.88	4.69	5.14	41.38	85.01	85.45	5.14	1.89	2.35
	Out	0.91	0.49	0.07	0.42									

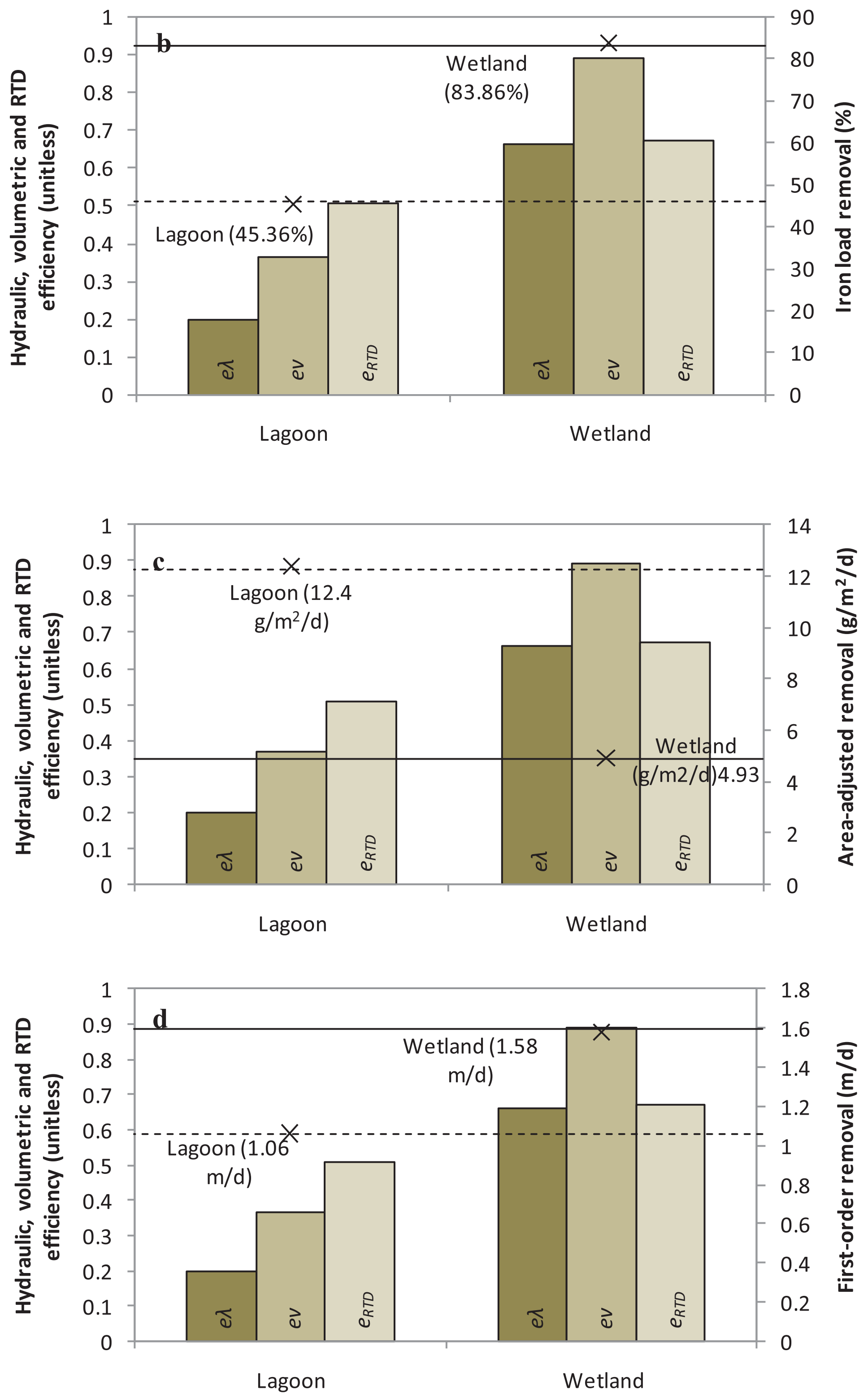
5.4.2 Hydraulic performance and iron removal in wetlands and lagoons

Within wetlands and lagoons varying in geometry, flow rates and influent iron characteristics, treatment performance in terms of iron removal (i.e. removal efficiency, area-adjusted removal, first-order removal and TIS removal) in relation to hydraulic performance metrics are illustrated in Figure 5.18. For the purpose of this comparison, mean values of each iron removal metric and hydraulic performance metric are used to illustrate the relationship in Figure 5.18. Generally, greater (mean) iron removal performance metrics (except for area-adjusted removal) correspond with greater hydraulic performance. Similarly, for lagoons, lower (mean) iron removal (except for area-adjusted removal) corresponds with lower hydraulic performance in the systems. Despite consistent patterns between iron removal (removal efficiency, load removal, first-order removal and TIS removal) and hydraulic performance metrics within both wetlands and lagoons (Figure 5.18a, Figure 5.18b, Figure 5.18d and Figure 5.18e), the area-adjusted removal indicates a contradictory results compared to other iron removal metrics (Figure 5.18c). This probably reflects the concentration-dependence for iron removal as discussed in section 5.3.

A greater volumetric efficiency (which largely reflects the hydraulic efficiency) in the wetland systems (compared to lagoons) may have an important influence on iron attenuation processes. The volumetric efficiency is a measure of relative mean residence time for comparing systems with different characteristics. Therefore greater volumetric efficiency is indicative of a longer residence time, and hence might be expected to result in greater removal of iron. This is occurring despite comparatively low influent iron concentrations which, according to a first-order kinetics model, might be expected to result in a lower rate of iron removal (*cf.* lower area-adjusted removal rate seen in wetlands in Figure 5.18c). The efficient iron removal in wetlands may also be associated with the wetland vegetation, which provides a greater capacity for physical filtration of precipitated iron and adsorption of iron onto plant material, but it is difficult to distinguish between the influence of reeds on hydraulics and influence in terms of iron removal. It has been reported that retention of iron in wetlands may be influenced by reeds colonisation i.e. whether vegetation have maturely colonised e.g. Fennesy et al. (2004), seasonal effects e.g. Goulet and Pick (2001), and the inlet concentration e.g. Wieder (1989) and Tarutis et al. (1999).

Despite higher oxidation and settlement rates in lagoons (as discussed in section 5.3), the systems appear to be less efficient in terms of their treatment efficiency, load removal, first-order removal and TIS removal rates with respect to iron compared to wetlands (Figure 5.18a, Figure 5.18b, Figure 5.18d and Figure 5.18e, respectively). This may in part be a consequence of the influences of hydraulic factors on treatment efficiency. In the lagoons there is evidence of a large degree of dispersion (i.e. greater D and hence lower e_{RTD} in Table 4.14) due to apparent short-circuiting effects compared to wetlands. The lagoon RTDs suggest rapid flow transmission across the system with a very short relative mean residence time i.e. considerably lower volumetric efficiency (Table 4.14). Consequently, lagoons have a lower effective volume for retention and treatment of iron, and hence the lower removal rates in such systems. This flow pattern effect has apparently limited the potential for greater removal of iron, which would otherwise appear to be possible given the high oxidation and settlement rates. Thus, evidence for the lagoon systems suggests that the flow pattern has a great influence on the iron removal processes, due principally to the largely ineffective volume in lagoons. This has significantly reduced the retention of iron and the degree of treatment received therefore lower removal efficiency. In addition, it is also recognised that pH may have a significant influence on the rates of iron removal in such systems. Specifically, the Fe(II) oxidation rates are much greater at higher pH. More details on this subject are provided in section *2.9.1.1* of Chapter 2. This issue has not been explored experimentally in this work, though it is recognised that the pH may have a significant overall influence on the rate of iron removal.




b
Hydraulic, volumetric and RTD efficiency (unitless)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Iron load removal (%)
90
80
70
60
50
40
30
20
10
0
Wetland (83.86%)
Lagoon (45.36%)
eλ
ev
eRTD
Lagoon
Wetland
c
Hydraulic, volumetric and RTD efficiency (unitless)
Area-adjusted removal (g/m²/d)
14
12
10
8
6
4
2
0
Lagoon (12.4 g/m²/d)
Wetland (g/m2/d)4.93
eλ
ev
eRTD
Lagoon
Wetland
d
Hydraulic, volumetric and RTD efficiency (unitless)
First-order removal (m/d)
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Wetland (1.58 m/d)
Lagoon (1.06 m/d)
eλ
ev
eRTD
Lagoon
Wetland

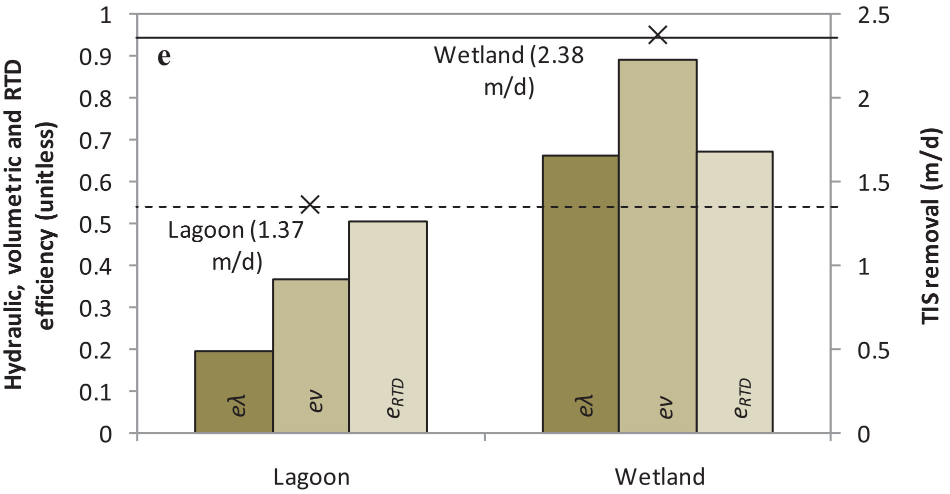
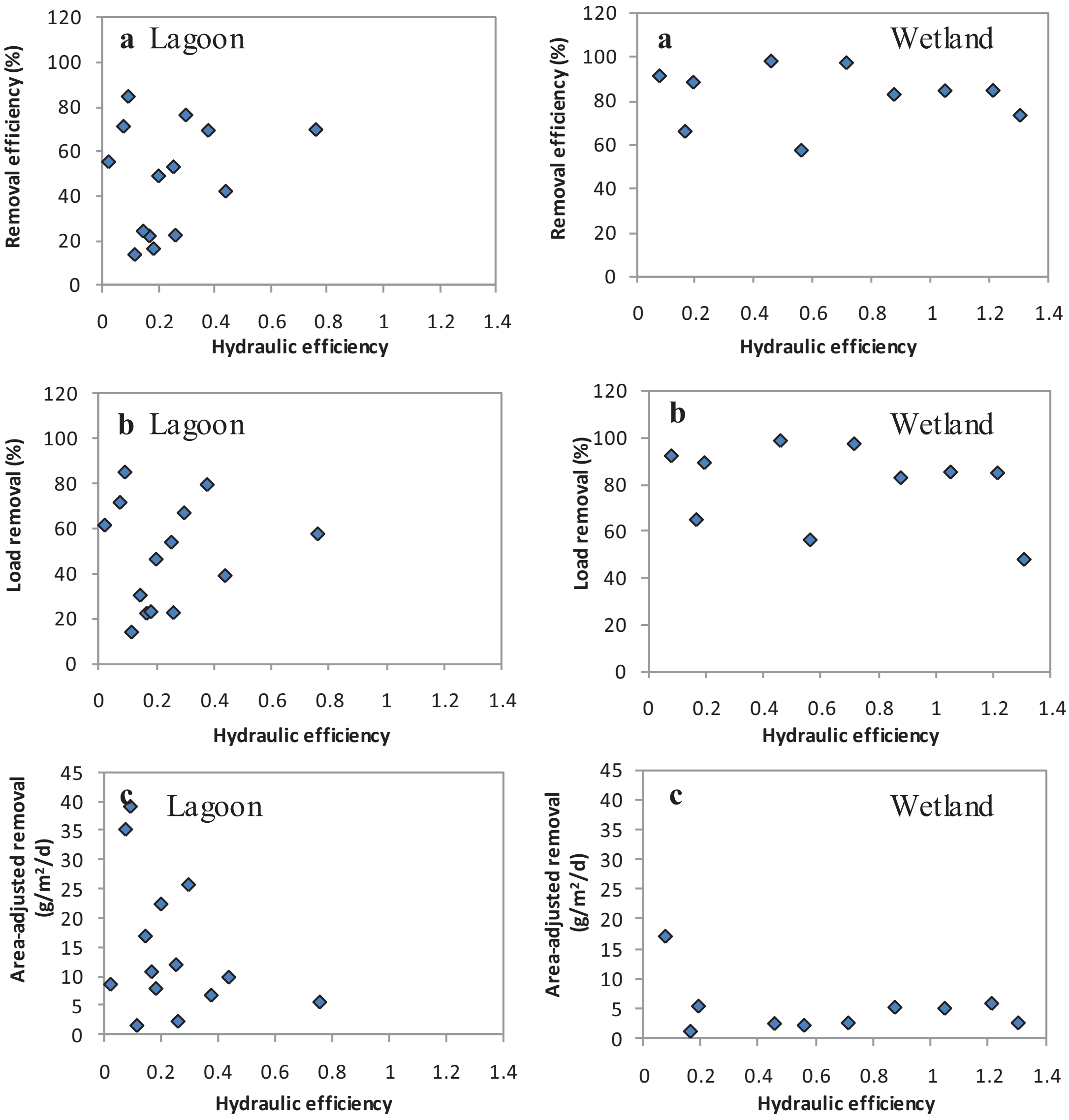


Figure 5.18 Iron removals in relation to hydraulic performance metrics for (a) iron removal efficiency (b) iron load removal (c) area-adjusted removal rate (d) first-order removal rate and (e) TIS removal rate. Mean values are used, *n* = 12 for lagoon and 10 for wetland

Additionally, illustration of iron removal performance and hydraulic efficiency for individual wetlands and lagoons are also shown (Figure 5.19). Note that when comparing the iron removal and hydraulic performance between individual lagoons and/or wetlands, there is no clear relationship found within these systems varying in design configurations and inflow characteristics (Figure 5.19). However, on average, wetlands are performing better than lagoons in terms of their iron removal and hydraulic performance compared to lagoons, as discussed earlier. This however, is not always the case for all wetland systems for instance, at Whittle and Allerdean Mill wetland cells, significantly low hydraulic efficiency was observed, whilst iron is greatly removed in the systems (see Appendix O). At Whittle, the low hydraulic efficiency was found to be due to apparent short-circuiting effects observed, possibly due to greatly dense wetland reeds, coupled with the presence of large ochre build up within the system, further enhancing the short-circuiting effects. The Whittle wetland receives greatly higher influent iron compared to other wetlands studied. At the Allerdean Mill wetland cell, the lower hydraulic efficiency observed was also associated with large extent of flow short-circuiting effect exiting the system through separate channels. This has been discussed in detail in section *4.3.2.2* of Chapter 4. In lagoons, although generally the systems appear to have lower iron removal and hydraulic efficiency compared to wetlands, there are exceptions to this trend. For instance, the Acomb lagoons have a rather high iron removal despite significantly low hydraulic efficiency (see Appendix O). This is because this treatment system is dosed with hydrogen peroxide to encourage ferrous iron oxidation of the initially high influent iron, and thus greater removal of iron as a consequence. Therefore, in light of these findings, it is again recognised that pH may also be a significant factor that influences such variations in iron removal between lagoons and wetlands (i.e. greater iron removal in wetlands (regardless of hydraulics) may be associated with higher pH in the systems).



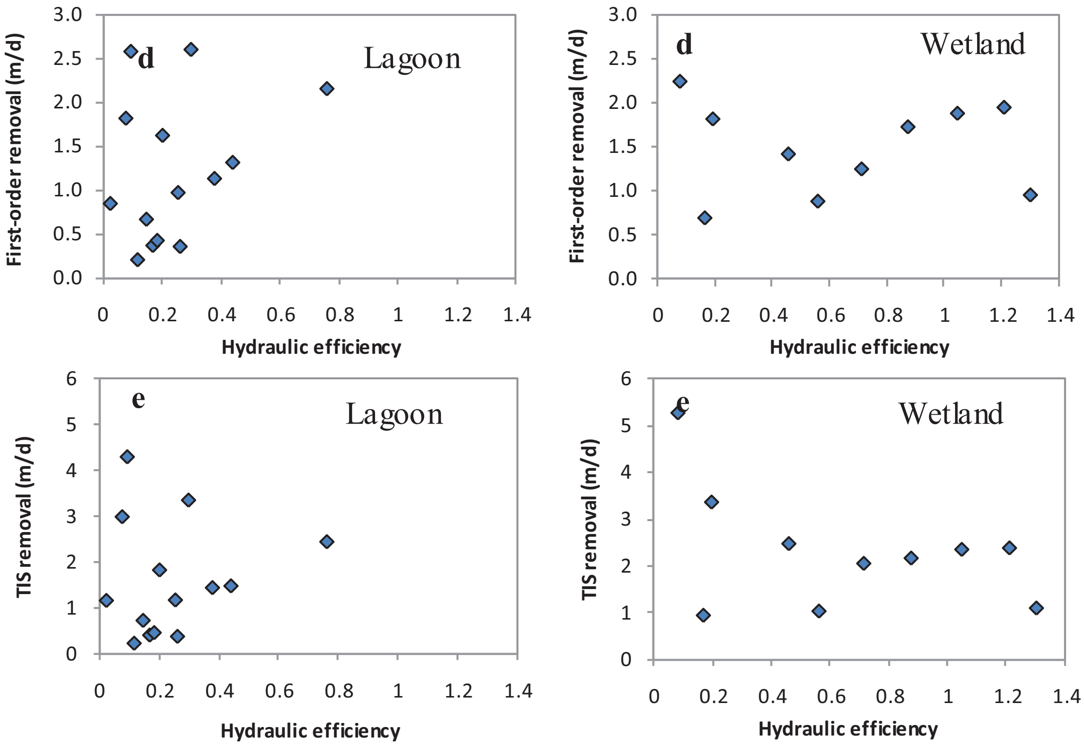


Figure 5.19 Scatter plots of iron removal metrics in relation to hydraulic efficiency for (a) iron removal efficiency (b) iron load removal (c) area-adjusted removal rate (d) first-order removal rate and (e) TIS removal rate

In essence, the results seem to suggest that the influence of hydraulics on the performance of mine water treatment systems is two-fold:

i. In terms of hydraulic performance, hydraulic efficiency is governed by the system effective volume, which ensures a better flow pattern across the system. This is reflected in a longer residence time relative to nominal residence time. In wetlands hydraulic efficiency appears to be greatly influenced by the vegetation distribution, although there are multiple factors interacting at the same time, such as system length-to-width ratio, flow and the age of the system (as shown by the partial correlations discussed in section *4.4.4.4* of Chapter 4). For lagoons, there is evidence that greater hydraulic efficiency is governed by greater length-to-width ratio and depth (as discussed in section *4.4.5.1* of Chapter 4).
ii. Hydraulic performance alone may not adequately explain the overall treatment efficiency. Treatment performance for iron removal appears to correspond to the hydraulic performance of the systems as discussed above, despite the geochemical control on the reaction rates for iron removal i.e. despite greater

dependence of iron removal rates on initial iron concentration, the absolute treatment efficiency is reflected by the hydraulic efficiency, as indicated by effective volume and retention time.

5.5 IMPLICATIONS FOR DESIGN AND MAINTENANCE OF MINE WATER TREATMENT SYSTEMS

5.5.1 Implications for design and sizing of lagoons and wetland

5.5.1.1 Lagoon systems

Table 5.7 shows the lagoon system area estimation and residence time using the different sizing formulae recommended by the PIRAMID Consortium (2003), compared to actual lagoon performance and the recommended design formula. Clearly there are substantial differences in system sizing using the different approaches, whereby the area-adjusted sizing formula gives a substantially larger lagoon area than either of the other design approaches. Measurements made in this work show that area-adjusted removal rates for iron are typically greater than the 10 g/m^2/d, suggesting that lagoons designed on this basis will have been over-sized. Additionally, for a system with high iron load, this approach gives an area which is impracticably large in most cases (PIRAMID Consortium, 2003). Therefore such approach is not likely to be favourable for the design of mine water treatment lagoons.

As discussed earlier, TIS first-order removal formula seems to be appropriate for design of mine water treatment systems. The TIS first-order removal formula gives a system area which is close to the nominal 48 hours retention time approach and the use of 100 m^2/L/s flow. Accordingly, the estimated residence times are close to one another between these approaches, compared to the area-adjusted removal formula. Therefore, the TIS first-order removal formula can be regarded as an alternative approach to the design of mine water treatment lagoons. Apparently, the actual residence times as measured from this study are greatly lower than any of these sizing formulae, suggesting poorer hydraulic performance of the lagoons. As noted earlier, the poor hydraulic performance in lagoon is attributable to a large ineffective volume in the systems, and hence shorter residence time. Current observation indicates a mean reduction of 63% lagoon effective volume, thus the considerably short residence time. This reduced effective volume however, varies greatly between systems from 25% up to 92% (refer to Table 4.12 of Chapter 4).

Irrespective of the design approaches, clearly residence time is an important design aspect for such systems. Currently, the low actual residence time in the lagoons seems to be an impediment to further improvements in treatment performance. Because effective volume is important for iron retention and attenuation in such systems, lagoon depth is also a critical design aspect that must be carefully considered. Similarly important for the design of lagoons is the system length and width, as it has been shown earlier that a larger length-to-width ratio may encourage a greater volumetric and hydraulic efficiency (see section *4.4.5.1* of Chapter 4). Therefore performance can be optimised by ensuring a greater volumetric efficiency (hence residence time) which can be achieved by providing a large length-to-width ratio system, but also a greater depth (i.e. maximum of 3.0 m), though only if systems are regularly maintained i.e. dredged.

5.5.1.2 Wetland system

The area-adjusted removal formula remains the most useful approach to the design of aerobic wetland systems for treatment of net-alkaline ferruginous mine waters (e.g. Younger et al., 2002). The evidence in this study suggests that lower area-adjusted removal rates in wetlands are likely the function of low initial iron concentration, which reflects the first-order kinetics of iron removal. Nevertheless, current wetland performance suggests generally good treatment efficiency, and good hydraulic performance, despite lower initial iron concentrations in the systems studied here. Comparison of the currently used design formulae and the recommended formula to the design of passive mine water treatment systems are presented in Table 5.8.

Apparently, the use of a first-order formula, by Tarutis et al. (1999) results in a substantially larger system design area. The use of this first-order design formula has received some criticism. For instance Younger et al. (2002) criticised use of the first-order formula on the grounds of the very large system area estimates derived when using the constant first-order removal rate suggested by Tarutis et al. (1999). Kadlec (2000) criticised the use of first-order expressions for the design of sewage treatment wetlands, reasoning that the plug-flow assumption does not apply for such systems, and that the contaminant removal processes differ between the fast- and slow-moving zones within the wetland. Goulet et al. (2001) found that the failure of a first-order removal model for a wetland treating agricultural and urban runoff was due to the seasonal variations that greatly affected the ideality of the flow. Thus, a TIS first-order removal model would be a better option for design, as it takes into account the flow pattern across the system in addition to the first-order assumption.

As shown in Table 5.8, the use of TIS first-order removal results in an area estimation which is by magnitude lower than first-order removal by Tarutis et al. (1999) but greater than the area-adjusted removal formula. The area from the TIS first-order removal formula is also close to the use of 100 m^2/L/s flow. However, whether the greater area resulting from using the recommended TIS first-order removal formula (compared to the commonly used area-adjusted removal formula), would enhance removal efficiency and hydraulic performance sufficiently to justify the increased system size (and therefore cost) is uncertain.

Therefore, on the evidence of the results in this study, the use of the area-adjusted removal formula appears to work well for wetlands such as those investigated here. This is supported by the high iron removal efficiency (mean of 85%) and efficient hydraulic performance of the systems (mean of 90% volumetric efficiency and 66% hydraulic efficiency), which is far better than lagoon treatment performance. Also noted from Table 5.8 is less variable residence times seen from the different approaches except for first-order removal criteria by Tarutis et al. (1999). The actual residence time measured in this study is also close to the estimated residence time from existing and recommended formula (except the first-order removal formula), suggesting that the wetland systems perform well in terms of their hydraulic performance as discussed earlier.

Importantly, there are very different results of the estimated design criteria using the different design formulae. The recommended TIS first-order removal formula does take account of the flow pattern effect on pollutant removal processes, in addition to the first-order (concentration-dependence) for iron removal. Both the TIS flow pattern and the concentration-dependent removal of iron have been shown to be appropriate for lagoons and wetlands studied. However, there is no evidence from actual systems to show whether such criteria (estimated treatment area and residence time) would enhance removal efficiency and hydraulic performance as stated earlier. Furthermore, use of the TIS first-order design formula requires reliable values of first-order removal rate constant and number of TIS, n, which was not possible to develop in this study. The first-order removal rate constant and n TIS used here are derived from only limited data from this study (i.e. median values of k_{TIS} and n found from this study). Therefore, such reliable values can only be derived if more data from tracer-tested sites are available to sufficiently justify the use of the TIS first-order removal formula in the design of passive mine water treatment systems. Nevertheless, the TIS model would only work if each system to be designed had the same number of tanks-in-series as a representation of its hydraulics (as well as the same pH, etc.). Whilst the TIS modelling approach appears to have worked well for the assessment of treatment systems in this study, it may not be possible to use it in the forward direction for design of treatment systems.

Table 5.7 Comparison of system area estimation (m^2) and the estimated residence time (d) for lagoon systems (existing performance, current design criteria and recommended design criteria)

A. Treatment area

Site	Design influent iron (mg/L)	Design flow (L/s)	Design depth (m)	Actual area (m^2)	This study TIS first-order basis[d]	Hedin et al. (1994) (10 $g/m^2/d$)	PIRAMID Consortium (2003) (48 hours retention)	PIRAMID Consortium (2003) (100 $m^2/L/s$ flow)
Acomb	40	15	3	750	1414	3240	864	1500
Allerdean Mill	28	10	2	883	1003	1555	1080	1000
Bates	60	76	3	2850	1554	5746	1094	1900
Strafford	20	20	2.5	850	1234	1728	1382	2000
Whittle	42	45	1.65	900	3010	8554	4712	4500
Mousewater	25	50	2.8	3036	4328	6480	3086	5000
Cuthill	30	45	1.55	1452	4907	7776	5017	4500

Area estimated for removing 50-80% of initial iron

[d] Required area using $k_{TIS} = 1.16$ m/d and $n = 2$, assuming 80% removal of iron from lagoon

B. Residence time

	Existing performance under current design		This study	Estimated residence time based on existing design criteria		
Site	Nominal residence time[a] (day)	Actual residence time[b] (day)	TIS first-order basis[d]	Hedin et al. (1994) (10 $g/m^2/d$)	PIRAMID Consortium (2003) (Nominal 48 hours retention)	PIRAMID Consortium (2003) (100 $m^2/L/s$ flow)
Acomb	2	0.56	3.27	7.5	2	1.91
Allerdean Mill	1.55	0.95	1.86	2.88	2	2.31
Bates	0.92	0.49	0.71	2.63	2	0.87
Strafford	1.43	0.89	1.78	2.50	2	2.89
Whittle	0.64	0.23	1.27	3.63	2	1.91
Mousewater	2.29	0.21	2.81	4.20	2	3.24
Cuthill	1.19	0.62	1.96	3.10	2	1.79

[a] Nominal residence time under current system design

[b] Actual residence time from tracer test (mean data)

Table 5.8 Comparison of system area estimation (m^2) and the estimated residence time (d) for wetland systems (existing performance, existing design criteria and recommended design criteria)

A. Treatment area

Site	Design influent iron (mg/L)	Flow design (L/s)	Actual area (m^2)	This study TIS first-order basis[a]	Hedin et al. (1994) (10 g/m^2/d)	Tarutis et al. (1999) (0.18 m/d)	PIRAMID Consortium (2003) (100 m^2/L/s flow)
Lambley	6	88	6845	7282	3802	75684	8800
Allerdean Mill	15	10	1066	1418	1210	12999	1000
Strafford	10	20	1690	2279	1555	22105	2000
Whittle	20	45	7200	7346	7387	64708	4500
Mousewater	10	50	8400	5699	3888	55262	5000
Cuthill	8	45	2744	4493	2722	44916	4500

[a] Required area using $k_{TIS} = 2.36$ m/d and $n = 4$, and target effluent Fe = 1 mg/L

B. Residence time

	Existing performance under current design		This study	Estimated residence time based on existing design criteria		
Site	Nominal residence time[a] (day)	Actual residence time[b] (day)	TIS first-order basis[c]	Hedin et al. (1994)[c] (10 g/m^2/d)	Tarutis et al. (1999)[c] (0.18 m/d)	Piramid Consortium (2003)[c] (100 m^2/L/s flow)
Lambley	0.32	0.38	0.29	0.15	2.99	0.35
Allerdean Mill	0.32	0.11	0.49	0.42	4.51	0.35
Strafford	0.23	0.36	0.40	0.27	3.83	0.35
Whittle	0.24	0.08	0.57	0.57	4.99	0.35
Mousewater	0.74	0.70	0.40	0.27	3.84	0.35
Cuthill	0.77	0.47	0.35	0.21	3.47	0.35

[a] Nominal residence time under current system design

[b] Actual residence time from tracer test (mean data)

[c] Required residence time assuming 0.3m wetland depth

5.5.2 Implications for system maintenance

The Coal Authority typically employs settlement lagoons as the preliminary treatment unit for removing 50-80% iron if properly sized and maintained. Current observations of 8 treatment sites show that settlement lagoons are only in fact currently removing a mean of 44.5% iron from these systems. As found in this study, performance of such systems is governed by both hydraulic and geochemical factors. A lower system hydraulic efficiency in lagoons is seen as an important metric to describe the hydraulic performance of lagoons. Poor hydraulic efficiency is typically due to low effective volume available for iron attenuation processes. Low effective volume is reflected in a lower relative mean residence time for a given volume and flow. Therefore, this suggests the need for regular ochre sludge removal from the lagoons to increase the lagoon effective volume and to retain a longer residence time for effective removal of iron. On the evidence of this study, sludge removal from a system may increase hydraulic efficiency by 53 – 82%, and lengthen residence time by up to 92% e.g. at Acomb lagoon where the second monitoring was conducted approximately 6 months after the sludge was removed from the system.

Measurements made here also show that lagoons have a significantly lower actual residence time than the nominal residence time, which is the basis on which they are often designed. Again, this points to a need of greater effective volume to improve the residence time in the system. A likely reason for the very short hydraulic residence time in lagoons is the apparent short-circuiting effect, which is typically associated with a reduced depth due to build up of ochre and debris. At the Allerdean Mill system, for example, a reduction of 39% effective volume was seen after just 18 months of operation, despite a rather low influent iron load (iron concentration of 10 mg/L and flow rate of 9 L/s). Thus, effective volume is reduced at a rate of approximately 2.2% per month. Therefore, a recommendation from this is that yearly sludge removal would be needed due to rapid lagoon depth reduction.

Another example is the Strafford lagoon, where 49% effective water depth (and hence volume) was lost in less than a year (approximately 8 months). The lagoon receives a low influent iron load; 6.6 mg/L iron and 14 L/s flow, and only removed 23% of iron during the monitoring conducted in this study. Thus, approximately 6.1% effective depth is reduced per month. Such a rapid effective depth reduction during early operation will clearly become worse if ochre sludge is not regularly removed. Therefore regular sludge removal (yearly) is highly important if efficient performance is to be maintained, because lagoon volume tends to decrease over time due to build up of ochre and debris. Overall, of the 8 treatment schemes investigated, on average the lagoons removed between 666-33000 g/year of iron and a depth reduction of approximately 7 – 49% per year was observed.

Most of the wetlands investigated serve as secondary treatment unit(s) following settlement lagoon(s). Pre-treatment with settlement lagoons is preferred as a way of minimising rapid accumulation of ochre in Coal Authority wetlands. Therefore these systems typically receive a low influent iron and act as polishing facilities for final iron removal prior to discharging into receiving streams. In contrast to the lagoon systems, the wetlands indicate a better performance both in terms of hydraulic efficiency and iron removal efficiency. Evidence from this study shows that they remove a high percentage of the influent iron, even where initial iron concentration is comparatively low (which, according to first-order iron removal kinetics, might result in less effective treatment).

It appears that the role of vegetation is important in ensuring a more distributed flow across wetland systems, and that vegetation may also result in deviations from an ideal flow pattern. Vegetation may assist in effective removal of precipitated iron through the physical filtering by plant stems and adsorption onto living or dead plant material. Conversely, accumulation of dead plant material may result in channelisation, and hence a rapid transit of flow, shortening the residence time. From this study, it appears that reed growth from initial colonisation through the second year of wetland operation is important in ensuring an efficient flow distribution and the development of effective iron attenuation processes. The maturity of the vegetation in the second year of operation, which is before reed cover becomes too dense, appears to be the period of optimum hydraulic performance. After this period, a return of short-circuiting and channelisation is possible, decreasing the efficiency of performance over time if the system is not regularly maintained. Despite the complex role of vegetation in wetlands, maintenance of such systems is important, and includes such matters as thinning of reeds whenever apparent channelisation might lead to short-circuiting and a reduction in the capacity for adsorption and settlement of precipitated iron hydroxide. Of the treatment systems investigated, on average the wetlands removed 0.5-15 kg/year of iron, which corresponds to 0.16-0.9% of effective depth reduction per year. In contrast to lagoons, this reduction in depth may be largely associated with dead vegetation and debris rather than ochre build-ups.

5.5.3 Managing abandoned coal mines in a broader context

The majority of the passive treatment systems in the UK typically comprise aeration, settlement lagoons and aerobic wetlands which have proved to work well with the net-alkaline, ferruginous mine waters (Jarvis and Rees, 2005; Johnston et al., 2007). In managing 44 treatment schemes the Coal Authority is responsible for more than 140,000 m^3 per day of mine water being discharged to the surface waters. From these treatment schemes over 1200 tonnes of iron are removed per day which would otherwise enter the environment (Johnston et al., 2007). Retention of such amounts of iron hydroxides (ochreous sludge) particularly in settlement lagoons is of issue when the treatment systems have reached their design capacity. Sludge removal is without doubt the most important long-term maintenance issue for passive treatment systems (PIRAMID Consortium, 2003). Removal of the ocherous sludge may involve large long-term maintenance cost i.e. manpower, equipments and even the costs of disposal to landfill. Construction of sludge drying beds is a common practice in the UK for sludge dewatering prior to disposal (examples in Figure 5.20).

Figure 5.20 Pictures show examples of sludge drying bed at (a) Acomb (b) Whittle treatment scheme

5.6 CHAPTER SUMMARY

Following the earlier discussions, comparisons between iron oxidation and settlement rates within lagoon systems can be summarised as follows:

Iron removal

- A large amount of iron is removed from the lagoons, between 666-33000 g/year. However, iron removal efficiency is significantly lower than in wetlands
- The area-adjusted removal rate in the lagoons studied indicates a removal rate that is greater than the 10 $g/m^2/d$ sometimes used for design purposes, suggesting that the rate of iron removal may approximate first-order kinetics for iron removal in such systems
- In lagoon systems the removal processes are primarily controlled by ferrous iron oxidation, whilst in wetlands the removal is controlled by iron settlement
- The time-dependence of iron removal in both lagoons and wetlands was investigated via laboratory column tests; oxidation and settlement rates of iron are clearly time-dependent, with faster rates evident in lagoons compared to wetlands
- At the influent to lagoons iron oxidation rates are higher than settlement rates due to the presence of a generally greater proportion of dissolved ferrous iron for oxidation. At lagoon effluents iron settlement rates become higher than oxidation rates, since a greater proportion of the remaining iron present is in the particulate form. Despite settlement rate dominance, in Acomb lagoon for instance, iron oxidation is still evident at the effluent point, suggesting that additional capacity is required for oxidation of ferrous iron if overall performance is to be improved.
- In wetlands, irrespective of wetland influent or effluent, settlement appears to be the dominant process for iron removal. This is because a large portion of ferrous iron has already been oxidised in settlement lagoon(s) prior to wetland treatment, thus most iron is initially present as particulate ferric hydroxide, while ferrous iron concentration is low. There is an exception to this trend i.e. Lambley wetland, which is constructed without pre-treatment in settlement lagoon, receives an influent iron which is largely in the dissolved

form and therefore greater oxidation than settlement rates at the system influent.

Relationship between hydraulic and geochemical factors in mine water treatment lagoons and wetlands

- In the Lambley wetland, performance over 4 years since commissioning indicates a very close relationship between hydraulic performance and treatment performance metrics. While the effects of varying system geometry and flow rates could not be accounted for in the system (since they were constant), the effect of vegetation seems to be of great importance for ensuring a good flow distribution across the system, and this has consequential impacts on iron attenuation processes. It is nevertheless difficult to distinguish between vegetation effects and the influence of seasonality.
- General trends (i.e. mean data for all wetlands compared to mean data for all lagoons) showed that efficient treatment performance for iron removal corresponds with greater system hydraulic efficiency in wetlands compared to lagoon systems. The greater hydraulic efficiency in wetlands was mainly attributed to a greater volumetric efficiency in the wetland systems, thus provided a longer relative mean residence time for retention and attenuation of iron. This is occurring despite comparatively low influent iron concentrations which, according to a first-order kinetics model, might be expected to result in a lower rate of iron removal. In contrast, shorter relative mean residence time was found in lagoons, thus a lower retention time for iron attenuation and lower removal efficiency as a consequence.

Implications for design and maintenance of mine water treatment systems

- For lagoons, residence time is an important aspect of the design of such systems. The low actual residence time in the lagoons seems to be an impediment to further improvements in treatment performance. Therefore performance can be optimised by ensuring a greater volumetric efficiency (hence residence time). This can be achieved by providing a large length-to-width ratio system, but also a greater depth (i.e. maximum of 3.0 m), though only if systems are regularly maintained i.e. dredged.

- On the evidence of the results in this study, for wetlands, the use of the area-adjusted removal rate formula appears to work well for the design of aerobic wetlands, despite the observed concentration-dependence of iron removal processes. This is based on the efficient hydraulic performance and treatment efficiency of the systems which is far better than lagoon systems. Note that the area-adjusted removal rate is based on zero-order kinetics whereas first-order kinetics appears to describe removal rate more accurately.
- First-order removal formula (TIS basis) would appear to be a more appropriate approach to the design of mine water treatment systems since it takes account of the flow pattern effect on pollutant removal processes, in addition to the first-order kinetics (concentration-dependence) for iron removal. From the systems studied, it has been shown that it is appropriate to take account of both the effect of flow pattern and first-order kinetics in the design of wetlands and lagoons. However, there is no evidence from actual systems to show whether such criteria (residence time and treatment area) estimated from this approach would enhance removal efficiency and hydraulic performance. Furthermore, use of this design formula requires reliable values of first-order removal rate constant and number of TIS. It was not possible to develop these reliable values from limited data in this study and within the timeframe of this study.
- Rapid depth reduction (7-49% effective depth reduction per year), particularly in lagoons, necessitates regular sludge removal (yearly) if efficient performance is to be maintained, because lagoon depth and volume appear to rapidly decrease over time due to the build up of ochre and debris. Thinning of reeds is recommended whenever apparent channelisation might lead to short-circuiting and a reduction in the capacity for adsorption and settlement of precipitated iron hydroxide.
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CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 INTRODUCTION

This chapter summarises the major findings of this thesis, and provides details of how the research aim and objectives have been met. Recommendations for how the outcomes may be applied to the design of treatment systems are made, and possible future research directions are discussed.

The overall aim of this study was to assess the hydraulic and geochemical factors that govern pollutant behaviour in passive systems for the treatment of net-alkaline, ferruginous mine waters. Such a study was undertaken to improve understanding of how these hydraulic and geochemical factors impact on the overall treatment performance, and thus may assist in optimising treatment efficiency (for both existing and future operations). The main contribution of this thesis is through the assessment of actual residence times within passive mine water treatment system, an assessment of which has not previously been explored for UK passive treatment systems. The UK is currently well advanced in the development of passive treatment systems for mine waters, with more full scale systems in place than in any other European country, and therefore the UK is an ideal location for such a study. A series of tracer tests have been undertaken at eight mine water treatment sites operated by the UK Coal Authority (at 6 wetland systems and at 7 lagoon systems) in the northern England and southern Scotland. Lambley wetland (Northumberland) was monitored on 4 successive years to evaluate temporal changes, Whittle wetland (Northumberland) was monitored twice, and other wetland systems were monitored on a one-off basis to make comparison between systems. For lagoons, Acomb and Whittle treatment systems (both Northumberland) were monitored twice. Simultaneous monitoring of mine water quality and iron removal during each tracer test was undertaken to assess the link between hydraulic and geochemical factors on overall treatment system performance. To explore the overall aim in detail 4 specific objectives were pursued, the fulfilment of which are discussed in detail in the following section.

6.2 FULFILMENT OF RESEARCH OBJECTIVES

6.2.1 Assessment of the most appropriate tracer to use and modelling approach for characterising treatment systems' hydraulic performance

During the early stage of this study, the use of the most appropriate tracer was assessed from several potential tracers; sodium bromide, Na-fluorescein and NaCl. This is important because the use of appropriate tracer will precisely determine the hydraulic flow characteristics of the systems studied, and in the fulfilment of the Objective (ii). In order to assess the hydraulic characteristics of the mine water treatment systems, a modelling approach was adopted (using a tank-in-series (TIS) model). This was applied to all the observed tracer test data for lagoons and wetlands, and for the different tracers used. The key findings are as follows:

- The trial tracer test employing different potential tracers at Lambley wetland indicated essentially identical results, but the selection of tracer appears to be best made based on site-specific considerations.
- The TIS modelling approach has been successfully applied to charaterise the flow pattern, an approach which has not been adopted in UK passive mine water treatment systems. Delayed TIS from least squares method yielded the best fit to actual RTDs, since it took account of the delay in tracer detection and gave realistic values of *n* and degree of dispersion. This modelling approach served as the basis for computing the system hydraulic efficiency. Further details are presented in section 4.4 of Chapter 4.

6.2.2 Assessment of the hydraulic performance of treatment systems and factors influencing the hydraulic performance

This objective was achieved by means of conducting tracer tests to experimentally determine the actual residence time within the treatment systems investigated, and in line with the Objective (i). The relative importance of residence time for measuring hydraulic performance of passive / semi passive treatment systems has been discussed in many studies (e.g. Kadlec, 1996; Thackston et al., 1988; Martinez and Wise, 2003; Persson et al., 1999; Goulet et al., 2001), but has not been widely investigated in UK mine water treatment systems. Therefore in light of the potential importance of hydraulic performance to overall system performance, tracer tests were conducted at six wetlands and at seven settlement lagoons. Key findings from this assessment of the hydraulic performance of UK mine water treatment systems are as follows:

- Variation in flow pattern has a significant impact on the residence time distribution across the systems. This was determined by modelling the flow movement within the systems using the TIS model. The tracer flow modelling approach showed that both lagoons and wetlands were greatly dispersed from an ideal plug-flow pattern. This effect was more pronounced in lagoons. Lagoons had dispersion in the range of 0.17-0.97, whereas wetlands had dispersion in the range 0.10-0.58. These correspond (as an inverse relationship) with n in the range 1.4-2.95 in lagoons and between 1.65-5.4 in wetlands. Accordingly, lagoons had hydraulic efficiency in the range 0.02-0.44, whilst in wetlands hydraulic efficiency ranged between 0.08-1.31. Therefore wetlands are more hydraulically efficient than lagoons. Further details and discussion are presented in sections 4.4.4, 4.4.5 and 4.4.6 of Chapter 4.
- Physical influences such as vegetation, seasonal variation, system geometry (i.e. length-to-width ratio and depth), flow rate, and age of system appear to have an influence on the hydraulic performance of the systems. This was assessed via partial correlation analysis, which allow for the independent assessment of the influence of one variable in light of the variation in other influential factors on hydraulic performance. Vegetation appears to be a key influence in wetlands' hydraulic performance, although there are multiple factors interacting at the same time. It should be noted that this vegetation effect on hydraulic performance is qualitative, and was assessed only through observations of the treatment systems studied. There was difficulty in distinguishing between vegetation effects and the effect of seasonal variation at Lambley wetland because the system was monitored during different seasons. Also, there was difficulty in establishing cause and effect relationships between the possible influences and hydraulic performance because some of these influences are constant engineered design aspects of the systems (i.e. design configuration). In lagoons, greater L/W and depth appear to have a significant influence on the greater lagoon hydraulic efficiency. Further details and discussion are presented in sections *4.4.4.4* and *4.4.5.1* of Chapter 4.

6.2.3 Assessment of the geochemical factors that influence treatment performance

In the absence of acidity (as is the case for the treatment systems investigated here) the most important contaminant in mine waters is iron, which is typically present at the point of discharge as ferrous iron. Therefore the objective here was achieved by evaluation of the rates of the key mechanisms that govern the removal of iron in the treatment systems. The issue was investigated in the field (section 5.3.2) and via laboratory experiments (section 5.3.3 of Chapter 5). Iron concentration (ferrous, ferric and total concentration) was measured at the influent and effluent points of treatment systems during the tracer tests. Findings from this assessment are as follows:

- Assessment of the controlling mechanisms (in the field) that govern iron removal in the mine water treatment systems indicated that oxidation and settlement rate was dependent on the available ferrous iron and total particulate iron, respectively. It was shown that in the lagoon systems studied, the removal processes were primarily controlled by the rate of ferrous iron oxidation, whilst in wetlands iron removal is controlled principally by the rate of iron settlement. Greater iron removal efficiency was found in wetlands compared to lagoons. This is occurring despite the lower initial concentration of iron in wetlands which, according to a first-order kinetics model (concentration-dependent removal, as shown from the field data and laboratory tests), might be expected to result in lower rates of removal. This good iron removal rate might be due to the greater hydraulic efficiency observed in the wetlands.
- The rates of iron oxidation and settlement are clearly dependent on time. This was shown via laboratory column tests to investigate the time- and concentration-dependent removal of iron under elevated pH and oxic conditions, such as those observed in the field. Reaction rates are faster in lagoons, and this appears to be due to the greater available initial iron concentration in lagoons, further strengthening the first-order kinetics removal model. However, field data indicated iron removal efficiency in lagoons which was comparatively lower than in wetlands. This was in part due to the influence of hydraulics (relatively shorter residence time) on iron attenuation processes in lagoons.

6.2.4 Evaluation of the links between hydraulic and geochemical factors governing treatment system performance

The coupled importance of hydraulic and geochemical factors on the treatment system performance was investigated by assessing the relationships between treatment performance for iron removal (section 5.3.1 of Chapter 5) and the hydraulic performance of the systems (section 4.4.6 of Chapter 4). The key findings are as follows:

- Performance of a wetland over 4 years of operation since commissioning revealed a very close relationship between iron removal and hydraulic characteristics and performance metrics. However, the individual effects of varying system geometry (i.e. length-to-width ratio and depth) and flow rates could not be accounted for. Vegetation appears to be a key factor in controlling the hydraulic performance (although seasonal effect and pH cannot be ruled out), but this vegetation effect was assessed only through observations of the system over the monitoring period.
- General trends (i.e. mean data for all wetlands compared to mean data for all lagoons) showed that efficient treatment performance for iron removal corresponds with greater system hydraulic efficiency in wetlands compared to lagoon systems. The greater hydraulic efficiency in wetlands was mainly attributed to a greater volumetric efficiency in the wetland systems, which thus results in a longer relative mean residence time for retention and attenuation of iron. This is occurring despite the lower initial iron concentration as stated above. In contrast, shorter relative mean residence time was found in lagoons, and thus a lower retention time for iron attenuation and lower removal efficiency as a consequence. Discussion on this is presented in section 5.4 of Chapter 5.
- However, comparing the geochemical and hydraulic performance between individual lagoons or/and wetlands revealed no clear relationships, within these systems of varying design configurations and inflow characteristics.

6.2.5 Implications of findings for the design and maintenance of mine water treatment systems

Implications of the findings of this study for the design and maintenance of mine water treatment systems were evaluated based on the hydraulic performance and treatment efficiency evidenced at the systems studied. This includes the implications for optimising design of such systems in the future, and for maintenance of efficient performance in existing systems (discussed in section 5.5 of Chapter 5). These are summarised as follows:

- For lagoons, residence time is an important variable for the design of such systems. Current observations showed that low actual residence time in the lagoons seems to be an impediment to further improvements in treatment performance. Therefore performance can be optimised by ensuring a greater volumetric efficiency (hence residence time). This appears to be achievable by providing a large length-to-width ratio system (up to a ratio of 4.7), but also a greater depth (i.e. maximum of 3.0 m), though only if systems are regularly maintained i.e. dredged.
- For wetlands, the use of the area-adjusted removal rate formula appears to work well for the design of aerobic wetlands, despite the observed concentration-dependence of iron removal processes i.e. the area-adjusted removal rate is based on zero-order kinetics whereas first-order kinetics appears to describe removal rate more accurately. This was observed from the efficient hydraulic performance and treatment efficiency of the wetland systems (compared to lagoon systems).
- Nevertheless, first-order removal formula (TIS basis) would appear to be a more appropriate approach to the design of mine water treatment systems since it takes account of the flow pattern effect on pollutant removal processes, in addition to the first-order kinetics (concentration-dependence) of iron removal. For the systems studied, it has been showed that it is appropriate to take account of both the flow pattern effect and first-order kinetics in designing lagoons and wetlands. However, there is no evidence from actual systems to show whether such criteria (residence time and treatment area) estimated from a TIS first-order approach would enhance removal efficiency and hydraulic performance. Furthermore, use of this design formula requires reliable values for the first-order removal rate constant and number of TIS. It was not possible

to derive such reliable values from the limited data from this study. Further research is required to address this issue in the future.

- Regular sludge removal, particularly from lagoons, is very important because of rapid depth reduction due to build up of ochre and debris (7-49% effective depth reduction per year). Such ochre accumulation significantly reduces the effective volume of the systems (which is especially pronounced in lagoons), whereby apparent streaming effects result in very short residence times in the systems, and hence reduce the time available for pollutant attenuation.
- In wetlands, thinning of reeds is also important to maintain effective flow movement so as to prevent short-circuiting effects, although at the same time the presence of reeds appears to provide significant potential for physical filtering of precipitated iron hydroxide and adsorption onto living and dead plant material. Thus, thinning of reeds is recommended whenever apparent channelisation would otherwise dominate the flow pattern, and therefore limits the capacity for adsorption and settlement of precipitated iron hydroxide.

6.3 RECOMMENDATIONS FOR FUTURE WORK

This study has successfully characterised the mine water treatment systems studied in terms of their hydraulic performance. This has been linked to the geochemical processes that govern pollutant removal in the systems, assessment of which has been shown to be central in the performance assessment of passive mine water treatment systems. Several issues relating to this thesis work and recommendations for future work are as follows:

- Monitoring hydraulic performance (actual residence time) in mine water treatment systems has indicated its significance to the overall hydraulic performance of such systems. Such monitoring should continue alongside treatment performance monitoring, because hydraulic and geochemical factors are both important in the overall performance assessment of mine water treatment systems.
- This study has shown that the hydraulic performance of a wetland system (i.e. Lambley wetland) appears to vary year-on-year, and between seasons, which is a rare insight into temporal changes in hydraulic performance. Vegetation appears to be a key influence, but there was difficulty in distinguishing

between vegetation and seasonal effects in terms of their role in governing overall hydraulic efficiency. A recommendation for this in the future is to conduct such year-to-year measurements in the same season each year. This would require frequent tracer tests in each season, at the same treatment system, over several years of its operation. Such an investigation was not feasible during the timeframe of this study.

- In the Lambley wetland, significant improvement of the hydraulic performance was seen during the second year of the wetland operation, whilst performance slightly decreased by the third year, and slightly improved during the fourth year of wetland operation. Whether this trend will continue is uncertain, and can be confirmed by further monitoring in future years. Monitoring other systems from commissioning would be useful to ascertain whether the pattern of hydraulic trends observed at the Lambley wetland are similar in other wetlands. Equivalent year-on-year hydraulic monitoring is also needed for lagoon systems, because hydraulic efficiency in lagoons appears to rapidly deteriorate after commissioning.
- There was difficulty in establishing cause and effect relationships between the possible influences on hydraulic performance using data available from this study. Additionally, some of these influences are constant engineered design aspects (i.e. design configuration). Varying the effect of design configuration might be possible via a simulation study, for instance, but in actual systems such effects are difficult to determine.
- General trends showed that efficient hydraulic performance in wetlands corresponded with efficient iron removal performance compared to lagoons (i.e. mean data for all wetlands compared to mean data for all lagoons). In the future, it may be possible to develop a better relationship that links the hydraulic and treatment performance for lagoons and wetlands, but this would require a large amount of data from tracer-tested treatment systems.

Recommendations for design and maintenance of current and future systems:

- Hydraulic assessment has shown that significant ineffective volume affected the overall hydraulic efficiency in lagoon systems. This has significantly reduced the available volume and hence time for iron attenuation. Regular sludge removal (yearly) is highly recommended if efficient hydraulic performance is to be maintained, because lagoon depth and volume appeared to rapidly decrease over time due to accumulation of ochre and debris. Similarly, thinning of reeds in wetlands is recommended when dense vegetation would otherwise lead to channelisation that influences the flow pattern, and reduces the capacity for adsorption and settlement of precipitated iron hydroxide. Monitoring hydraulic and treatment performance following the maintenance works is important to assess the degree of improvement for long-term operation.

- According to first-order kinetics for iron removal (which has been shown to be appropriate for the treatment systems studied), longer residence time would result in greater removal of iron. As shown in this study, it appears that a greater volumetric efficiency (and hence residence time) can be achieved by providing a greater length-to-width ratio system (up to a ratio of 4.7) and also a greater depth (up to 3.0 m).
- Because it has been shown in the field and in the laboratory that iron removal processes follow a first-order removal model, a first-order removal formula appears to be more appropriate to represent this concentration-dependent removal of iron. A TIS first-order removal design approach is recommended as it takes account of the flow pattern effect in addition to concentration-dependent removal of iron. When adopting this design formula, reliable values of first-order removal rate constant and number of TIS, n are needed. This requires a large amount of data from tracer-tested systems in the future to develop such reliable values, which has not been feasible within the timeframe of this study.
- Even when reliable values for the first-order design formula are available, performance monitoring and assessment in actual systems would be useful. This will confirm whether the design criteria from the design formula (estimated treatment area and residence time) would enhance hydraulic and treatment efficiency.

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APPENDICES

APPENDIX A

List of publications/disseminations

- F. M. Kusin, Adam P. Jarvis and Catherine J. Gandy (2010) Hydraulic residence time and iron removal in a wetland receiving ferruginous mine water over a 4 year period from commissioning. *Water Science and Technology*. 62(8), 1937-1946.
- F. M. Kusin, A. P. Jarvis and C. J. Gandy (2010) Effects of residence time on hydraulic performance and iron removal in wetlands and lagoons for remediation of coal mine waters. *Proceedings of the 12th IWA International Conference on Wetland Systems for Water Pollution Control,* 4-7 Oct, 2010, Venice, Italy.
- F. M. Kusin and A. P. Jarvis (2010) Residence time distribution for determination of hydraulic performance of a wetland receiving ferruginous mine water over a 3 year period from commissioning. *Proceedings of the 9th IWA International Conference on Sustainable Solutions for Small Water and Wastewater Treatment Systems (S2Small2010)*, 19-22 April, 2010, Girona, Spain.
- Faradiella M. Kusin, Adam P. Jarvis and Catherine J. Gandy (2010) Hydraulic performances of wetlands and settlement lagoons for remediation of mine-impacted waters. *Proceedings of the UK-Malaysia-Ireland Science Engineering Conference (UMIES)*, 23-25 June, 2010, Belfast, Northern Ireland.
- Faradiella M. Kusin, Adam P. Jarvis and Catherine J. Gandy (2010) Hydraulic performances of wetlands and settlement lagoons receiving ferruginous coal mine waters. *PGR Conference*, 24 June, 2010, School of Civil Engineering and Geosciences, Newcastle University, UK.
- Tobias Roetting, Faradiella Mohd Kusin and Adam Jarvis (2009) *Behaviour of iron in saline waters.* Report to the UK Coal Authority Ref KH091418, December 2009.
- Faradiella M. Kusin, Natalie Kruse, William M. Mayes and Adam P. Jarvis (2009) A comparative study of hydraulic residence time using a multi-tracer approach at a coal mine water treatment wetland, Lambley, Northumberland, UK. *Proceedings of the 8th International Conference on Acid Rock Drainage (ICARD)*, 22-26 June, 2009, Skellefteå, Sweden.
- Faradiella M. Kusin and Adam P. Jarvis (2009) A Comparative Study of Hydraulic Residence Time at Multiple Coal Mine Water Treatment Systems, North-East England. *PGR Conference*, 4 July, 2009, School of Civil Engineering and Geosciences, Newcastle University, UK.

APPENDIX B

Example of tracer mass estimation for Lambley wetland

Design parameters/Equations	Amount
Area (m^2)	4388
Design volume (m^3)	2054
Design flow rate (m^3/h),Qd	316.8
Length (m)	65
Width (m)	23
Actual flow rate (m^3/h),Q	302.4
Calculated time to fill (h),tn	6.483585859
Expected time to peak tracer (h),tp	5.186868687
Expected peak tracer conc. (mg/m^3),Cp	25
Tracer transport distance (m),L	65
Calculated velocity (m/h),vp	12.53164557
Tracer mass:	
NaBr	
Detection limit 0.05 mg/L	
Background at Lambley < LOD	
Guess method	
M = D.L x flow x t_n (NaBr g)	120.45
0.05 to 1 mg/L tracer spike (NaBr g)	2409.000
Bromide g	1870.545
95% tracer mass detection above background	1777.018
	0.738 mg/L
Na-flourescein	
Detection limit 0.2 ug/L	
Background at Lambley 0.25 ug/L	
Guess method	
M = D.L x flow x t_n (NaF ug)	410800.00
0.2 to 25 ug/L tracer spike (NaF ug)	51350000.00
NaF g	51.35
95% tracer mass detection above background	48.78
	23.7500 ug/L
Tracer mass equation method	
$^*M = 0.56[QCptp/1000]^{0.91}$	16.47
$^*M = 0.56[QCpL/1000vp]^{0.91}$	16.47
$^*M = 17[QCpL/3.6x10^6]^{0.93}$	2.79
$^*M = QL/3600$	5.72
$^*M = Q2L/3600q$	5.992380952
$^*M = CpTpQL/2500vp$	19.7184
$^*M = QCpTpT\rho t/747.23$	19.79149659

*In this case, 95% tracer mass detection below the Na-fluorescein background concentration

APPENDIXC

Hydrochemistry data of mine water treatment systems

1. Hydrochemistry data of Lambley wetland

Table H1. Hydrochemical composition of Lambley wetland (average values)

A.Total concentration						**mg/L**							
Sampling Date	**Location**	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Si**	**Zn**	**Cl^-**	**SO_4^{2-}**	**Electro-neutrality (%)**
26/02/2007	Influent	<LOD	54.34	6.22	5.55	23.97	0.85	7.91	n.d	<LOD	14.46	43.37	7.11
	Effluent	<LOD	53.50	3.11	5.55	23.60	0.85	8.32	n.d	<LOD	11.82	35.45	9.72
29/07/2008	Influent	<LOD	47.73	5.86	4.95	20.29	0.77	7.47	4.77	<LOD	13.76	44.96	1.73
	Effluent	<LOD	47.50	0.82	4.84	20.22	0.55	7.49	3.85	<LOD	13.58	44.26	0.16
17/10/2009	Influent	<LOD	50.50	6.58	4.85	21.53	0.83	7.80	4.28	<LOD	11.57	70.68	2.32
	Effluent	<LOD	50.09	1.10	4.81	21.41	0.73	7.75	4.07	<LOD	11.11	65.64	0.57
27/04/2010	Influent	<LOD	49.851	6.07	4.99	20.86	0.77	8.14	4.28	<LOD	15.07	52.11	2.14
	Effluent	<LOD	49.627	0.90	4.95	20.84	0.52	8.12	4.08	<LOD	14.76	50.07	3.37
B. Dissolved concentration						**mg/L**							
26/02/2007	Influent	<LOD	53.90	5.90	5.15	23.72	0.84	7.91	n.d	<LOD	14.46	43.37	6.50
	Effluent	<LOD	52.95	2.39	5.22	23.23	0.87	7.96	n.d	<LOD	11.82	35.45	8.69
29/07/2008	Influent	<LOD	47.68	5.85	4.97	20.29	0.77	7.55	4.15	<LOD	n.d	n.d	1.84
	Effluent	<LOD	47.63	0.82	5.09	20.37	0.82	7.80	3.92	<LOD	n.d	n.d	2.75
17/10/2009	Influent	<LOD	49.52	6.31	4.58	21.06	0.82	7.55	4.16	<LOD	11.80	70.92	1.04
	Effluent	<LOD	50.11	0.38	4.83	21.46	0.73	7.96	4.09	<LOD	10.95	63.23	1.03
27/04/2010	Influent	<LOD	49.87	5.90	4.97	20.94	0.78	8.09	4.35	<LOD	14.94	52.09	2.17
	Effluent	<LOD	49.94	0.49	4.99	21.05	0.52	8.21	4.12	<LOD	22.41	51.56	0.92

Table H2. Average physicochemical data of Lambley wetland

		pH	Conductivity	Eh	Temperature	Alkalinity
Sampling Date	**Influent/ Effluent**		**µS/cm**	**mV**	**ºC**	**mg/l $CaCO_3$**
26/02/2007	Influent	7.73	441.2	-71	9.8	171
(winter)	Effluent	6.96	423.3	-59	8.4	164
29/07/2008	Influent	6.65	440.8	-24	17.5	164
(summer)	Effluent	6.40	434.2	32	17.0	162
17/10/2009	Influent	6.09	462.1	77	11.2	151
(fall)	Effluent	6.65	447.2	71	9.2	154
27/04/2010	Influent	6.35	459.0	-14	11.7	162
(spring)	Effluent	6.65	442.2	-5	11.9	149

2. Hydrochemistry data of Acomb lagoon

Table H3. Hydrochemical composition of Acomb lagoon (average values)

A.Total concentration						**mg/L**							
Sampling Date	**Location**	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Si**	**Zn**	**Cl^-**	**SO_4^{2-}**	**Electro-neutrality (%)**
26/02/2007	Lag east influent	<LOD	254.24	33.69	15.02	62.58	0.69	44.48	n.d	<LOD	29.79	606.37	7.95
	Lag east effluent	<LOD	250.07	8.79	14.99	61.77	0.66	44.49	n.d	<LOD	28.49	595.19	6.46
	Lag west influent	<LOD	254.24	33.69	15.02	62.58	0.69	44.48	n.d	<LOD	29.79	606.37	7.95
	Lag west effluent	<LOD	254.34	18.01	15.53	62.64	0.68	43.71	n.d	<LOD	33.53	612.32	6.10
17/02/2009	Lag east influent	<LOD	216.70	6.99	14.75	54.71	0.61	40.08	6.97	<LOD	31.46	552.83	2.72
	Lag east effluent	<LOD	216.30	6.02	12.73	54.57	0.61	39.90	7.07	<LOD	30.67	539.09	3.47
	Lag west influent	<LOD	220.05	29.67	12.15	55.33	0.65	38.84	7.56	<LOD	31.89	549.19	5.58
	Lag west effluent	<LOD	217.9	13.42	12.47	54.88	0.62	39.35	7.07	<LOD	30.82	538.74	4.31
02/06/2009	Lag east influent	<LOD	231.83	23.97	11.68	58.37	0.63	42.29	7.43	<LOD	31.62	592.07	1.22
	Lag east effluent	<LOD	232.87	26.16	12.09	58.86	0.60	43.26	7.33	<LOD	30.50	574.6	2.67
	Lag west influent	<LOD	225.99	32.01	11.73	57.11	0.64	42.13	7.77	<LOD	32.27	565.55	1.80
	Lag west effluent	<LOD	229.60	24.88	11.99	58.22	0.63	42.95	7.50	<LOD	31.02	559.82	2.81

B. Dissolved concentration						mg/L							
Sampling Date	**Location**	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Si**	**Zn**	**Cl^-**	**SO_4^{2-}**	**Electro-neutrality (%)**
26/02/2007	Lag east influent	<LOD	245.06	0.01	14.55	60.81	0.66	43.93	n.d	<LOD	29.79	529.04	8.06
	Lag east effluent	<LOD	248.07	<LOD	14.92	61.54	0.65	43.09	n.d	<LOD	28.49	582.12	5.99
	Lag west influent	<LOD	245.06	0.01	14.55	60.81	0.66	43.93	n.d	<LOD	29.79	529.04	8.06
	Lag west effluent	<LOD	251.41	<LOD	15.11	62.35	0.67	42.83	n.d	<LOD	33.53	603.32	4.50
17/02/2009	Lag east influent	<LOD	212.70	<LOD	15.61	54.10	0.60	39.45	6.80	<LOD	30.57	550.72	1.49
	Lag east effluent	<LOD	217.43	<LOD	15.83	54.71	0.60	39.87	6.85	<LOD	29.55	550.72	3.87
	Lag west influent	<LOD	218.50	10.84	15.45	55.01	0.63	40.55	6.87	<LOD	30.88	540.18	4.55
	Lag west effluent	<LOD	215.16	4.42	15.82	54.45	0.61	39.44	6.72	<LOD	28.83	518.76	4.63
02/06/2009	Lag east influent	<LOD	258.52	15.10	11.84	65.59	0.61	41.57	6.75	<LOD	30.57	590.76	5.29
	Lag east effluent	<LOD	230.78	14.29	11.76	58.39	0.59	41.89	6.75	<LOD	28.5	570.60	1.41
	Lag west influent	<LOD	234.46	30.32	11.71	59.441	0.61	42.24	7.66	<LOD	30.17	563.55	3.50
	Lag west effluent	<LOD	229.30	15.99	11.96	57.965	0.61	41.51	6.87	<LOD	30.54	555.28	2.01

Table H4. Average physicochemical data of Acomb lagoon

		pH	Conductivity	Eh	Temperature	Alkalinity
Sampling Date	**Location**		**µS/cm**	**mV**	**ºC**	**mg/l $CaCO_3$**
26/02/2007	Lag east influent	7.09	1477	257	11.2	242
	Lag east effluent	6.94	1470	101	11.1	232
	Lag west influent	7.09	1477	257	11.2	242
	Lag west effluent	7.05	1473	149	10.5	240
17/02/2009	Lag east influent	7.16	1420	85	11	222
	Lag east effluent	7.22	1426	107	10.6	219
	Lag west influent	6.63	1463	-43	11.4	219
	Lag west effluent	7.09	1442	-39	10.6	221
02/06/2009	Lag east influent	6.43	1504	-30	13.2	299
	Lag east effluent	6.92	1484	-76	16.3	291
	Lag west influent	6.93	1487	-84	16.7	289
	Lag west effluent	6.95	1476	-84	16.2	292

3. Hydrochemistry data of Whittle treatment systems

Table H5. Hydrochemical composition of Whittle treatment systems (average values)

A.Total concentration							**mg/L**						
Sampling Date	**Location**	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Si**	**Zn**	**Cl^-**	**SO_4^{2-}**	**Electro-neutrality (%)**
26/02/2007	Lagoon influent	<LOD	304.19	32.59	54.13	197.76	0.91	584.48	n.d	<LOD	276.09	2334.84	-4.99
	Lagoon effluent	<LOD	297.76	22.97	56.01	194.87	0.89	588.93	n.d	<LOD	210.37	2344.85	-3.93
	Wetland influent[†]	<LOD	303.97	22.99	40.47	201.56	0.86	569.57	n.d	<LOD	255.40	2279.20	-3.97
	Wetland effluent	<LOD	268.92	2.42	34.27	171.28	0.57	507.86	n.d	<LOD	530.21	2029.97	-12.42
23/02/2010	Lagoon influent	<LOD	234.77	19.57	29.22	144.81	0.57	531.43	4.14	<LOD	55.79	1914.36	-0.20
	Lagoon effluent	<LOD	235.53	16.34	30.22	146.97	0.57	515.97	4.11	<LOD	51.46	1729.54	4.18
	Wetland influent[‡]	<LOD	227.29	7.44	27.99	139.01	0.45	505.99	3.617	<LOD	45.58	1647.01	3.88
	Wetland effluent	<LOD	225.51	0.83	28.09	138.64	0.25	509.43	3.417	<LOD	45.16	1631.82	4.27
B. Dissolved concentration							**mg/L**						
26/02/2007	Lagoon influent	<LOD	297.74	29.52	49.22	194.19	0.89	572.13	n.d	<LOD	276.09	2331.44	-6.17
	Lagoon effluent	<LOD	296.86	5.16	55.51	193.57	0.86	586.40	n.d	<LOD	210.37	2271.96	-3.51
	Wetland influent[†]	<LOD	302.93	1.56	40.09	199.48	0.85	565.60	n.d	<LOD	255.40	2276.31	-4.93
	Wetland effluent	<LOD	268.65	<LOD	32.95	170.23	0.48	505.49	n.d	<LOD	530.21	1965.48	-11.71
23/02/2010	Lagoon influent	<LOD	234.56	17.03	30.74	145.99	0.59	511.76	4.21	<LOD	64.09	2291.74	-8.74
	Lagoon effluent	<LOD	234.65	2.89	30.44	146.52	0.57	507.85	3.86	<LOD	46.71	1689.67	4.32
	Wetland influent[‡]	<LOD	221.41	<LOD	28.19	136.39	0.433	510.56	3.44	<LOD	63.25	1653.94	2.50
	Wetland effluent	<LOD	219.63	<LOD	27.75	135.94	0.24	503.49	3.38	<LOD	45.25	1625.53	3.53

[†] Sampling undertaken at Wetland 1

[‡] Sampling undertaken at Wetland 3

Table H6. Average physicochemical data of Whittle wetland

		pH	Conductivity	Eh	Temperature	Alkalinity
Sampling Date	**Location**		**µS/cm**	**mV**	**ºC**	**mg/l $CaCO_3$**
26/02/2007	Lagoon influent	7.40	4186	-117	10.5	477
	Lagoon effluent	7.30	4234	-188	10.3	454
	Wetland influent[†]	7.38	4124	-83	10.5	441
	Wetland effluent	7.86	3597	224	9.3	398
23/02/2010	Lagoon influent	7.06	3619	-64	12.3	356
	Lagoon effluent	7.33	3599	-57	10.7	326
	Wetland influent[‡]	7.76	3436	50	8.71	346
	Wetland effluent	8.11	3448	20	6.81	336

4. Hydrochemistry data of Allerdean Mill treatment systems

Table H7. Hydrochemical composition of Allerdean Mill treatment systems (average values)

A. Total concentration						**mg/L**						
Sampling Date	**Location**	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Si**	**Zn**	**Cl^-**	**SO_4^{2-}**	**Electro-neutrality (%)**
09/10/2008	Lag influent	<LOD	190.21	15.30	7.22	54.40	0.81	21.21	6.62	<LOD	48.31	457.32	1.69
	Lag north effluent†	<LOD	188.22	3.10	7.32	53.60	0.61	21.11	5.72	<LOD	43.42	451.43	6.25
	Lag south effluent‡	<LOD	188.34	2.50	7.42	53.60	0.61	20.91	5.62	<LOD	44.25	459.26	1.05
	Pond effluent*	<LOD	71.30	4.10	5.32	35.90	0.81	21.11	4.61	<LOD	54.14	205.13	2.05
	Wet north influent	<LOD	185.32	0.40	6.42	53.20	0.00	21.21	4.91	<LOD	46.17	444.18	1.36
	Wet south effluent	<LOD	135.21	0.10	6.92	45.50	0.00	21.01	5.21	<LOD	49.23	328.22	-0.08
20/04/2009	Lag influent	<LOD	177.03	9.72	6.16	51.16	0.64	22.06	5.04	<LOD	51.95	408.40	3.84
	Lag north effluent†	<LOD	174.74	3.21	6.09	50.2	0.58	21.26	4.43	<LOD	50.31	417.38	0.51
	Lag south effluent‡	<LOD	180.47	3.21	6.23	52.02	0.56	22.41	4.48	<LOD	48.58	399.96	2.84
	Pond effluent*	<LOD	82.3	4.40	6.30	36.90	0.80	21.10	4.60	<LOD	53.46	225.77	1.84
	Wet north influent	<LOD	179.8	0.93	6.15	51.7	0.40	22.15	4.22	<LOD	48.83	397.36	4.75
	Wet south effluent	<LOD	154.69	1.02	5.8	48.09	0.39	22.54	4.13	<LOD	51.28	375.49	-1.55

Sampling Date	Location	Al	Ca	Fe	K	Mg	Mn	Na	Si	Zn	Cl-	SO42-	Electro-neutrality (%)
23/04/2009	Lag influent	<LOD	142.41	10.00	6.10	41.01	0.64	17.45	5.08	<LOD	48.95	407.46	-9.69
	Lag north effluent[†]	<LOD	140.33	3.01	6.13	40.45	0.59	16.86	4.49	<LOD	49.52	410.56	-8.87
	Lag south effluent[‡]	<LOD	143.41	3.00	6.09	41.17	0.54	17.97	4.36	<LOD	49.28	408.96	-9.76
	Pond effluent[*]	<LOD	154.59	6.55	5.73	27.62	0.89	16.72	4.45	<LOD	49.77	406.67	-5.11
	Wet north effluent	<LOD	144.39	1.01	6.17	41.41	0.39	18.87	4.16	<LOD	53.33	357.12	-5.35
	Wet south effluent	<LOD	117.61	1.01	5.55	37.90	0.36	17.56	3.99	<LOD	50.83	204.27	13.30

[†] Lagoon north effluent = wetland influent 1
[‡] Lagoon south effluent = wetland influent 2
[*] Pond effluent = wetland influent 3

Table H8. Average physicochemical data of Allerdean Mill treatment systems

		pH	Conductivity	Eh	Temperature	Alkalinity
Sampling Date	**Location**		**µS/cm**	**mV**	**ºC**	**mg/l $CaCO_3$**
09/10/2008	Lag influent	6.4	1291	-33	11.3	216
	Lag north effluent[†]	7.23	1242	-21	10.9	136
	Lag south effluent[‡]	7.24	1232	-2	10.9	198
	Pond effluent[*]	7.15	725	-51	10.7	84
	Wet north influent	7.48	1226	51	10.9	192
	Wet south effluent	7.35	1053	46	10.6	172

		pH	**Conductivity**	**Eh**	**Temperature**	**Alkalinity**
Sampling Date	**Location**		**µS/cm**	**mV**	**ºC**	**mg/l CaCO3**
20/04/2009	Lag influent	6.72	1214	36	11.1	178
	Lag north effluent[†]	7.41	1199	35	13.3	194
	Lag south effluent[‡]	7.44	1201	60	12.6	206
	Pond effluent[*]	7.4	726	-14	15	97
	Wet north influent	7.47	1200	143	14.8	175
	Wet south effluent	7.49	1071	106	14.2	203
23/04/2009	Lag influent	6.65	1221	29	10.1	226
	Lag north effluent[†]	7.33	1215	63	11.5	184
	Lag south effluent[‡]	7.35	1216	88	11.6	214
	Pond effluent[*]	7.14	724	-14	11.2	125
	Wet north influent	7.39	1217	126	11.9	204
	Wet south effluent	7.33	1094	12	12	98

5. Hydrochemistry data of Bates treatment systems

Table H9. Hydrochemical composition of Bates treatment systems (average values)

A.Total concentration						**mg/L**						
Sampling Date	**Location**	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Si**	**Zn**	**Cl^-**	**SO_4^{2-}**	**Electro-neutrality (%)**
13/07/2009	Lag right1 influent	<LOD	448.558	18.967	117.781	504.519	4.114	2216.02	4.776	<LOD	3184.485	3055.809	-1.71
	Lag right1 effluent[†]	<LOD	401.348	9.605	112.566	494.962	3.967	2201.06	4.451	<LOD	3068.689	2949.724	-1.19
	Lag right2 effluent	<LOD	417.277	5.53	111.976	503.041	3.672	2250.01	4.211	<LOD	3150.533	3012.040	-1.32
	Lag left1 influent	<LOD	417.48	18.828	115.939	519.553	4.063	2281.71	4.737	<LOD	3061.859	2886.763	1.31
	Lag left1 effluent[‡]	<LOD	393.236	4.361	112.445	488.949	3.691	2156.6	4.266	<LOD	3060.943	2880.617	-4.08
	Lag left2 effluent	<LOD	380.9	1.297	114.205	477.971	3.699	2110.17	4.179	<LOD	3077.352	2945.644	-3.35
	Wet out	<LOD	367.986	0.038	112.926	526.457	0.073	2387.75	3.689	<LOD	3520.6111	3320.609	-3.60
B. Dissolved concentration						**mg/L**							
13/07/2009	Lag right1 influent	<LOD	441.967	16.871	107.948	498.132	3.35	2146.46	4.495	<LOD	3004.435	3005.812	-1.19
	Lag right1 effluent†	<LOD	440.4	4.151	119.468	491.641	3.494	2137.28	4.531	<LOD	3018.239	2859.734	-0.53
	Lag right2 effluent	<LOD	456.475	0.843	111.237	505.041	3.597	2192.38	4.584	<LOD	3654.013	3002.120	-5.47
	Lag left1 influent	<LOD	428.067	<LOD	116.644	485.14	3.275	2097.66	4.408	<LOD	3001.869	2766.463	-0.79
	Lag left1 effluent[‡]	<LOD	449.779	<LOD	111.863	502.129	3.588	2173.45	4.661	<LOD	2976.543	2680.614	-0.72
	Lag left2 effluent	<LOD	430.939	<LOD	110.599	486.649	3.525	2152.28	4.583	<LOD	2964.475	2895.609	-0.47
	Wet out	<LOD	368.623	<LOD	111.396	480.197	0.054	2140.07	3.801	<LOD	2907.607	2920.123	-0.53

[†] Effluent of lagoon right1 = influent of lagoon right2

[‡] Effluent of lagoon left1 = influent of lagoon left2

Table H10. Average physicochemical data of Bates treatment systems

		pH	Conductivity	Eh	Temperature	Alkalinity
Sampling Date	**Location**		**µS/cm**	**mV**	**ºC**	**mg/l $CaCO_3$**
13/07/2009	Lag right1 influent	6.73	13910	-37	15.8	852
	Lag right1 effluent[†]	6.97	13900	-26	16.1	822
	Lag right2 effluent	7.19	13880	-15	18	834
	Lag left1 influent	6.65	13960	108	16.2	818
	Lag left1 effluent[‡]	7.05	13800	80	16.7	1224
	Lag left2 effluent	7.29	13900	87	18.1	816
	Wet out	7.65	13890	120	19.4	663

6. Hydrochemistry data of Strafford treatment systems

Table H11. Hydrochemical composition of Strafford treatment systems (average values)

A. Total concentration						**mg/L**							
Sampling Date	**Location**	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Si**	**Zn**	**Cl^-**	**SO_4^{2-}**	**Electro-neutrality (%)**
11/08/2009	Lagoon influent	<LOD	65.47	6.60	8.44	40.24	0.78	412.33	5.06	<LOD	86.88	501.19	2.01
	Lagoon effluent[†]	<LOD	65.49	5.11	8.49	40.47	0.77	403.47	4.98	<LOD	82.78	498.24	2.47
	Wetland effluent	<LOD	62.85	1.34	8.68	39.86	0.45	410.98	4.49	<LOD	95.73	591.87	-3.84

B. Dissolved concentration						**mg/L**							
Sampling Date	**Location**	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Si**	**Zn**	**Cl^-**	**SO_4^{2-}**	
11/08/2009	Lagoon influent	<LOD	63.07	3.3689	8.40	39.34	0.76	399.87	4.98	<LOD	82.27	504.76	0.39
	Lagoon effluent[†]	<LOD	54.28	<LOD	8.57	33.34	0.74	393.55	4.85	<LOD	82.69	505.22	-1.56
	Wetland effluent	<LOD	59.80	<LOD	8.37	38.86	0.44	390.47	4.50	<LOD	83.00	510.56	-2.29

[†] Effluent of lagoon = influent of wetland

Table H12. Average physicochemical data of Strafford treatment systems

		pH	**Conductivity**	**Eh**	**Temperature**	**Alkalinity**
Sampling Date	**Location**		**µS/cm**	**mV**	**ºC**	**mg/l $CaCO_3$**
11/08/2009	Lagoon influent	6.88	2184	-55	15.6	558
	Lagoon effluent†	7.38	2181	-35	16.9	536
	Wetland effluent	7.70	2194	-33	18.6	578

7. Hydrochemistry data of Mousewater treatment systems

Table H13. Hydrochemical composition of Mousewater treatment system (average values)

A.Total concentration					**mg/L**								
Sampling Date	**Location**	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Si**	**Zn**	**Cl^-**	**SO_4^{2-}**	**Electro-neutrality (%)**
6/07/2010	Lagoon influent	<LOD	119.245	14.578	7.459	51.006	1.887	10.176	4.564	<LOD	17.222	295.681	1.38
	Lagoon effluent	<LOD	120.766	6.451	7.67	50.032	1.838	10.429	4.252	<LOD	17.171	289.216	3.56
	Wetland influent	<LOD	117.375	8.408	7.854	50.845	1.942	10.681	4.649	<LOD	17.062	289.868	1.84
	Wetland effluent	<LOD	117.358	0.183	6.996	50.463	0.774	10.659	3.658	<LOD	16.593	291.235	1.11
B. Dissolved concentration						**mg/L**							
6/07/2010	Lagoon influent	<LOD	120.035	6.407	7.404	48.689	1.844	10.143	4.350	<LOD	16.021	290.281	0.03
	Lagoon effluent	<LOD	120.596	0.616	7.848	50.496	1.894	10.683	4.332	<LOD	16.124	286.118	3.29
	Wetland influent	<LOD	115.974	8.399	7.798	50.919	1.91	10.75	4.341	<LOD	16.042	286.267	2.04
	Wetland effluent	<LOD	112.637	<0.1	6.986	50.129	0.757	10.709	3.677	<LOD	15.991	281.343	0.91

Table H14. Average physicochemical data of Mousewater treatment systems

		pH	Conductivity	Eh	Temperature	Alkalinity
Sampling Date	**Location**		**µS/cm**	**mV**	**ºC**	**mg/l $CaCO_3$**
6/07/2010	Lagoon influent	5.81	936.4	84	10.8	224
	Lagoon effluent	6.47	904.9	69	12.3	194
	Wetland influent	6.11	908.2	35	15.2	211
	Wetland effluent	6.61	892.7	50	14.3	199

8. Hydrochemistry data of Cuthill treatment systems

Table H15. Hydrochemical composition of Cuthill treatment systems (average values)

A. Total concentration						**mg/L**							
Sampling Date	**Location**	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Si**	**Zn**	**Cl^-**	**SO_4^{2-}**	**Electro-neutrality (%)**
6/07/2010	Lagoon influent	<LOD	350.13	17.413	19.927	97.607	1.106	76.978	9.858	<LOD	47.58	1006.092	-1.02
	Lagoon effluent	<LOD	351.568	8.105	20.239	97.574	1.108	77.467	9.824	<LOD	42.674	886.564	2.81
	Wetland influent	<LOD	321.656	7.869	19.539	89.066	1.064	70.902	9.468	<LOD	42.334	878.705	-0.64
	Wetland effluent	<LOD	301.267	<0.1	17.123	87.906	<0.1	69.947	7.133	<LOD	39.899	851.281	-2.10
B. Dissolved concentration						**mg/L**							
6/07/2010	Lagoon influent	<LOD	349.993	5.187	20.789	97.67	1.132	79.219	9.694	<LOD	44.182	887.540	2.80
	Lagoon effluent	<LOD	349.927	0.337	17.432	97.62	1.124	76.754	9.431	<LOD	41.274	876.154	2.49
	Wetland influent	<LOD	312.765	0.15	20.143	86.98	1.029	68.233	8.749	<LOD	40.031	875.577	-2.25
	Wetland effluent	<LOD	298.436	<0.1	17.682	87.099	<0.1	69.471	7.518	<LOD	38.291	850.001	-2.38

Table H16. Average physicochemical data of Cuthill treatment systems

		pH	**Conductivity**	**Eh**	**Temperature**	**Alkalinity**
Sampling Date	**Location**		**µS/cm**	**mV**	**ºC**	**mg/l $CaCO_3$**
6/07/2010	Lagoon influent	7.18	2041	-120	14.4	424
	Lagoon effluent	7.02	2008	8	14.7	431
	Wetland influent	6.84	2037	87	14.6	413
	Wetland effluent	7.43	1970	125	13.4	406

APPENDIX D

Flow data (Examples from Lambley wetland, flow data for other sites are provided in the enclosed CD)

Note:

i. Timely flow data calculated from water head measured using a CTD Diver and a Barometer
   a. Corrected level = water head [(water pressure + atmospheric pressure measured by CTD Diver) – (atmospheric pressure measured by BaroDiver)]
   b. Flow (L/s) = $1.342H^{2.48}$; H = water head (m)

ii. Flow calculated using a mean-section method from measurement of flow channel width, depth and velocity using a flow impeller
   a. Flow (m^3/s), $Q = \sum_{i=1}^{n} \frac{(v_{i-1}+v_i)}{2} \frac{(d_{i-1}+d_i)}{2} (b_i - b_{i-1})$; v = velocity (m/s); d = water depth (m); b = section width (m)

iii. Abbreviation :
   v = velocity
   d = depth
   b = section width
   s.d = standard deviation

1. Lambley

Timely flow data for Lambley wetland on 26-27/02/2007

Date/Time	Corrected level (cm)	Flow (L/s)
26/02/2007 11:15	32.2	71.17732357
26/02/2007 11:30	32.4	74.09660004
26/02/2007 11:45	34	70.6018559
26/02/2007 12:00	33.5	71.75558129
26/02/2007 12:15	32.8	74.09660004
26/02/2007 12:30	33.3	71.17732357
26/02/2007 12:45	32.7	75.28396306
26/02/2007 13:00	32.9	77.69256971
26/02/2007 13:15	33.3	70.02917389
26/02/2007 13:30	32.8	70.02917389
26/02/2007 13:45	33.5	74.09660004
26/02/2007 14:00	33.9	82.01704937
26/02/2007 14:15	32.6	80.76720938
26/02/2007 14:30	32.6	83.27835999
26/02/2007 14:45	33.3	82.64626873
26/02/2007 15:00	34.6	78.30180499
26/02/2007 15:15	34.4	72.33663344
26/02/2007 15:30	34.8	75.28396306
26/02/2007 15:45	34.7	74.68887346
26/02/2007 16:00	34	79.52880597
26/02/2007 16:15	33	77.69256971
26/02/2007 16:30	33.5	77.69256971
26/02/2007 16:45	33.4	80.76720938
26/02/2007 17:00	34.2	83.9133274
26/02/2007 17:15	33.9	72.33663344
26/02/2007 17:30	33.9	85.19190755
26/02/2007 17:45	34.4	85.19190755
26/02/2007 18:00	34.9	86.48204296

26/02/2007 18:15	33	95.15189752
26/02/2007 18:30	35.1	85.19190755
26/02/2007 18:45	35.1	86.48204296
26/02/2007 19:00	35.3	97.919467
26/02/2007 19:15	36.6	85.19190755
26/02/2007 19:30	35.1	84.55117518
26/02/2007 19:45	35.3	89.09711411
26/02/2007 20:00	37	89.7581564
26/02/2007 20:15	35.1	83.27835999
26/02/2007 20:30	35	81.39069767
26/02/2007 20:45	35.7	85.19190755
26/02/2007 21:00	35.8	85.83552874
26/02/2007 21:15	34.8	89.09711411
26/02/2007 21:30	34.5	84.55117518
26/02/2007 21:45	35.1	85.19190755
26/02/2007 22:00	35.2	91.08899963
26/02/2007 22:15	35.7	87.13145441
26/02/2007 22:30	35	94.46739369
26/02/2007 22:45	35.1	93.78583704
26/02/2007 23:00	36	94.46739369
26/02/2007 23:15	35.4	87.13145441
26/02/2007 23:30	36.5	85.83552874
26/02/2007 23:45	36.4	91.08899963
27/02/2007 00:00	36.5	91.75880888
27/02/2007 00:15	35.4	90.42211685
27/02/2007 00:30	35.2	90.42211685
27/02/2007 00:45	36	81.39069767
27/02/2007 01:00	36.1	72.33663344
27/02/2007 01:15	35.9	82.01704937
27/02/2007 01:30	35.9	85.83552874
27/02/2007 01:45	34.5	85.19190755
27/02/2007 02:00	33	83.9133274
27/02/2007 02:15	34.6	83.9133274
27/02/2007 02:30	35.2	79.52880597
27/02/2007 02:45	35.1	86.48204296
27/02/2007 03:00	34.9	71.75558129
27/02/2007 03:15	34.9	82.01704937
27/02/2007 03:30	34.2	86.48204296
26/02/2007 11:15	35.3	81.39069767
26/02/2007 11:30	32.9	82.01704937
26/02/2007 11:45	34.6	85.83552874
26/02/2007 12:00	35.3	79.52880597
26/02/2007 12:15	34.5	78.91388231
26/02/2007 12:30	34.6	72.92048438
26/02/2007 12:45	35.2	85.19190755
27/02/2007 03:45	34.2	80.14658023
27/02/2007 04:00	34.1	74.09660004
27/02/2007 04:15	33.1	72.33663344
27/02/2007 04:30	35.1	77.08617218
27/02/2007 04:45	34.3	71.17732357
27/02/2007 05:00	33.3	75.28396306
27/02/2007 05:15	33	82.64626873
27/02/2007 05:30	33.8	70.6018559
27/02/2007 05:45	32.8	72.92048438

27/02/2007 06:00	33.5	77.69256971
27/02/2007 06:15	34.7	74.68887346

Timely flow data for Lambley wetland on 29-30/07/2008

Date/Time	Corrected level (cm)	Flow (L/s)
29/07/2008 12:20	32.2	67.76621472
29/07/2008 12:40	32.4	68.89214934
29/07/2008 13:00	34	78.30180499
29/07/2008 13:20	33.5	75.28396306
29/07/2008 13:40	32.8	71.17732357
29/07/2008 14:00	33.3	74.09660004
29/07/2008 14:20	32.7	70.6018559
29/07/2008 14:40	32.9	71.75558129
29/07/2008 15:00	33.3	74.09660004
29/07/2008 15:20	32.8	71.17732357
29/07/2008 15:40	33.5	75.28396306
29/07/2008 16:00	33.9	77.69256971
29/07/2008 16:20	32.6	70.02917389
29/07/2008 16:40	32.6	70.02917389
29/07/2008 17:00	33.3	74.09660004
29/07/2008 17:20	34.6	82.01704937
29/07/2008 17:40	34.4	80.76720938
29/07/2008 18:00	34.8	83.27835999
29/07/2008 18:20	34.7	82.64626873
29/07/2008 18:40	34	78.30180499
29/07/2008 19:00	33	72.33663344
29/07/2008 19:20	33.5	75.28396306
29/07/2008 19:40	33.4	74.68887346
29/07/2008 20:00	34.2	79.52880597
29/07/2008 20:20	33.9	77.69256971
29/07/2008 20:40	33.9	77.69256971
29/07/2008 21:00	34.4	80.76720938
29/07/2008 21:20	34.9	83.9133274
29/07/2008 21:40	33	72.33663344
29/07/2008 22:00	35.1	85.19190755
29/07/2008 22:20	35.1	85.19190755
29/07/2008 22:40	35.3	86.48204296
29/07/2008 23:00	36.6	95.15189752
29/07/2008 23:20	35.1	85.19190755
29/07/2008 23:40	35.3	86.48204296
30/07/2008 00:00	37	97.919467
30/07/2008 00:20	35.1	85.19190755
30/07/2008 00:40	35	84.55117518
30/07/2008 01:00	35.7	89.09711411
30/07/2008 01:20	35.8	89.7581564
30/07/2008 01:40	34.8	83.27835999
30/07/2008 02:00	34.5	81.39069767
30/07/2008 02:20	35.1	85.19190755
30/07/2008 02:40	35.2	85.83552874
30/07/2008 03:00	35.7	89.09711411
30/07/2008 03:20	35	84.55117518
30/07/2008 03:40	35.1	85.19190755
30/07/2008 04:00	36	91.08899963

30/07/2008 04:20	35.4	87.13145441
30/07/2008 04:40	36.5	94.46739369
30/07/2008 05:00	36.4	93.78583704
30/07/2008 05:20	36.5	94.46739369
30/07/2008 05:40	35.4	87.13145441
30/07/2008 06:00	35.2	85.83552874
30/07/2008 06:20	36	91.08899963
30/07/2008 06:40	36.1	91.75880888
30/07/2008 07:00	35.9	90.42211685
30/07/2008 07:20	35.9	90.42211685
30/07/2008 07:40	34.5	81.39069767
30/07/2008 08:00	33	72.33663344
30/07/2008 08:20	34.6	82.01704937
30/07/2008 08:40	35.2	85.83552874
30/07/2008 09:00	35.1	85.19190755
30/07/2008 09:20	34.9	83.9133274
30/07/2008 09:40	34.9	83.9133274
30/07/2008 10:00	34.2	79.52880597
30/07/2008 10:20	35.3	86.48204296
30/07/2008 10:40	32.9	71.75558129
30/07/2008 11:00	34.6	82.01704937
30/07/2008 11:20	35.3	86.48204296
30/07/2008 11:40	34.5	81.39069767
30/07/2008 12:00	34.6	82.01704937
30/07/2008 12:20	35.2	85.83552874
30/07/2008 12:40	34.2	79.52880597
30/07/2008 13:00	34.1	78.91388231
30/07/2008 13:20	33.1	72.92048438
30/07/2008 13:40	35.1	85.19190755
30/07/2008 14:00	34.3	80.14658023
30/07/2008 14:20	33.3	74.09660004
30/07/2008 14:40	33	72.33663344
30/07/2008 15:00	33.8	77.08617218
30/07/2008 15:20	32.8	71.17732357
30/07/2008 15:40	33.5	75.28396306
30/07/2008 16:00	34.7	82.64626873
30/07/2008 16:20	32.7	70.6018559
30/07/2008 16:40	33.1	72.92048438
30/07/2008 17:00	33.9	77.69256971
30/07/2008 17:20	33.4	74.68887346
30/07/2008 17:40	33.1	72.92048438
30/07/2008 18:00	33.8	77.08617218
30/07/2008 18:20	33	72.33663344
30/07/2008 18:40	33.3	74.09660004
30/07/2008 19:00	33.1	72.92048438
30/07/2008 19:20	33.9	77.69256971
30/07/2008 19:40	33.9	77.69256971
30/07/2008 20:00	33.8	77.08617218
30/07/2008 20:20	33.4	74.68887346
30/07/2008 20:40	33.7	76.4826081
30/07/2008 21:00	32.7	70.6018559
30/07/2008 21:20	33.5	75.28396306
30/07/2008 21:40	33.7	76.4826081
30/07/2008 22:00	33.8	77.08617218

30/07/2008 22:20	35.3	86.48204296
30/07/2008 22:40	35.6	88.4389858
30/07/2008 23:00	33.8	77.08617218
30/07/2008 23:20	34.9	83.9133274

Inflow measurement using impeller (mean-section method)

Inflow data for Lambley wetland on 29/07/2008

Channel 1

Distance (m)	Depth (m)	Velocity (m/s)	s.d.	vi-1 + vi/2	di-1 +di/2	bi-bi-1	Flow (m^3/s)	Area (m^2)
0	0	0	0	0	0	0	0	0
0.2	0.6	0.141	0.115	0.0705	0.3	0.2	0.00423	0.06
0.4	0.6	0.139	0.055	0.14	0.6	0.2	0.0168	0.12
0.58	0	0	0	0.0695	0.3	0.18	0.003753	0.054
						Flow	0.024783	m^3/s
						Flow	**24.783**	L/s

Channel 2

Distance (m)	Depth (m)	Velocity (m/s)	s.d.	vi-1 + vi/2	di-1 +di/2	bi-bi-1	Flow (m^3/s)	Area (m^2)
0	0	0	0	0	0	0	0	0
0.2	0.6	0.114	0.004	0.057	0.3	0.2	0.00342	0.06
0.4	0.6	0.371	0.011	0.2425	0.6	0.2	0.0291	0.12
0.61	0	0	0	0.1855	0.3	0.21	0.011687	0.063
						Flow	0.044207	m^3/s
						Flow	**44.2065**	L/s

Channel 3

Distance (m)	Depth (m)	Velocity (m/s)	s.d.	vi-1 + vi/2	di-1 +di/2	bi-bi-1	Flow (m^3/s)	Area (m^2)
0	0	0	0	0	0	0	0	0
0.2	0.59	0.062	0.012	0.031	0.295	0.2	0.001829	0.059
0.4	0.52	0.042	0.012	0.052	0.555	0.2	0.005772	0.111
0.6	0	0	0	0.021	0.26	0.2	0.001092	0.052
						Flow	0.008693	m^3/s
						Flow	**8.693**	L/s

Channel 4

Distance (m)	Depth (m)	Velocity (m/s)	s.d.	vi-1 + vi/2	di-1 +di/2	bi-bi-1	Flow (m^3/s)	Area (m^2)
0	0	0.024	0	0	0	0	0	0
0.2	0.59	0.012	0.007	0.018	0.295	0.2	0.001062	0.059
0.4	0.59	0.023	0.007	0.0175	0.59	0.2	0.002065	0.118
0.6	0	0	0	0.0115	0.295	0.2	0.000679	0.059
						Flow	0.003806	m^3/s
						Flow	**3.8055**	L/s

Total inflow **81.488** L/s

Timely flow data for Lambley wetland on 17-19/10/2009

Date/Time	Corrected level (cm)	Flow (L/s)
17/11/2009 14:30	30.3	69.45927317
17/11/2009 15:00	30.2	68.89214934
17/11/2009 15:30	30.9	72.92048438
17/11/2009 16:00	30.1	68.32779799
17/11/2009 16:30	30.1	68.32779799
17/11/2009 17:00	29.5	64.99966457
17/11/2009 17:30	30.5	70.6018559
17/11/2009 18:00	31.4	75.88187317
17/11/2009 18:30	30.4	70.02917389
17/11/2009 19:00	30.3	69.45927317
17/11/2009 19:30	31.5	76.4826081
17/11/2009 20:00	30.7	71.75558129
17/11/2009 20:30	30.3	69.45927317
17/11/2009 21:00	30.3	69.45927317
17/11/2009 21:30	30.1	68.32779799
17/11/2009 22:00	31	73.50713846
17/11/2009 22:30	30.9	72.92048438
17/11/2009 23:00	30.7	71.75558129
17/11/2009 23:30	31.5	76.4826081
18/11/2009 00:00	30.5	70.6018559
18/11/2009 00:30	31.8	78.30180499
18/11/2009 01:00	31.5	76.4826081
18/11/2009 01:30	32.5	82.64626873
18/11/2009 02:00	33	85.83552874
18/11/2009 02:30	32.5	82.64626873
18/11/2009 03:00	33.6	89.7581564
18/11/2009 03:30	34.8	97.919467
18/11/2009 04:00	33.1	86.48204296
18/11/2009 04:30	33.3	87.7837673
18/11/2009 05:00	33.5	89.09711411
18/11/2009 05:30	33.7	90.42211685
18/11/2009 06:00	33.1	86.48204296
18/11/2009 06:30	34.8	97.919467
18/11/2009 07:00	34.7	97.22313329
18/11/2009 07:30	34.1	93.10722345
18/11/2009 08:00	31	73.50713846
18/11/2009 08:30	33.2	87.13145441
18/11/2009 09:00	31.3	75.28396306
18/11/2009 09:30	31.7	77.69256971
18/11/2009 10:00	32.5	82.64626873
18/11/2009 10:30	32.1	80.14658023
18/11/2009 11:00	31	73.50713846
18/11/2009 11:30	31	73.50713846
18/11/2009 12:00	32	79.52880597
18/11/2009 12:30	32.1	80.14658023
18/11/2009 13:00	32.1	80.14658023
18/11/2009 13:30	30.9	72.92048438
18/11/2009 14:00	30.4	70.02917389
18/11/2009 14:30	31.5	76.4826081
18/11/2009 15:00	32	79.52880597
18/11/2009 15:30	32.2	80.76720938
18/11/2009 16:00	30.9	72.92048438

18/11/2009 16:30	32.2	80.76720938
18/11/2009 17:00	32.2	80.76720938
18/11/2009 17:30	29.9	67.2073951
18/11/2009 18:00	32.7	83.9133274
18/11/2009 18:30	30.4	70.02917389
18/11/2009 19:00	32.1	80.14658023
18/11/2009 19:30	32.2	80.76720938
18/11/2009 20:00	31.3	75.28396306
18/11/2009 20:30	31.3	75.28396306
18/11/2009 21:00	30.8	72.33663344
18/11/2009 21:30	30.6	71.17732357
18/11/2009 22:00	32.1	80.14658023
18/11/2009 22:30	31.7	77.69256971
18/11/2009 23:00	30.7	71.75558129
18/11/2009 23:30	32.1	80.14658023
19/11/2009 00:00	31.3	75.28396306
19/11/2009 00:30	32.1	80.14658023
19/11/2009 01:00	32	79.52880597
19/11/2009 01:30	30.7	71.75558129
19/11/2009 02:00	32.6	83.27835999
19/11/2009 02:30	31.6	77.08617218
19/11/2009 03:00	32.6	83.27835999
19/11/2009 03:30	30.5	70.6018559
19/11/2009 04:00	31.5	76.4826081
19/11/2009 04:30	31.9	78.91388231
19/11/2009 05:00	31.4	75.88187317
19/11/2009 05:30	31.7	77.69256971
19/11/2009 06:00	30.7	71.75558129
19/11/2009 06:30	31.5	76.4826081
19/11/2009 07:00	32.5	82.64626873
19/11/2009 07:30	33.3	87.7837673
19/11/2009 08:00	32.5	82.64626873
19/11/2009 08:30	33.2	87.13145441
19/11/2009 09:00	32.5	82.64626873
19/11/2009 09:30	32.7	83.9133274
19/11/2009 10:00	32	79.52880597
19/11/2009 10:30	32.3	81.39069767
19/11/2009 11:00	32.4	82.01704937
19/11/2009 11:30	31.9	78.91388231
19/11/2009 12:00	30.9	72.92048438
19/11/2009 12:30	32.4	82.01704937
19/11/2009 13:00	31.2	74.68887346
19/11/2009 13:30	31	73.50713846
19/11/2009 14:00	31.1	74.09660004

Inflow data for Lambley wetland on 17/10/2009

Channel 1

Distance (m)	Depth (m)	Velocity (m/s)	s.d.	vi-1 + vi/2	di-1 +di/2	bi-bi-1	Flow (m^3/s)	Area (m^2)
0	0	0	0	0	0	0	0	0
0.2	0.61	0.139	0.017	0.0695	0.305	0.2	0.00424	0.061
0.4	0.6	0.135	0.023	0.137	0.605	0.2	0.016577	0.121
0.58	0	0	0	0.0675	0.3	0.18	0.003645	0.054
						Flow	0.024462	m^3/s
						Flow	**24.4615**	L/s

Channel 2

Distance (m)	Depth (m)	Velocity (m/s)	s.d.	vi-1 + vi/2	di-1 +di/2	bi-bi-1	Flow (m^3/s)	Area (m^2)
0	0	0	0	0	0	0	0	0
0.2	0.54	0.168	0.011	0.084	0.27	0.2	0.004536	0.054
0.4	0.59	0.297	0.016	0.2325	0.565	0.2	0.026273	0.113
0.61	0	0	0	0.1485	0.295	0.21	0.0092	0.06195
						Flow	0.040008	m^3/s
						Flow	**40.00808**	L/s

Channel 3

Distance (m)	Depth (m)	Velocity (m/s)	s.d.	vi-1 + vi/2	di-1 +di/2	bi-bi-1	Flow (m^3/s)	Area (m^2)
0	0	0	0	0	0	0	0	0
0.2	0.6	0.059	0.012	0.0295	0.3	0.2	0.00177	0.06
0.4	0.6	0.042	0.012	0.0505	0.6	0.2	0.00606	0.12
0.6	0	0	0	0.021	0.3	0.2	0.00126	0.06
						Flow	0.00909	m^3/s
						Flow	**9.09**	L/s

Channel 4

Distance (m)	Depth (m)	Velocity (m/s)	s.d.	vi-1 + vi/2	di-1 +di/2	bi-bi-1	Flow (m^3/s)	Area (m^2)
0	0	0	0	0	0	0	0	0
0.2	0.6	0.013	0.007	0.0065	0.3	0.2	0.00039	0.06
0.4	0.6	0.024	0.009	0.0185	0.6	0.2	0.00222	0.12
0.6	0	0	0	0.012	0.3	0.2	0.00072	0.06
						Flow	0.00333	m^3/s
						Flow	3.33	L/s

Total inflow **76.88958** L/s

Timely flow data for Lambley wetland on 27-28/04/2010

Date/Time		Corrected level (cm)	Flow (L/s)
27/04/2010	11:00:00	34.9	84.55117518
27/04/2010	11:05:00	32.1	67.76621472
27/04/2010	11:10:00	33.3	74.68887346
27/04/2010	11:15:00	32.7	71.17732357
27/04/2010	11:20:00	32.5	70.02917389
27/04/2010	11:25:00	31.4	63.9122658
27/04/2010	11:30:00	33.1	73.50713846
27/04/2010	11:35:00	33.4	75.28396306
27/04/2010	11:40:00	33	72.92048438
27/04/2010	11:45:00	33.9	78.30180499
27/04/2010	11:50:00	33.4	75.28396306
27/04/2010	11:55:00	33.3	74.68887346
27/04/2010	12:00:00	33.4	75.28396306
27/04/2010	12:05:00	33.5	75.88187317
27/04/2010	12:10:00	32.4	69.45927317
27/04/2010	12:15:00	33.6	76.4826081
27/04/2010	12:20:00	32.1	67.76621472
27/04/2010	12:25:00	32.1	67.76621472
27/04/2010	12:30:00	32.5	70.02917389
27/04/2010	12:35:00	31.1	62.30165028
27/04/2010	12:40:00	31.9	66.65133472
27/04/2010	12:45:00	33.2	74.09660004
27/04/2010	12:50:00	31.9	66.65133472
27/04/2010	12:55:00	33.6	76.4826081
27/04/2010	13:00:00	34.5	82.01704937
27/04/2010	13:05:00	32.3	68.89214934
27/04/2010	13:10:00	33.8	77.69256971
27/04/2010	13:15:00	33.3	74.68887346
27/04/2010	13:20:00	34.3	80.76720938
27/04/2010	13:25:00	33.3	74.68887346
27/04/2010	13:30:00	32.9	72.33663344
27/04/2010	13:35:00	32.3	68.89214934
27/04/2010	13:40:00	33.3	74.68887346
27/04/2010	13:45:00	33.1	73.50713846
27/04/2010	13:50:00	34.3	80.76720938
27/04/2010	13:55:00	32.5	70.02917389
27/04/2010	14:00:00	34.3	80.76720938
27/04/2010	14:05:00	32.8	71.75558129
27/04/2010	14:10:00	26.1	38.96515384
27/04/2010	14:15:00	32.4	69.45927317
27/04/2010	14:20:00	32.1	67.76621472
27/04/2010	14:25:00	32.3	68.89214934
27/04/2010	14:30:00	33.3	74.68887346
27/04/2010	14:35:00	33.2	74.09660004

27/04/2010	14:40:00	33.9	78.30180499
27/04/2010	14:45:00	33.7	77.08617218
27/04/2010	14:50:00	33	72.92048438
27/04/2010	14:55:00	33.3	74.68887346
27/04/2010	15:00:00	34.1	79.52880597
27/04/2010	15:05:00	34.1	79.52880597
27/04/2010	15:10:00	33.9	78.30180499
27/04/2010	15:15:00	34	78.91388231
27/04/2010	15:20:00	32.6	70.6018559
27/04/2010	15:25:00	33.3	74.68887346
27/04/2010	15:30:00	33.7	77.08617218
27/04/2010	15:35:00	33.7	77.08617218
27/04/2010	15:40:00	33.2	74.09660004
27/04/2010	15:45:00	32.3	68.89214934
27/04/2010	15:50:00	32.7	71.17732357
27/04/2010	15:55:00	33.5	75.88187317
27/04/2010	16:00:00	33.2	74.09660004
27/04/2010	16:05:00	32.8	71.75558129
27/04/2010	16:10:00	32.9	72.33663344
27/04/2010	16:15:00	33.6	76.4826081
27/04/2010	16:20:00	33.7	77.08617218
27/04/2010	16:25:00	32.7	71.17732357
27/04/2010	16:30:00	33.6	76.4826081
27/04/2010	16:35:00	32.8	71.75558129
27/04/2010	16:40:00	33.9	78.30180499
27/04/2010	16:45:00	32.7	71.17732357
27/04/2010	16:50:00	33.3	74.68887346
27/04/2010	16:55:00	32.8	71.75558129
27/04/2010	17:00:00	32.1	67.76621472
27/04/2010	17:05:00	34.7	83.27835999
27/04/2010	17:10:00	33.4	75.28396306
27/04/2010	17:15:00	33.5	75.88187317
27/04/2010	17:20:00	33.9	78.30180499
27/04/2010	17:25:00	32.9	72.33663344
27/04/2010	17:30:00	33.5	75.88187317
27/04/2010	17:35:00	33.3	74.68887346
27/04/2010	17:40:00	33.4	75.28396306
27/04/2010	17:45:00	33.9	78.30180499
27/04/2010	17:50:00	32.6	70.6018559
27/04/2010	17:55:00	34.3	80.76720938
27/04/2010	18:00:00	33.9	78.30180499
27/04/2010	18:05:00	34.5	82.01704937
27/04/2010	18:10:00	34.1	79.52880597
27/04/2010	18:15:00	33.6	76.4826081
27/04/2010	18:20:00	32.7	71.17732357
27/04/2010	18:25:00	33.4	75.28396306

27/04/2010	18:30:00	33.9	78.30180499
27/04/2010	18:35:00	34.1	79.52880597
27/04/2010	18:40:00	33.5	75.88187317
27/04/2010	18:45:00	32.9	72.33663344
27/04/2010	18:50:00	33	72.92048438
27/04/2010	18:55:00	33.5	75.88187317
27/04/2010	19:00:00	34.3	80.76720938
27/04/2010	19:05:00	33.7	77.08617218
27/04/2010	19:10:00	33.5	75.88187317
27/04/2010	19:15:00	34.4	81.39069767
27/04/2010	19:20:00	34.4	81.39069767
27/04/2010	19:25:00	33.1	73.50713846
27/04/2010	19:30:00	33.7	77.08617218
27/04/2010	19:35:00	32.3	68.89214934
27/04/2010	19:40:00	32.2	68.32779799
27/04/2010	19:45:00	33.7	77.08617218
27/04/2010	19:50:00	34	78.91388231
27/04/2010	19:55:00	33.6	76.4826081
27/04/2010	20:00:00	33.7	77.08617218
27/04/2010	20:05:00	34.3	80.76720938
27/04/2010	20:10:00	33.5	75.88187317
27/04/2010	20:15:00	32.1	67.76621472
27/04/2010	20:20:00	33.5	75.88187317
27/04/2010	20:25:00	33.2	74.09660004
27/04/2010	20:30:00	33.4	75.28396306
27/04/2010	20:35:00	33.5	75.88187317
27/04/2010	20:40:00	33.7	77.08617218
27/04/2010	20:45:00	34.1	79.52880597
27/04/2010	20:50:00	33.1	73.50713846
27/04/2010	20:55:00	33.2	74.09660004
27/04/2010	21:00:00	31.9	66.65133472
27/04/2010	21:05:00	34.2	80.14658023
27/04/2010	21:10:00	33	72.92048438
27/04/2010	21:15:00	33.3	74.68887346
27/04/2010	21:20:00	33.1	73.50713846
27/04/2010	21:25:00	33.8	77.69256971
27/04/2010	21:30:00	33.3	74.68887346
27/04/2010	21:35:00	32.9	72.33663344
27/04/2010	21:40:00	33.2	74.09660004
27/04/2010	21:45:00	32.4	69.45927317
27/04/2010	21:50:00	33.9	78.30180499
27/04/2010	21:55:00	33.7	77.08617218
27/04/2010	22:00:00	32.3	68.89214934
27/04/2010	22:05:00	32.8	71.75558129
27/04/2010	22:10:00	33.9	78.30180499
27/04/2010	22:15:00	32.6	70.6018559

27/04/2010	22:20:00	33.7	77.08617218
27/04/2010	22:25:00	32.3	68.89214934
27/04/2010	22:30:00	32.9	72.33663344
27/04/2010	22:35:00	34.1	79.52880597
27/04/2010	22:40:00	34.6	82.64626873
27/04/2010	22:45:00	33.6	76.4826081
27/04/2010	22:50:00	33.7	77.08617218
27/04/2010	22:55:00	33.9	78.30180499
27/04/2010	23:00:00	33.4	75.28396306
27/04/2010	23:05:00	32.7	71.17732357
27/04/2010	23:10:00	32.7	71.17732357
27/04/2010	23:15:00	33.2	74.09660004
27/04/2010	23:20:00	34.3	80.76720938
27/04/2010	23:25:00	33.4	75.28396306
27/04/2010	23:30:00	33.3	74.68887346
27/04/2010	23:35:00	33.3	74.68887346
27/04/2010	23:40:00	33.2	74.09660004
27/04/2010	23:45:00	32.8	71.75558129
27/04/2010	23:50:00	33.7	77.08617218
27/04/2010	23:55:00	32.3	68.89214934
28/04/2010	00:00:00	33.3	74.68887346
28/04/2010	00:05:00	33.5	75.88187317
28/04/2010	00:10:00	33.3	74.68887346
28/04/2010	00:15:00	33.1	73.50713846
28/04/2010	00:20:00	33.5	75.88187317
28/04/2010	00:25:00	33.3	74.68887346
28/04/2010	00:30:00	33.6	76.4826081
28/04/2010	00:35:00	33.8	77.69256971
28/04/2010	00:40:00	33.1	73.50713846
28/04/2010	00:45:00	33.4	75.28396306
28/04/2010	00:50:00	34.5	82.01704937
28/04/2010	00:55:00	34.7	83.27835999
28/04/2010	01:00:00	33.6	76.4826081
28/04/2010	01:05:00	34.8	83.9133274
28/04/2010	01:10:00	34.6	82.64626873
28/04/2010	01:15:00	33.4	75.28396306
28/04/2010	01:20:00	34.5	82.01704937
28/04/2010	01:25:00	32.9	72.33663344
28/04/2010	01:30:00	34.6	82.64626873
28/04/2010	01:35:00	34.6	82.64626873
28/04/2010	01:40:00	34.7	83.27835999
28/04/2010	01:45:00	32.7	71.17732357
28/04/2010	01:50:00	33.1	73.50713846
28/04/2010	01:55:00	34.1	79.52880597
28/04/2010	02:00:00	34.3	80.76720938
28/04/2010	02:05:00	33.9	78.30180499

28/04/2010	02:10:00	33.7	77.08617218
28/04/2010	02:15:00	34.6	82.64626873
28/04/2010	02:20:00	34.5	82.01704937
28/04/2010	02:25:00	34.1	79.52880597
28/04/2010	02:30:00	34.5	82.01704937
28/04/2010	02:35:00	34	78.91388231
28/04/2010	02:40:00	34.5	82.01704937
28/04/2010	02:45:00	34.1	79.52880597
28/04/2010	02:50:00	33.3	74.68887346
28/04/2010	02:55:00	33.9	78.30180499
28/04/2010	03:00:00	33.7	77.08617218
28/04/2010	03:05:00	34.3	80.76720938
28/04/2010	03:10:00	33.3	74.68887346
28/04/2010	03:15:00	33.9	78.30180499
28/04/2010	03:20:00	34.5	82.01704937
28/04/2010	03:25:00	34.7	83.27835999
28/04/2010	03:30:00	34.7	83.27835999
28/04/2010	03:35:00	34.2	80.14658023
28/04/2010	03:40:00	34.6	82.64626873
28/04/2010	03:45:00	33.9	78.30180499
28/04/2010	03:50:00	33.3	74.68887346
28/04/2010	03:55:00	33.3	74.68887346
28/04/2010	04:00:00	34.7	83.27835999
28/04/2010	04:05:00	33	72.92048438
28/04/2010	04:10:00	33.7	77.08617218
28/04/2010	04:15:00	34.8	83.9133274
28/04/2010	04:20:00	33.4	75.28396306
28/04/2010	04:25:00	34.5	82.01704937
28/04/2010	04:30:00	34.7	83.27835999
28/04/2010	04:35:00	36.1	92.43154877
28/04/2010	04:40:00	34.5	82.01704937
28/04/2010	04:45:00	34.2	80.14658023
28/04/2010	04:50:00	34.3	80.76720938
28/04/2010	04:55:00	34.9	84.55117518
28/04/2010	05:00:00	34.6	82.64626873
28/04/2010	05:05:00	34.3	80.76720938
28/04/2010	05:10:00	35.1	85.83552874
28/04/2010	05:15:00	33.7	77.08617218
28/04/2010	05:20:00	34.9	84.55117518
28/04/2010	05:25:00	33.1	73.50713846
28/04/2010	05:30:00	32.4	69.45927317
28/04/2010	05:35:00	33.1	73.50713846
28/04/2010	05:40:00	33.5	75.88187317
28/04/2010	05:45:00	33.6	76.4826081
28/04/2010	05:50:00	32.6	70.6018559
28/04/2010	05:55:00	34.1	79.52880597

28/04/2010	06:00:00	32.9	72.33663344
28/04/2010	06:05:00	33.3	74.68887346
28/04/2010	06:10:00	33.2	74.09660004
28/04/2010	06:15:00	33.5	75.88187317
28/04/2010	06:20:00	33.1	73.50713846
28/04/2010	06:25:00	32.8	71.75558129
28/04/2010	06:30:00	33.9	78.30180499
28/04/2010	06:35:00	33.3	74.68887346
28/04/2010	06:40:00	33.1	73.50713846
28/04/2010	06:45:00	33.5	75.88187317
28/04/2010	06:50:00	33.1	73.50713846
28/04/2010	06:55:00	34	78.91388231
28/04/2010	07:00:00	33.3	74.68887346
28/04/2010	07:05:00	33.9	78.30180499
28/04/2010	07:10:00	34.2	80.14658023
28/04/2010	07:15:00	34	78.91388231
28/04/2010	07:20:00	33.6	76.4826081
28/04/2010	07:25:00	34.1	79.52880597
28/04/2010	07:30:00	33.5	75.88187317
28/04/2010	07:35:00	32.9	72.33663344
28/04/2010	07:40:00	33.4	75.28396306
28/04/2010	07:45:00	34.3	80.76720938
28/04/2010	07:50:00	34.5	82.01704937
28/04/2010	07:55:00	33.7	77.08617218
28/04/2010	08:00:00	34.7	83.27835999
28/04/2010	08:05:00	33.9	78.30180499
28/04/2010	08:10:00	34.7	83.27835999
28/04/2010	08:15:00	33.5	75.88187317
28/04/2010	08:20:00	33.8	77.69256971
28/04/2010	08:25:00	35.4	87.7837673
28/04/2010	08:30:00	34.5	82.01704937
28/04/2010	08:35:00	34.1	79.52880597
28/04/2010	08:40:00	35.2	86.48204296
28/04/2010	08:45:00	33.7	77.08617218
28/04/2010	08:50:00	33.5	75.88187317
28/04/2010	08:55:00	35	85.19190755
28/04/2010	09:00:00	34	78.91388231
28/04/2010	09:05:00	34.9	84.55117518
28/04/2010	09:10:00	33.6	76.4826081
28/04/2010	09:15:00	33.4	75.28396306
28/04/2010	09:20:00	34.3	80.76720938
28/04/2010	09:25:00	34	78.91388231
28/04/2010	09:30:00	33.5	75.88187317
28/04/2010	09:35:00	33.4	75.28396306
28/04/2010	09:40:00	33.5	75.88187317
28/04/2010	09:45:00	33.9	78.30180499

28/04/2010	09:50:00	33.2	74.09660004
28/04/2010	09:55:00	34.6	82.64626873
28/04/2010	10:00:00	33.7	77.08617218
28/04/2010	10:05:00	33.5	75.88187317
28/04/2010	10:10:00	34.1	79.52880597
28/04/2010	10:15:00	35.2	86.48204296
28/04/2010	10:20:00	33.5	75.88187317
28/04/2010	10:25:00	34.1	79.52880597
28/04/2010	10:30:00	34.2	80.14658023
28/04/2010	10:35:00	34.9	84.55117518
28/04/2010	10:40:00	33.5	75.88187317
28/04/2010	10:45:00	34.6	82.64626873
28/04/2010	10:50:00	34	78.91388231
28/04/2010	10:55:00	33.2	74.09660004
28/04/2010	11:00:00	33.9	78.30180499
28/04/2010	11:05:00	34.5	82.01704937
28/04/2010	11:10:00	34.1	79.52880597
28/04/2010	11:15:00	33.1	73.50713846
28/04/2010	11:20:00	33.7	77.08617218
28/04/2010	11:25:00	33.7	77.08617218
28/04/2010	11:30:00	32.8	71.75558129
28/04/2010	11:35:00	33.5	75.88187317
28/04/2010	11:40:00	33.3	74.68887346
28/04/2010	11:45:00	33.5	75.88187317
28/04/2010	11:50:00	33.9	78.30180499
28/04/2010	11:55:00	34.4	81.39069767
28/04/2010	12:00:00	34.3	80.76720938
28/04/2010	12:05:00	33.1	73.50713846
28/04/2010	12:10:00	33.3	74.68887346
28/04/2010	12:15:00	33.5	75.88187317
28/04/2010	12:20:00	31.5	64.45459669
28/04/2010	12:25:00	33.4	75.28396306
28/04/2010	12:30:00	33.7	77.08617218
28/04/2010	12:35:00	32.7	71.17732357
28/04/2010	12:40:00	33.2	74.09660004
28/04/2010	12:45:00	32.9	72.33663344
28/04/2010	12:50:00	32.9	72.33663344
28/04/2010	12:55:00	33.1	73.50713846
28/04/2010	13:00:00	33.4	74.68887346
28/04/2010	13:05:00	34.5	82.01704937

Inflow data for Lambley wetland on 27/04/2010

Channel 1 (Right)

Distance (m)	Depth (m)	Velocity (m/s)	s.d.	vi-1 + vi/2	di-1 +di/2	bi-bi-1	Flow (m^3/s)	Area (m^2)
0	0	0	0	0	0	0	0	0
0.2	0.6	0.139	0.115	0.0695	0.3	0.2	0.00417	0.06
0.4	0.6	0.139	0.055	0.139	0.6	0.2	0.01668	0.12
0.58	0	0	0	0.0695	0.3	0.18	0.003753	0.054
						Flow	0.024603	m^3/s
						Flow	**24.603**	L/s

Channel 2

Distance (m)	Depth (m)	Velocity (m/s)	s.d.	vi-1 + vi/2	di-1 +di/2	bi-bi-1	Flow (m^3/s)	Area (m^2)
0	0	0	0	0	0	0	0	0
0.2	0.6	0.105	0.004	0.0525	0.3	0.2	0.00315	0.06
0.4	0.6	0.39	0.011	0.2475	0.6	0.2	0.0297	0.12
0.61	0	0	0	0.195	0.3	0.21	0.012285	0.063
						Flow	0.045135	m^3/s
						Flow	**45.135**	L/s

Channel 3

Distance (m)	Depth (m)	Velocity (m/s)	s.d.	vi-1 + vi/2	di-1 +di/2	bi-bi-1	Flow (m^3/s)	Area (m^2)
0	0	0	0	0	0	0	0	0
0.2	0.5	0.06	0.012	0.03	0.25	0.2	0.0015	0.05
0.4	0.5	0.01	0.012	0.035	0.5	0.2	0.0035	0.1
0.6	0	0	0	0.005	0.25	0.2	0.00025	0.05
						Flow	0.00525	m^3/s
						Flow	**5.25**	L/s

Channel 4

Distance (m)	Depth (m)	Velocity (m/s)	s.d.	vi-1 + vi/2	di-1 +di/2	bi-bi-1	Flow (m^3/s)	Area (m^2)
0	0	0.024	0	0	0	0	0	0
0.2	0.59	0.012	0.007	0.018	0.295	0.2	0.001062	0.059
0.4	0.59	0.024	0.007	0.018	0.59	0.2	0.002124	0.118
0.6	0	0	0	0.012	0.295	0.2	0.000708	0.059
						Flow	0.003894	m^3/s
						Flow	**3.894**	L/s

Total inflow **78.882** L/s

APPENDIX E

Tracer modelling data (examples from Lambley wetland), modelling data for other treatment site are included in the enclosed CD.

Note:

i. Calculations on moment analysis and the modelling approach are shown as examples.

ii. Data from tracer test at Lambley treatment scheme on July 2008 (bromide, Na-fluorescein and NaCl)

iii. Terms used:

  a. Moment calculation

  M_o = zeroth moment (recovered tracer) $\cong \sum_{i=1}^{n} Q_i\,(t)C_i\,(t)\Delta t$; $Q(t)$ = flow rate (m^3/d); $C(t)$ = tracer concentration(g/m^3)

  M_1= first moment (mean residence time) $\cong \sum_{i=1}^{n} tE_i\,(t)\Delta t$; t = time (d); $E(t)$ = residence time distribution (RTD) (d^{-1})

  M_2 = second moment (variance) $\cong \sum_{i=1}^{n}(t-\tau_m)^2 E_i\,(t)\,\Delta t$; τ_m = tracer mean residence time (d)

  RTD = residence time distribution, $(t) = \frac{Q(t)C(t)}{\int_0^\infty Q(t)C(t)dt}$; $Q(t)$ = flow rate (m^3/d); $C(t\ )$ = tracer concentration (g/m^3)

  b. TIS modelling approach

  Gammadist = Gamma distribution function, $(t) = \frac{1}{\beta^\alpha\,\Gamma(\alpha)}\,t^{\alpha-1} exp\left(-\frac{t}{\beta}\right)$; α (shape parameter) = n = number of tanks-in-series (unitless); β (scaling parameter) = τ_i = mean residence time in one tank (d)

  i. Mean residence time for the whole system, $\tau_m = n\,.\,\tau_i$

  ii. Spread of tracer from the mean (variance), $\sigma^2 = n\,.\,{\tau_i}^2$

  iii. Time for the peak tracer (mode), $\tau_p = (n-1)\tau_i$

  c. Hydraulic performance metric

  i. $e_v = \frac{t_m}{t_n}$

  ii. $eRTD$ = residence time distribution efficiency = $(1 - \sigma_\theta^2)$; σ_θ^2 = dimensionless variance, $\frac{\sigma^2}{{t_m}^2}$

  iii. $e\lambda = ev.eRTD$

iv. Abbreviation:

conc. = concentration
cond. = conductivity
b/c = background concentration
min = minute
VAR = variance
dVAR = dimensionless variance

Lambley August 2008 (Na-fluorescein)

Time elapsed (min)	t (day)	Conc. (ug/L)	Conc. - b/c (ug/L)	Δt (day)	ΔC (ug/L)	Area, CΔt (mg/L.day)	Flow, Q (L/s)	RTD (d^{-1})	M_o QCΔt (g)	M_1 tRTDΔt (d)	M_2 $(t-\tau_m)^2$RTDΔt (d^2)	Gammadist	Error
0	0	0.2	0	0.003472	0	0	67.77	0	0	0	0		
5	0.003472	0.2	0	0.003472	0	0	68.89	0	0	0	0		
10	0.006944	0.2	0	0.003472	0	0	78.3	0	0	0	0		
15	0.010417	0.2	0	0.003472	0	0	75.28	0	0	0	0		
20	0.013889	0.2	0	0.003472	0	0	71.18	0	0	0	0		
25	0.017361	0.2	0	0.003472	0	0	74.1	0	0	0	0		
30	0.020833	0.2	0	0.003472	0	0	70.6	0	0	0	0		
35	0.024306	0.2	0	0.003472	0	0	71.76	0	0	0	0		
40	0.027778	0.2	0	0.003472	0	0	74.1	0	0	0	0		
45	0.03125	0.2	0	0.003472	0	0	71.18	0	0	0	0		
50	0.034722	0.2	0	0.003472	0	0	75.28	0	0	0	0		
55	0.038194	0.2	0	0.003472	0	0	77.69	0	0	0	0		
60	0.041667	0.2	0	0.003472	0	0	70.03	0	0	0	0		
65	0.045139	0.2	0	0.003472	0	0	70.03	0	0	0	0		
70	0.048611	0.2	0	0.003472	0	0	74.1	0	0	0	0		
75	0.052083	0.2	0	0.003472	0	0	82.02	0	0	0	0		
80	0.055556	0.2	0	0.003472	0	0	80.77	0	0	0	0		
85	0.059028	0.2	0	0.003472	0	0	83.28	0	0	0	0		
90	0.0625	0.2	0	0.003472	0	0	82.65	0	0	0	0		
95	0.065972	0.2	0	0.003472	0	0	78.3	0	0	0	0		
100	0.069444	0.2	0	0.003472	0	0	72.34	0	0	0	0		
105	0.072917	0.2	0	0.003472	0	0	75.28	0	0	0	0		

110	0.076389	0.2	0	0.003472	0	0	74.69	0	0	0	0		
115	0.079861	0.2	0	0.003472	0	0	79.53	0	0	0	0		
120	0.083333	0.2	0	0.003472	0	0	77.69	0	0	0	0		
125	0.086806	0.2	0	0.003472	0	0	77.69	0	0	0	0		
130	0.090278	0.2	0	0.003472	0	0	80.77	0	0	0	0		
135	0.09375	0.2	0	0.003472	0	0	83.91	0	0	0	0		
140	0.097222	0.2	0	0.003472	0	0	72.34	0	0	0	0		
145	0.100694	0.2	0	0.003472	0	0	85.19	0	0	0	0		
150	0.104167	0.2	0	0.003472	0	0	85.19	0	0	0	0		
155	0.107639	0.2	0	0.003472	0	0	86.48	0	0	0	0		
160	0.111111	0.2	0	0.003472	0	0	95.15	0	0	0	0		
165	0.114583	0.2	0	0.003472	0	0	85.19	0	0	0	0		
170	0.118056	0.2	0	0.003472	0	0	86.48	0	0	0	0		
175	0.121528	0.2	0	0.003472	0	0	97.92	0	0	0	0		
180	0.125	0.2	0	0.003472	0	0	85.19	0	0	0	0		
185	0.128472	0.2	0	0.003472	0	0	84.55	0	0	0	0		
190	0.131944	0.2	0	0.003472	0	0	89.1	0	0	0	0		
195	0.135417	0.2	0	0.003472	0	0	89.76	0	0	0	0		
200	0.138889	0.2	0	0.003472	0	0	83.28	0	0	0	0		
205	0.142361	0.2	0	0.003472	0	0	81.39	0	0	0	0	0	0
210	0.145833	0.2	0	0.003472	0.05	0.0000868	85.19	0	0.000638884	0	0	1.32418E-06	1.75345E-12
215	0.149306	0.25	0.05	0.003472	0	0.0001736	85.84	0.001988462	0.001287518	1.0308E-06	8.80367E-07	2.41256E-05	3.85862E-06
220	0.152778	0.25	0.05	0.003472	0.04	0.00024304	89.1	0.002063979	0.00187098	1.09483E-06	8.96118E-07	0.000128899	3.74454E-06
225	0.15625	0.29	0.09	0.003472	0	0.00031248	84.55	0.003525444	0.002282704	1.91255E-06	1.50073E-06	0.000416948	9.66274E-06
230	0.159722	0.29	0.09	0.003472	0.05	0.00039928	85.19	0.003552129	0.002938867	1.96985E-06	1.48225E-06	0.001024454	6.38915E-06
235	0.163194	0.34	0.14	0.003472	0.35	0.00109368	91.09	0.005908216	0.008607454	3.34765E-06	2.41628E-06	0.002115252	1.43866E-05
240	0.166667	0.69	0.49	0.003472	-0.1	0.00152768	87.13	0.01977978	0.011500424	1.14459E-05	7.92644E-06	0.0038741	0.000252991

245	0.170139	0.59	0.39	0.003472	0.05	0.00144088	94.47	0.017069318	0.011760762	1.00832E-05	6.70117E-06	0.006497457	0.000111764
250	0.173611	0.64	0.44	0.003472	0.39	0.00220472	93.79	0.019119075	0.017865852	1.15245E-05	7.35167E-06	0.010190015	7.97281E-05
255	0.177083	1.03	0.83	0.003472	0.29	0.0033852	94.47	0.036327011	0.027630707	2.2335E-05	1.36785E-05	0.015157195	0.000448161
260	0.180556	1.32	1.12	0.003472	-0.63	0.00279496	87.13	0.045210925	0.021040548	2.83423E-05	1.66665E-05	0.02160264	0.000557351
265	0.184028	0.69	0.49	0.003472	1.17	0.0037324	85.84	0.019486931	0.027681628	1.24511E-05	7.03136E-06	0.029716102	0.000104636
270	0.1875	1.86	1.66	0.003472	0.79	0.00713496	91.09	0.070054565	0.056153391	4.56055E-05	2.47358E-05	0.039680927	0.000922558
275	0.190972	2.65	2.45	0.003472	-0.49	0.00765576	91.76	0.104154285	0.060695355	6.906E-05	3.59798E-05	0.051664215	0.002755208
280	0.194444	2.16	1.96	0.003472	-0.1	0.00663152	90.42	0.08210663	0.051807344	5.5431E-05	2.77425E-05	0.065816156	0.00026538
285	0.197917	2.06	1.86	0.003472	2.06	0.01003408	90.42	0.077917516	0.078389123	5.35424E-05	2.57442E-05	0.082273374	1.89735E-05
290	0.201389	4.12	3.92	0.003472	0.24	0.01402688	81.39	0.147813727	0.098638367	0.000103355	4.77449E-05	0.101138069	0.002178617
295	0.204861	4.36	4.16	0.003472	1.33	0.0167524	72.34	0.139421416	0.104705448	9.91673E-05	4.40147E-05	0.122505608	0.000286145
300	0.208333	5.69	5.49	0.003472	-2.26	0.01513792	82.02	0.208617032	0.107275294	0.000150899	6.43515E-05	0.146445877	0.003865253
305	0.211806	3.43	3.23	0.003472	-2.84	0.00628432	85.84	0.128454666	0.046608137	9.44643E-05	3.87061E-05	0.173015657	0.001985682
310	0.215278	0.59	0.39	0.003472	5.24	0.01045072	85.19	0.015392561	0.076921647	1.15051E-05	4.52942E-06	0.202227508	0.034907297
315	0.21875	5.83	5.63	0.003472	1.57	0.02227288	83.91	0.21886674	0.16147446	0.000166229	6.28767E-05	0.234096148	0.000231935
320	0.222222	7.4	7.2	0.003472	0.39	0.02567544	83.91	0.279900627	0.186142421	0.000215959	7.84813E-05	0.268609331	0.000127493
325	0.225694	7.79	7.59	0.003472	2.06	0.02992864	79.53	0.279660038	0.205651417	0.000219144	7.65095E-05	0.305735989	0.000679955
330	0.229167	9.85	9.65	0.003472	1.23	0.03564008	86.48	0.386634539	0.266298116	0.000307633	0.000103174	0.345439056	0.001697068
335	0.232639	11.08	10.88	0.003472	1.03	0.03956344	71.76	0.361717049	0.24529586	0.000292167	9.41226E-05	0.387630119	0.000671487
340	0.236111	12.11	11.91	0.003472	-2.11	0.03768856	82.02	0.452573562	0.267081036	0.00037101	0.000114796	0.432239257	0.000413484
345	0.239583	10	9.8	0.003472	2.3	0.0380184	86.48	0.392644402	0.284068618	0.000326614	9.70528E-05	0.479171304	0.007486905
350	0.243056	12.3	12.1	0.003472	2.8	0.046872	81.39	0.456261761	0.329608404	0.000385035	0.000109861	0.528332692	0.005194219
355	0.246528	15.1	14.9	0.003472	-6.37	0.04067448	82.02	0.566191945	0.288240841	0.000484629	0.000132759	0.57957551	0.00017912
360	0.25	8.73	8.53	0.003472	2.5	0.03395616	85.84	0.339231672	0.251838441	0.000294453	7.74309E-05	0.632783824	0.086172866
365	0.253472	11.23	11.03	0.003472	1.12	0.04024048	79.53	0.406409778	0.276508112	0.000357663	9.02692E-05	0.687818977	0.079191138
370	0.256944	12.35	12.15	0.003472	7.5	0.0552048	78.91	0.444187134	0.37637661	0.000396264	9.597E-05	0.744534731	0.090208679
375	0.260417	19.85	19.65	0.003472	-3.58	0.06200992	72.92	0.663845274	0.390680355	0.000600228	0.000139463	0.802795508	0.019307167

380	0.263889	16.27	16.07	0.003472	7.99	0.06966568	85.19	0.634252442	0.512768386	0.000581116	0.000129511	0.862410069	0.052055902
385	0.267361	24.26	24.06	0.003472	-4.21	0.07622776	80.15	0.89342233	0.527874189	0.000829344	0.000177246	0.923233406	0.0008887
390	0.270833	20.05	19.85	0.003472	1.03	0.07070728	74.1	0.681453729	0.452684976	0.000640793	0.000131295	0.98510115	0.092201757
395	0.274306	21.08	20.88	0.003472	-0.25	0.07206136	72.34	0.69978826	0.450396183	0.000666472	0.000130881	1.047865376	0.121157679
400	0.277778	20.83	20.63	0.003472	6.62	0.08311968	77.09	0.736809008	0.553624946	0.000710612	0.000133713	1.111323052	0.140260769
405	0.28125	27.45	27.25	0.003472	1.32	0.09690352	71.18	0.898632546	0.595951997	0.000877515	0.000158164	1.175325484	0.076558982
410	0.284722	28.77	28.57	0.003472	5.45	0.10865624	75.28	0.996431628	0.706721047	0.000985027	0.00017001	1.239707088	0.059182949
415	0.288194	34.22	34.02	0.003472	0.29	0.11862088	82.65	1.302671226	0.847066959	0.001303465	0.000215353	1.30430415	2.66644E-06
420	0.291667	34.51	34.31	0.003472	4.21	0.12643288	70.6	1.122233096	0.771220339	0.001136449	0.000179665	1.368974177	0.060881161
425	0.295139	38.72	38.52	0.003472	0.74	0.13502608	72.92	1.301339439	0.850703192	0.001333512	0.000201656	1.43352206	0.017472245
430	0.298611	39.46	39.26	0.003472	3.63	0.1426124	77.69	1.413100565	0.957273756	0.001465071	0.000211836	1.497812476	0.007176108
435	0.302083	43.09	42.89	0.003472	1.22	0.151032	74.69	1.484144404	0.974642119	0.001556618	0.000215113	1.561695909	0.006014236
440	0.305556	44.31	44.11	0.003472	0.89	0.15469496	72.92	1.490189061	0.9746228	0.001580927	0.000208709	1.625045903	0.018186368
445	0.309028	45.2	45	0.003472	3.03	0.16150008	77.09	1.607193668	1.075683557	0.001724431	0.000217381	1.687686673	0.006479124
450	0.3125	48.23	48.03	0.003472	1.13	0.16872184	72.34	1.609714086	1.054541195	0.00174654	0.000210129	1.749502976	0.019540934
455	0.315972	49.36	49.16	0.003472	3.83	0.1773324	74.1	1.687670797	1.135324585	0.001851467	0.000212487	1.810367257	0.015054421
460	0.319444	53.19	52.99	0.003472	1.27	0.186186	72.92	1.790186315	1.173025422	0.001985513	0.00021725	1.870158231	0.006395507
465	0.322917	54.46	54.26	0.003472	1.91	0.19170648	77.69	1.953001443	1.286813644	0.002189642	0.000228285	1.928777794	0.000586785
470	0.326389	56.37	56.17	0.003472	2.26	0.1989456	77.69	2.021748822	1.335405629	0.002291091	0.000227461	1.986084012	0.001271979
475	0.329861	58.63	58.43	0.003472	1.52	0.20550768	77.09	2.08685169	1.368799521	0.002390024	0.000225816	2.041992563	0.002012341
480	0.333333	60.15	59.95	0.003472	1.56	0.21085456	74.69	2.074480229	1.36069002	0.002400863	0.000215735	2.096408919	0.000480867
485	0.336806	61.71	61.51	0.003472	2.99	0.21875336	76.48	2.179471828	1.445494202	0.002548654	0.000217648	2.149260431	0.000912728
490	0.340278	64.7	64.5	0.003472	5.1	0.2327976	70.6	2.109706636	1.420028112	0.002492503	0.000202143	2.20043592	0.008231803
495	0.34375	69.8	69.6	0.003472	-2.15	0.2379188	75.28	2.427428817	1.547469556	0.002897136	0.000222965	2.249876991	0.031524651
500	0.347222	67.65	67.45	0.003472	-0.49	0.23333576	76.48	2.389942689	1.541852835	0.002881207	0.00021025	2.297516632	0.008542576
505	0.350694	67.16	66.96	0.003472	0.83	0.233926	77.09	2.391504178	1.558081901	0.002911918	0.00020131	2.343294577	0.002324166
510	0.354167	67.99	67.79	0.003472	4.85	0.24378648	86.48	2.716057552	1.821541374	0.003339849	0.000218544	2.38716956	0.108167311

515	0.357639	72.84	72.64	0.003472	3.09	0.25757032	88.44	2.976337819	1.96815045	0.003695786	0.000228688	2.429069206	0.299502935
520	0.361111	75.93	75.73	0.003472	-5.34	0.25366432	77.09	2.704728366	1.689550482	0.003391127	0.000198231	2.468965705	0.055584033
525	0.364583	70.59	70.39	0.003472	10.93	0.26336856	83.91	2.736417377	1.909375707	0.003463845	0.000191083	2.506824549	0.052712866
530	0.368056	81.52	81.32	0.003472	-9.46	0.26592048	67.77	2.553245111	1.557051632	0.003262767	0.000169667	2.542627274	0.000112738
535	0.371528	72.06	71.86	0.003472	6.32	0.26046944	68.89	2.29351218	1.550339112	0.002958505	0.000144853	2.57633063	0.079986276
540	0.375	78.38	78.18	0.003472	0.39	0.272118	78.3	2.836057825	1.840910924	0.003692547	0.000170016	2.607928242	0.052043107
545	0.378472	78.77	78.57	0.003472	1.67	0.27569416	75.28	2.740274169	1.79316775	0.00360087	0.000155707	2.637408557	0.010581334
550	0.381944	80.44	80.24	0.003472	-4.71	0.27041672	71.18	2.646101854	1.663049848	0.003509021	0.000142306	2.664765238	0.000348322
555	0.385417	75.73	75.53	0.003472	1.92	0.26557328	74.1	2.592957186	1.700263876	0.003469812	0.000131773	2.690003896	0.009418064
560	0.388889	77.65	77.45	0.003472	2.89	0.27392344	70.6	2.533283395	1.670889156	0.003420497	0.000121458	2.713113403	0.032338832
565	0.392361	80.54	80.34	0.003472	6.52	0.2902592	71.76	2.670987839	1.799625617	0.003638626	0.000120604	2.734109265	0.003984314
570	0.395833	87.06	86.86	0.003472	-6.52	0.2902592	74.1	2.98191793	1.858309061	0.004098146	0.00012657	2.753003703	0.052401723
575	0.399306	80.54	80.34	0.003472	2.15	0.28267288	71.18	2.649399588	1.738424644	0.003673102	0.000105502	2.769817532	0.014500481
580	0.402778	82.69	82.49	0.003472	-2.1	0.28275968	75.28	2.876991424	1.839123249	0.004023315	0.000107257	2.784561163	0.008543353
585	0.40625	80.59	80.39	0.003472	-4.61	0.27111112	77.69	2.893508773	1.81981062	0.004081294	0.000100765	2.797263407	0.009263171
590	0.409722	75.98	75.78	0.003472	6.03	0.27357624	70.03	2.458648139	1.655298209	0.003497562	7.97878E-05	2.807951279	0.122012683
595	0.413194	82.01	81.81	0.003472	1.37	0.28642264	70.03	2.654288787	1.733026534	0.003807868	8.0061E-05	2.816654912	0.026362759
600	0.416667	83.38	83.18	0.003472	-2.45	0.28454776	74.1	2.855582931	1.821743051	0.00413108	7.98334E-05	2.823408996	0.001035162
605	0.420139	80.93	80.73	0.003472	-2.06	0.2767184	82.02	3.067696358	1.96097269	0.004474918	7.92551E-05	2.828245338	0.057336791
610	0.423611	78.87	78.67	0.003472	-0.59	0.272118	80.77	2.943858195	1.898983082	0.00432976	7.00564E-05	2.831204298	0.012690901
615	0.427083	78.28	78.08	0.003472	-6.52	0.25977504	83.28	3.012577128	1.869183245	0.004467146	6.58047E-05	2.832326245	0.032490381
620	0.430556	71.76	71.56	0.003472	0.54	0.24939376	82.65	2.740127953	1.780910864	0.004096191	5.47268E-05	2.83165313	0.008376858
625	0.434028	72.3	72.1	0.003472	8.63	0.26531288	78.3	2.615499733	1.794873471	0.003941415	4.75645E-05	2.829229572	0.045680444
630	0.4375	80.93	80.73	0.003472	-8.97	0.26472264	72.34	2.705646849	1.654563091	0.004109878	4.45961E-05	2.825101486	0.01426941
635	0.440972	71.96	71.76	0.003472	15.29	0.27569416	75.28	2.502762815	1.79316775	0.003831867	3.71993E-05	2.819316166	0.100206024
640	0.444444	87.25	87.05	0.003472	-12.01	0.28138824	74.69	3.012235262	1.815859093	0.004648209	4.01461E-05	2.811922163	0.040125338
645	0.447917	75.24	75.04	0.003472	4.12	0.2676912	79.53	2.764912941	1.83941117	0.004299904	3.28344E-05	2.802966315	0.001448059

650	0.451389	79.36	79.16	0.003472	-4.7	0.26668432	77.69	2.849236901	1.790096097	0.004465388	2.99376E-05	2.792504344	0.003218583
655	0.454861	74.66	74.46	0.003472	-1.87	0.2552788	77.69	2.680067959	1.713537502	0.004232571	2.47177E-05	2.780585201	0.010103716
660	0.458333	72.79	72.59	0.003472	2.4	0.25619888	80.77	2.716342525	1.787891058	0.004322603	2.17906E-05	2.767260796	0.00259267
665	0.461806	75.19	74.99	0.003472	-3.43	0.2544108	83.91	2.915242777	1.844433524	0.004674272	2.01288E-05	2.752579077	0.026459479
670	0.465278	71.76	71.56	0.003472	7.36	0.26123328	72.34	2.398316469	1.632753977	0.003874349	1.40814E-05	2.736601194	0.114436556
675	0.46875	79.12	78.92	0.003472	-7.36	0.26123328	85.19	3.114822823	1.922785614	0.005069374	1.53305E-05	2.719375979	0.156378206
680	0.472222	71.76	71.56	0.003472	-4.46	0.24071376	85.19	2.824337572	1.771753411	0.004630656	1.14553E-05	2.700956359	0.015222924
685	0.475694	67.3	67.1	0.003472	3.04	0.23824864	86.48	2.688412181	1.780163342	0.004440207	8.80114E-06	2.681395204	4.9238E-05
690	0.479167	70.34	70.14	0.003472	-11.71	0.22319752	95.15	3.091948186	1.834897884	0.005143975	7.96199E-06	2.660739118	0.18594126
695	0.482639	58.63	58.43	0.003472	5.44	0.2123128	85.19	2.306121357	1.56271053	0.00386442	4.52078E-06	2.63905244	0.110843106
700	0.486111	64.07	63.87	0.003472	-0.39	0.2210796	86.48	2.558999791	1.651878473	0.004319022	3.6576E-06	2.616381439	0.003292654
705	0.489583	63.68	63.48	0.003472	0.34	0.2209928	97.92	2.879824195	1.869662734	0.004895218	2.82796E-06	2.59277772	0.082395679
710	0.493056	64.02	63.82	0.003472	5.44	0.23102688	85.19	2.518854442	1.700453944	0.004312003	1.55738E-06	2.568285167	0.002443397
715	0.496528	69.46	69.26	0.003472	-9.26	0.22439536	84.55	2.71302473	1.639235032	0.004677106	9.18113E-07	2.54296834	0.028919176
720	0.5	60.2	60	0.003472	5.09	0.21715624	89.1	2.476775299	1.671720853	0.004299682	3.52295E-07	2.516870057	0.00160759
725	0.503472	65.29	65.09	0.003472	-2.35	0.22191288	89.76	2.70679128	1.720992969	0.004731619	8.06034E-08	2.490039307	0.046981418
730	0.506944	62.94	62.74	0.003472	2.26	0.22175664	83.28	2.420710668	1.595625953	0.004260716	2.48182E-09	2.462524262	0.001748377
735	0.510417	65.2	65	0.003472	-4.02	0.21870128	81.39	2.45099293	1.537928396	0.004343571	1.37277E-07	2.434364022	0.000276521
740	0.513889	61.18	60.98	0.003472	-3.98	0.20481328	85.19	2.406765024	1.507510943	0.004294205	4.68589E-07	2.40562119	1.30836E-06
745	0.517361	57.2	57	0.003472	2.65	0.2025044	85.84	2.266847049	1.501889273	0.004071886	9.45486E-07	2.376333152	0.011987207
750	0.520833	59.85	59.65	0.003472	-8.77	0.19188008	89.1	2.462327443	1.477138907	0.004452706	1.78075E-06	2.346544308	0.013405734
755	0.524306	51.08	50.88	0.003472	6.62	0.18814768	84.55	1.993050798	1.37444138	0.003628131	2.21854E-06	2.316289241	0.104483091
760	0.527778	57.7	57.5	0.003472	-7.46	0.18668944	85.19	2.26941602	1.374111941	0.004158581	3.60084E-06	2.285627668	0.000262818
765	0.53125	50.24	50.04	0.003472	2.6	0.17825248	91.09	2.111765334	1.40287839	0.003895151	4.52749E-06	2.254592126	0.020399492
770	0.534722	52.84	52.64	0.003472	2.99	0.18795672	87.13	2.124913462	1.414944203	0.003945018	5.91767E-06	2.223222677	0.009664702
775	0.538194	55.83	55.63	0.003472	-5.93	0.18285288	94.47	2.434785062	1.49248324	0.004549663	8.54505E-06	2.191558244	0.059159285
780	0.541667	49.9	49.7	0.003472	1.67	0.17545752	93.79	2.159586371	1.421812293	0.004061465	9.32551E-06	2.159627368	1.68082E-09

785	0.545139	51.57	51.37	0.003472	-3.63	0.17205496	94.47	2.248335586	1.404348371	0.004255476	1.17145E-05	2.127485047	0.014604853
790	0.548611	47.94	47.74	0.003472	3.24	0.17137792	87.13	1.927115666	1.290138466	0.003670726	1.19214E-05	2.095157547	0.028238074
795	0.552083	51.18	50.98	0.003472	-3.24	0.17137792	85.84	2.027436185	1.271037368	0.003886255	1.46901E-05	2.062679115	0.001242064
800	0.555556	47.94	47.74	0.003472	-3.63	0.1594516	91.09	2.01470178	1.254912155	0.003886139	1.69018E-05	2.030073412	0.000236287
805	0.559028	44.31	44.11	0.003472	3.19	0.15868776	91.76	1.875202252	1.258086717	0.003639665	1.80323E-05	1.997391104	0.014930115
810	0.5625	47.5	47.3	0.003472	-6.13	0.15358392	90.42	1.981450816	1.199841815	0.003869773	2.16511E-05	1.96465352	0.000282149
815	0.565972	41.37	41.17	0.003472	4.71	0.1511188	90.42	1.724658142	1.180583588	0.003389048	2.125E-05	1.931890189	0.042945121
820	0.569444	46.08	45.88	0.003472	-4.51	0.151466	81.39	1.730023932	1.065123453	0.003420447	2.38732E-05	1.899129471	0.028596683
825	0.572917	41.57	41.37	0.003472	4.9	0.15214304	72.34	1.386505762	0.950920777	0.002757993	2.1299E-05	1.866389151	0.230288067
830	0.576389	46.47	46.27	0.003472	-8.43	0.14601496	82.02	1.758234987	1.034739102	0.00351862	2.99026E-05	1.833714145	0.005697103
835	0.579861	38.04	37.84	0.003472	1.37	0.1337588	85.84	1.504868287	0.992032306	0.003029717	2.81958E-05	1.801119946	0.087765046
840	0.583333	39.41	39.21	0.003472	0.3	0.13665792	85.19	1.547544385	1.005859141	0.003134291	3.1801E-05	1.768630359	0.048879008
845	0.586806	39.71	39.51	0.003472	0.29	0.13768216	83.91	1.535954689	0.998171428	0.003129339	3.44769E-05	1.736258786	0.040121731
850	0.590278	40	39.8	0.003472	1.86	0.14141456	83.91	1.547228464	1.025230671	0.00317096	3.77941E-05	1.704045491	0.02459158
855	0.59375	41.86	41.66	0.003472	0.3	0.14516432	79.53	1.534998309	0.997480947	0.003164399	4.06638E-05	1.672001683	0.018769925
860	0.597222	42.16	41.96	0.003472	-9.66	0.12891536	86.48	1.681159092	0.963239069	0.003485975	4.81465E-05	1.640146865	0.001682003
865	0.600694	32.5	32.3	0.003472	3.38	0.11801328	71.76	1.073847488	0.731689889	0.002239627	3.31501E-05	1.608499512	0.285852786
870	0.604167	35.88	35.68	0.003472	-2.16	0.1201312	82.02	1.355820712	0.851313112	0.002844061	4.49947E-05	1.577068076	0.048950396
875	0.607639	33.72	33.52	0.003472	0.1	0.11655504	86.48	1.343004118	0.87088434	0.002833366	4.77912E-05	1.545887148	0.041161524
880	0.611111	33.82	33.62	0.003472	2.16	0.1204784	81.39	1.267728958	0.847215675	0.002689839	4.82598E-05	1.514963169	0.061124755
885	0.614583	35.98	35.78	0.003472	-0.74	0.12294352	82.02	1.359620658	0.871242697	0.002901202	5.52473E-05	1.484310725	0.015547613
890	0.618056	35.24	35.04	0.003472	-3.23	0.1160516	85.84	1.393514396	0.860705511	0.002990329	6.03185E-05	1.453934786	0.003650623
895	0.621528	32.01	31.81	0.003472	-4.22	0.1031184	79.53	1.17206664	0.708566949	0.002529256	5.39373E-05	1.423865628	0.063402731
900	0.625	27.79	27.59	0.003472	3.68	0.10218096	78.91	1.0086521	0.696651801	0.002188775	4.92591E-05	1.394106382	0.148575003
905	0.628472	31.47	31.27	0.003472	-0.54	0.107632	72.92	1.056409248	0.678112598	0.002305143	5.46562E-05	1.364668124	0.095023534
910	0.631944	30.93	30.73	0.003472	0.83	0.10813544	85.19	1.212854857	0.795921823	0.002661136	6.63707E-05	1.335561113	0.015056825
915	0.635417	31.76	31.56	0.003472	-1.42	0.1071112	80.15	1.171920563	0.741740776	0.002585453	6.77279E-05	1.306786584	0.018188844

920	0.638889	30.34	30.14	0.003472	-1.47	0.10209416	67.77	0.946320802	0.597794794	0.00209915	5.76732E-05	1.278369813	0.110256545
925	0.642361	28.87	28.67	0.003472	1.57	0.10226776	68.89	0.915043059	0.608707525	0.0020408	5.87281E-05	1.250310425	0.112404207
930	0.645833	30.44	30.24	0.003472	-1.37	0.10261496	78.3	1.096986296	0.694202518	0.002459808	7.40472E-05	1.222615667	0.015782739
935	0.649306	29.07	28.87	0.003472	-4.51	0.09240728	75.28	1.006894683	0.601034691	0.002269934	7.13939E-05	1.195284278	0.035490639
940	0.652778	24.56	24.36	0.003472	2.4	0.08874432	71.18	0.80332803	0.545773308	0.001820699	5.97614E-05	1.168337883	0.133232193
945	0.65625	26.96	26.76	0.003472	-1.23	0.09077544	74.1	0.918675153	0.581166153	0.002093201	7.16229E-05	1.141773805	0.049773008
950	0.659722	25.73	25.53	0.003472	2.01	0.09212952	70.6	0.835051324	0.561975331	0.001912731	6.81551E-05	1.115596669	0.07870569
955	0.663194	27.74	27.54	0.003472	-2.84	0.09068864	71.76	0.91559628	0.562275372	0.002108261	7.81519E-05	1.089810506	0.030350597
960	0.666667	24.9	24.7	0.003472	1.37	0.08813672	74.1	0.847955018	0.564272434	0.001962734	7.56201E-05	1.06441152	0.046853417
965	0.670139	26.27	26.07	0.003472	-1.71	0.08754648	71.18	0.859719284	0.53840665	0.002000328	8.00272E-05	1.039417252	0.03229136
970	0.673611	24.56	24.36	0.003472	4.36	0.09214688	75.28	0.849600086	0.599341	0.001987025	8.24747E-05	1.014822718	0.027298518
975	0.677083	28.92	28.72	0.003472	-5.24	0.0906192	77.69	1.033730215	0.608273768	0.002430126	0.00010456	0.990629804	0.001857645
980	0.680556	23.68	23.48	0.003472	0.05	0.08160936	70.03	0.761798077	0.493784941	0.001800045	8.0222E-05	0.966833122	0.042039369
985	0.684028	23.73	23.53	0.003472	-0.05	0.08160936	70.03	0.763420305	0.493784941	0.001813081	8.36302E-05	0.943447321	0.032409727
990	0.6875	23.68	23.48	0.003472	-2.16	0.0777728	74.1	0.806072219	0.497920131	0.001924094	9.17884E-05	0.920466001	0.013085937
995	0.690972	21.52	21.32	0.003472	2.16	0.0777728	82.02	0.810148475	0.551139125	0.001943591	9.58238E-05	0.897889253	0.007698444
1000	0.694444	23.68	23.48	0.003472	-0.59	0.08049832	80.77	0.878629597	0.56175978	0.002118472	0.00010787	0.875716775	8.48454E-06
1005	0.697917	23.09	22.89	0.003472	-2.06	0.07589792	83.28	0.883169704	0.546115286	0.002140068	0.00011247	0.853941673	0.000854278
1010	0.701389	21.03	20.83	0.003472	-1.08	0.07044688	82.65	0.797608514	0.503058352	0.001942354	0.00010529	0.832575448	0.001222686
1015	0.704861	19.95	19.75	0.003472	0.1	0.0687456	78.3	0.716451037	0.465072233	0.001753354	9.79747E-05	0.811610397	0.009055304
1020	0.708333	20.05	19.85	0.003472	0.78	0.07027328	72.34	0.665268053	0.439220368	0.001636115	9.41864E-05	0.791044824	0.015819796
1025	0.711806	20.83	20.63	0.003472	1.13	0.07358904	75.28	0.719509432	0.478637245	0.001778189	0.0001054	0.770870977	0.002638008
1030	0.715278	21.96	21.76	0.003472	-1.67	0.0726516	74.69	0.752972307	0.468836468	0.001869965	0.000114062	0.75109819	3.51231E-06
1035	0.71875	20.29	20.09	0.003472	-1.61	0.06695752	79.53	0.740233222	0.460091367	0.001847252	0.000115891	0.731718045	7.25082E-05
1040	0.722222	18.68	18.48	0.003472	1.32	0.06645408	77.69	0.665157882	0.44606743	0.00166792	0.000107571	0.712727739	0.002262891
1045	0.725694	20	19.8	0.003472	-2.55	0.0643188	77.69	0.712669159	0.431734542	0.001795648	0.000118992	0.694124231	0.000343914
1050	0.729167	17.45	17.25	0.003472	1.08	0.06176688	80.77	0.645500875	0.431041902	0.001634194	0.000111218	0.675899069	0.00092405

1055	0.732639	18.53	18.33	0.003472	0.34	0.064232	83.91	0.712580345	0.465670695	0.001812607	0.000126633	0.65805928	0.002972547
1060	0.736111	18.87	18.67	0.003472	-0.64	0.0637112	72.34	0.625720633	0.398206213	0.001599203	0.000114636	0.640595903	0.000221274
1065	0.739583	18.23	18.03	0.003472	-1.22	0.06048224	85.19	0.711609928	0.445174447	0.001827295	0.000134342	0.623505101	0.00776246
1070	0.743056	17.01	16.81	0.003472	1.03	0.0601524	85.19	0.66345884	0.442746687	0.001711651	0.000129011	0.606778111	0.003212705
1075	0.746528	18.04	17.84	0.003472	-1.13	0.0599788	86.48	0.714773075	0.448153916	0.001852653	0.000143097	0.590420411	0.015463585
1080	0.75	16.91	16.71	0.003472	-0.15	0.05775672	95.15	0.736618965	0.474815685	0.001918156	0.000151766	0.574422838	0.026307583
1085	0.753472	16.76	16.56	0.003472	0.2	0.05784352	85.19	0.653591814	0.42575237	0.001709832	0.000138526	0.558780974	0.008989095
1090	0.756944	16.96	16.76	0.003472	-0.15	0.05793032	86.48	0.671502059	0.432847936	0.001764781	0.00014635	0.543490282	0.016387015
1095	0.760417	16.81	16.61	0.003472	-0.88	0.05614224	97.92	0.753526778	0.474979519	0.001989437	0.000168811	0.528541865	0.050618211
1100	0.763889	15.93	15.73	0.003472	0.1	0.05478816	85.19	0.620833287	0.403263649	0.001646588	0.000142912	0.513939594	0.011426262
1105	0.767361	16.03	15.83	0.003472	-0.74	0.05367712	84.55	0.620086363	0.392117803	0.001652082	0.000146616	0.499674294	0.014499066
1110	0.770833	15.29	15.09	0.003472	-0.05	0.05230568	89.1	0.622908988	0.402661678	0.001667111	0.000151229	0.485741069	0.018815038
1115	0.774306	15.24	15.04	0.003472	0	0.05221888	89.76	0.62544386	0.4049712	0.001681437	0.000155859	0.472131084	0.023504807
1120	0.777778	15.24	15.04	0.003472	0.15	0.05247928	83.28	0.580291496	0.377608991	0.001567045	0.000148379	0.458847157	0.014748727
1125	0.78125	15.39	15.19	0.003472	-0.39	0.05206264	81.39	0.572778194	0.366109482	0.001553661	0.00015023	0.445880253	0.016103087
1130	0.784722	15	14.8	0.003472	-1.18	0.04933712	85.19	0.584127949	0.363141727	0.001591489	0.000157102	0.433225264	0.02277162
1135	0.788194	13.82	13.62	0.003472	1.13	0.04925032	85.84	0.541657137	0.365268741	0.001482304	0.000149336	0.420877049	0.01458783
1140	0.791667	14.95	14.75	0.003472	-1.32	0.04892048	89.1	0.608873928	0.376601596	0.001673592	0.000172032	0.408827012	0.040018769
1145	0.795139	13.63	13.43	0.003472	-0.2	0.04628176	84.55	0.526074532	0.338093811	0.001452346	0.000152278	0.397076905	0.016640388
1150	0.798611	13.43	13.23	0.003472	0.44	0.0466984	85.19	0.522163025	0.343719651	0.001447842	0.000154802	0.385618018	0.018644539
1155	0.802083	13.87	13.67	0.003472	-0.73	0.04619496	91.09	0.576895126	0.363562466	0.001606556	0.000175117	0.374445145	0.040985995
1160	0.805556	13.14	12.94	0.003472	-0.15	0.04466728	87.13	0.522347648	0.336256713	0.001460949	0.000162305	0.363549984	0.025216698
1165	0.809028	12.99	12.79	0.003472	-0.05	0.04432008	94.47	0.559786104	0.361749712	0.001572408	0.000177999	0.352933608	0.042787955
1170	0.8125	12.94	12.74	0.003472	-1.37	0.04185496	93.79	0.553584112	0.339169827	0.001561661	0.000180089	0.342587652	0.044519506
1175	0.815972	11.57	11.37	0.003472	0.68	0.04065712	94.47	0.497636278	0.33185187	0.001409831	0.000165582	0.332506941	0.027267698
1180	0.819444	12.25	12.05	0.003472	-0.78	0.04048352	87.13	0.48642111	0.304761234	0.001383921	0.000165501	0.322686322	0.026809081
1185	0.822917	11.47	11.27	0.003472	0.69	0.04032728	85.84	0.448199408	0.299090337	0.001280581	0.000155899	0.313117948	0.018247001

1190	0.826389	12.16	11.96	0.003472	-0.2	0.04117792	91.09	0.504730484	0.324077478	0.001448184	0.000179435	0.303802229	0.040372163
1195	0.829861	11.96	11.76	0.003472	-0.69	0.03963288	91.76	0.499940569	0.314212009	0.001440467	0.00018161	0.294731305	0.042110842
1200	0.833333	11.27	11.07	0.003472	0.05	0.03852184	90.42	0.463734895	0.300943708	0.001341739	0.000172094	0.285900146	0.031625198
1205	0.836806	11.32	11.12	0.003472	-0.58	0.03760176	90.42	0.465829452	0.293755778	0.001353416	0.000176564	0.277301318	0.035542857
1210	0.840278	10.74	10.54	0.003472	-0.54	0.03565744	81.39	0.39743793	0.250746541	0.001159503	0.000153824	0.268934823	0.016513049
1215	0.84375	10.2	10	0.003472	0	0.03472	72.34	0.335147634	0.217006111	0.000981815	0.000132427	0.260793248	0.005528575
1220	0.847222	10.2	10	0.003472	0.78	0.03607408	82.02	0.379994594	0.255639978	0.001117775	0.000153254	0.25287174	0.01616022
1225	0.850694	10.98	10.78	0.003472	-0.44	0.03666432	85.84	0.428712477	0.271923716	0.001266249	0.000176443	0.245165494	0.033689495
1230	0.854167	10.54	10.34	0.003472	-0.44	0.03513664	85.19	0.408100203	0.258620287	0.00121029	0.000171365	0.237667631	0.029047262
1235	0.857639	10.1	9.9	0.003472	0	0.0343728	83.91	0.384863362	0.24919675	0.001146016	0.000164851	0.230377772	0.023865798
1240	0.861111	10.1	9.9	0.003472	0	0.0343728	83.91	0.384863362	0.24919675	0.001150656	0.000168126	0.22328909	0.026106245
1245	0.864583	10.1	9.9	0.003472	-0.59	0.03334856	79.53	0.364773962	0.229151028	0.00109499	0.000162485	0.216397006	0.022015721
1250	0.868056	9.51	9.31	0.003472	0	0.03232432	86.48	0.373012182	0.241523182	0.001124218	0.000169392	0.209695099	0.02667247
1255	0.871528	9.51	9.31	0.003472	1.37	0.03470264	71.76	0.309520747	0.215158589	0.000936593	0.000143271	0.203182769	0.011307765
1260	0.875	10.88	10.68	0.003472	-1.57	0.03435544	82.02	0.405834226	0.243460788	0.001232924	0.000191442	0.196853668	0.043672874
1265	0.878472	9.31	9.11	0.003472	-0.63	0.03053624	86.48	0.364999031	0.228162877	0.001113267	0.000175438	0.190703464	0.030378945
1270	0.881944	8.68	8.48	0.003472	0.54	0.03038	81.39	0.319760308	0.213635076	0.000979141	0.000156576	0.184727894	0.018233753
1275	0.885417	9.22	9.02	0.003472	-0.94	0.0296856	82.02	0.342755124	0.210367836	0.001053687	0.000170954	0.178921113	0.026841583
1280	0.888889	8.28	8.08	0.003472	0.15	0.02831416	85.84	0.321335511	0.20999412	0.000991713	0.000163221	0.173282331	0.021919744
1285	0.892361	8.43	8.23	0.003472	-0.54	0.02763712	79.53	0.303241385	0.189905485	0.000939526	0.000156839	0.16780579	0.0183428
1290	0.895833	7.89	7.69	0.003472	0.3	0.02722048	78.91	0.281135725	0.185584442	0.000874425	0.000148033	0.162487494	0.014077403
1295	0.899306	8.19	7.99	0.003472	-0.2	0.02739408	72.92	0.269929961	0.172590593	0.000842827	0.000144679	0.157322049	0.012680542
1300	0.902778	7.99	7.79	0.003472	0.39	0.02772392	85.19	0.307456536	0.204059584	0.000963706	0.000167719	0.152308572	0.024070891
1305	0.90625	8.38	8.18	0.003472	-0.54	0.02746352	80.15	0.303748739	0.190183777	0.000955745	0.000168611	0.147441762	0.024431871
1310	0.909722	7.84	7.64	0.003472	-0.05	0.02643928	74.1	0.262282443	0.169270616	0.000828433	0.000148133	0.142717901	0.01429568
1315	0.913194	7.79	7.59	0.003472	-0.14	0.02610944	72.34	0.254377054	0.163188595	0.00080653	0.000146152	0.138133334	0.013512602
1320	0.916667	7.65	7.45	0.003472	-0.2	0.0255192	77.09	0.266079841	0.169972571	0.000846844	0.000155498	0.133683219	0.017528865

1325	0.920139	7.45	7.25	0.003472	0.25	0.025606	71.18	0.239085723	0.157475671	0.000763813	0.000142097	0.129366602	0.012038285
1330	0.923611	7.7	7.5	0.003472	-0.35	0.0254324	75.28	0.261576381	0.165417213	0.000838817	0.000158084	0.125178738	0.018604317
1335	0.927083	7.35	7.15	0.003472	0.05	0.0249116	82.65	0.273783047	0.177892739	0.000881262	0.000168227	0.12111625	0.023307151
1340	0.930556	7.4	7.2	0.003472	-0.78	0.02364432	70.6	0.235502136	0.144226569	0.000760882	0.000147104	0.11717471	0.01400138
1345	0.934028	6.62	6.42	0.003472	0.44	0.02305408	72.92	0.216889906	0.145247344	0.000703362	0.000137705	0.113353147	0.010719861
1350	0.9375	7.06	6.86	0.003472	0.19	0.02414776	77.69	0.246914668	0.162089811	0.000803707	0.000159324	0.109647233	0.018842349
1355	0.940972	7.25	7.05	0.003472	-0.34	0.02388736	74.69	0.243954723	0.154150294	0.000797013	0.00015996	0.106053862	0.019016647
1360	0.944444	6.91	6.71	0.003472	-0.05	0.02321032	72.92	0.226687114	0.146231701	0.000743332	0.000151022	0.102569991	0.01540506
1365	0.947917	6.86	6.66	0.003472	-0.1	0.02294992	77.09	0.237864663	0.152859686	0.000782853	0.000160992	0.099191686	0.019230194
1370	0.951389	6.76	6.56	0.003472	-0.29	0.02227288	72.34	0.219856848	0.13920942	0.000726236	0.000151153	0.095917982	0.015360842
1375	0.954861	6.47	6.27	0.003472	-0.24	0.0213528	74.1	0.21525012	0.13670575	0.000713614	0.000150304	0.092745043	0.015007494
1380	0.958333	6.23	6.03	0.003472	0.73	0.02220344	72.92	0.203714351	0.139888067	0.000677825	0.00014446	0.089670086	0.013006094
1385	0.961806	6.96	6.76	0.003472	-0.83	0.02202984	77.69	0.243315329	0.14787345	0.000812525	0.000175205	0.086689546	0.024531636
1390	0.965278	6.13	5.93	0.003472	0.1	0.02076256	77.69	0.213440814	0.13936694	0.000715335	0.000156045	0.083802479	0.016806098
1395	0.96875	6.23	6.03	0.003472	0.04	0.0210056	77.09	0.215363952	0.139909395	0.000724377	0.000159843	0.081005416	0.018052216
1400	0.972222	6.27	6.07	0.003472	-0.49	0.0202244	74.69	0.210043286	0.130512422	0.000709013	0.000158244	0.078295821	0.017357395
1405	0.975694	5.78	5.58	0.003472	0.1	0.01954736	76.48	0.197715051	0.129166453	0.000669781	0.000151185	0.075671215	0.014894698
1410	0.979167	5.88	5.68	0.003472	0.15	0.01998136	70.6	0.185785019	0.121883099	0.000631607	0.000144173	0.073128461	0.0126915
1415	0.982639	6.03	5.83	0.003472	-0.44	0.01947792	75.28	0.20333204	0.126688131	0.000693713	0.000160116	0.07066666	0.017600103
1420	0.986111	5.59	5.39	0.003472	0.15	0.01897448	76.48	0.190982818	0.125380935	0.000653883	0.000152592	0.068282765	0.015055303
1425	0.989583	5.74	5.54	0.003472	-0.05	0.01914808	77.09	0.197863398	0.127537242	0.000679825	0.000160386	0.065974529	0.017394674
1430	0.993056	5.69	5.49	0.003472	-0.05	0.01897448	86.48	0.219960997	0.141774886	0.000758401	0.000180871	0.063739125	0.024405273
1435	0.996528	5.64	5.44	0.003472	-0.1	0.01871408	88.44	0.222897546	0.142998328	0.000771213	0.00018591	0.061575702	0.026024737
1440	1	5.54	5.34	0.003472	-0.05	0.01845368	77.09	0.190720315	0.122912138	0.000662181	0.000161334	0.059481522	0.017223621
1445	1.003472	5.49	5.29	0.003472	-0.15	0.01810648	83.91	0.20564921	0.131268793	0.000716493	0.000176419	0.057454552	0.021961657
1450	1.006944	5.34	5.14	0.003472	0.15	0.01810648	67.77	0.161383176	0.106019379	0.000564213	0.000140385	0.055492811	0.011212769
1455	1.010417	5.49	5.29	0.003472	-0.05	0.01828008	68.89	0.168837732	0.108804791	0.000592311	0.000148915	0.053593831	0.013281157

1460	1.013889	5.44	5.24	0.003472	-0.15	0.01793288	78.3	0.19008625	0.121318085	0.000669146	0.000169974	0.051756824	0.01913503
1465	1.017361	5.29	5.09	0.003472	-0.14	0.01742944	75.28	0.177523171	0.113364424	0.000627061	0.00016092	0.049979403	0.016267413
1470	1.020833	5.15	4.95	0.003472	-0.25	0.0167524	71.18	0.163237839	0.103026456	0.000578569	0.000149988	0.048259784	0.013219953
1475	1.024306	4.9	4.7	0.003472	0	0.0163184	74.1	0.161351765	0.104474313	0.00057383	0.000150264	0.046595758	0.013168941
1480	1.027778	4.9	4.7										
								Sum	**144.49023**	**0.5064006**	**0.0270271**		
									M_o	***M_1***	***M_2***		

Na-fluorescein background = 0.2 ug/L
Tracer added = 120.45 g
Tracer recovery = 119.67%

Tracer flow modelling parameters:							Hydraulic parameters:	
ALPHA α	5.052367	MEAN	0.340723	MEAN (delayed)	0.490028527	d	e_{RTD}	0.802073
BETA β	0.067438	VAR	0.022978	dVAR	0.197927039		e_v	1.139548
ERROR	7.088918	MODE	0.273285	MODE (delayed)	0.422590238	d	e_λ	0.914001
RMS error	0.16722							

Lambley July 2008 (Bromide)

Time elapsed (min)	t (day)	Conc. (ug/L)	Δt (day)	ΔC (ug/L)	Area, CΔt (mg/L.day)	Flow, Q (L/s)	RTD (d^{-1})	M_o QCΔt (g)	M_1 tRTDΔt (d)	M_2 $(t-\tau_m)^2$RTDΔt (d^2)	Gammadist	Error
0	0	0	0.01389	0	0	78.3	0	0	0	0		
20	0.013889	0	0.01389	0	0	75.28	0	0	0	0		
40	0.027778	0	0.01389	0	0	71.18	0	0	0	0		
60	0.041667	0	0.01389	0	0	74.1	0	0	0	0		
80	0.055556	0	0.01389	0	0	70.6	0	0	0	0		
100	0.069444	0	0.01389	0	0	71.76	0	0	0	0		
120	0.083333	0	0.01389	0	0	74.1	0	0	0	0		
140	0.097222	0	0.01389	0	0	71.18	0	0	0	0		
160	0.111111	0	0.01389	0	0	75.28	0	0	0	0		
180	0.125	0	0.01389	0	0	77.69	0	0	0	0		
200	0.138889	0	0.01389	0	0	70.03	0	0	0	0		
220	0.152778	0	0.01389	0	0	70.03	0	0	0	0		
240	0.166667	0	0.01389	0	0	74.1	0	0	0	0	0	0
260	0.180556	0	0.01389	0.0554	0.000384753	82.02	0	2.726562908	0	0	0.0015535	2.41336E-06
280	0.194444	0.0554	0.01389	0.0521	0.001131341	80.77	0.17993497	7.895091357	0.000485973	0.000157923	0.019782314	0.025648873
300	0.208333	0.1075	0.01389	0.0796	0.002045997	83.28	0.360001997	14.72175045	0.001041754	0.000282011	0.079618389	0.078614968
320	0.222222	0.1871	0.01389	0.0438	0.00290301	82.65	0.621831007	20.73027829	0.001919383	0.000431806	0.19994182	0.177990487
340	0.236111	0.2309	0.01389	0.0076	0.003259983	78.3	0.72701174	22.05417619	0.002384294	0.000444073	0.387749515	0.115098857
360	0.25	0.2385	0.01389	0.172	0.004507305	72.34	0.693781343	28.17144954	0.002409156	0.0003695	0.638562738	0.003049094
380	0.263889	0.4105	0.01389	0.0782	0.006244944	75.28	1.242649074	40.61831481	0.004554829	0.000571265	0.939426763	0.09194377
400	0.277778	0.4887	0.01389	0.1055	0.007520741	74.69	1.467778518	48.53296293	0.005663183	0.000575664	1.272514357	0.038128092
420	0.291667	0.5942	0.01389	0.0831	0.008830568	79.53	1.900287706	60.67829087	0.007698549	0.000627183	1.618356165	0.079485394
440	0.305556	0.6773	0.01389	-0.0007	0.009402836	77.69	2.115933068	63.11574346	0.008980386	0.000578178	1.958309194	0.024845286

460	0.319444	0.6766	0.01389	0.1023	0.010108448	77.69	2.113746219	67.85210473	0.009378855	0.000468863	2.276174478	0.026382939
480	0.333333	0.7789	0.01389	0.0515	0.011176589	80.77	2.529807731	77.99613579	0.011712998	0.000444581	2.559189007	0.000863259
500	0.347222	0.8304	0.01389	0.078	0.012075966	83.91	2.801926833	87.54862813	0.013513451	0.000378308	2.798206243	1.38428E-05
520	0.361111	0.9084	0.01389	0.0654	0.013071879	72.34	2.642477869	81.7015444	0.013254225	0.000263339	2.987691814	0.119172668
540	0.375	0.9738	0.01389	-0.0343	0.013287869	85.19	3.335908402	97.80423991	0.017375913	0.000232359	3.125331265	0.044342731
560	0.388889	0.9395	0.01389	0.0745	0.013567058	85.19	3.21840824	99.8591871	0.017384773	0.000144862	3.211512667	4.75489E-05
580	0.402778	1.014	0.01389	-0.0766	0.013552473	86.48	3.526219678	101.2623435	0.019727741	9.07159E-05	3.2487513	0.076988701
600	0.416667	0.9374	0.01389	0.0075	0.013072574	95.15	3.586653899	107.4691038	0.020757776	4.23244E-05	3.241120178	0.119393552
620	0.430556	0.9449	0.01389	-0.0447	0.01281422	85.19	3.236906808	94.31798624	0.019358071	1.04677E-05	3.19372742	0.00186446
640	0.444444	0.9002	0.01389	-0.0222	0.012349599	86.48	3.130476287	92.27462298	0.019325454	8.1658E-08	3.11227053	0.00033145
660	0.458333	0.878	0.01389	-0.0352	0.011950956	97.92	3.457177274	101.1085296	0.022009239	7.52552E-06	3.002637639	0.20660628
680	0.472222	0.8428	0.01389	-0.0509	0.011352992	85.19	2.887146849	83.56274028	0.018937268	2.79659E-05	2.870651213	0.000272106
700	0.486111	0.7919	0.01389	-0.0196	0.010863369	84.55	2.692400631	79.35821415	0.018179309	6.07266E-05	2.721829887	0.000866081
720	0.5	0.7723	0.01389	-0.0773	0.010190399	89.1	2.767065679	78.44813335	0.019217271	0.000112847	2.561243363	0.042362826
740	0.513889	0.695	0.01389	0.0299	0.009861206	89.76	2.508553556	76.47625201	0.01790585	0.000161472	2.393419237	0.013255911
760	0.527778	0.7249	0.01389	-0.0912	0.009435477	83.28	2.427585557	67.89195572	0.017796233	0.000226526	2.222295895	0.042143845
780	0.541667	0.6337	0.01389	-0.0774	0.00826455	81.39	2.074008273	58.117109	0.015604329	0.00026468	2.051211398	0.000519697
800	0.555556	0.5563	0.01389	-0.0431	0.007427678	85.19	1.905695055	54.67079631	0.014705625	0.000318785	1.882919252	0.000518737
820	0.569444	0.5132	0.01389	-0.0241	0.006960974	85.84	1.771462999	51.626589	0.014011523	0.000376079	1.719634712	0.002686171
840	0.583333	0.4891	0.01389	-0.0488	0.006454683	89.1	1.752391329	49.68969886	0.014198743	0.000460316	1.563035326	0.035855696
860	0.597222	0.4403	0.01389	-0.0296	0.005910195	84.55	1.496986991	43.1746837	0.012418126	0.000476668	1.414385996	0.006822924
880	0.611111	0.4107	0.01389	-0.032	0.005482383	85.19	1.406918855	40.35261955	0.011942394	0.000533948	1.274548764	0.017521841
900	0.625	0.3787	0.01389	-0.0368	0.005004567	91.09	1.387144601	39.38682309	0.012042149	0.000618629	1.144052018	0.059094004
920	0.638889	0.3419	0.01389	-0.0342	0.004511472	87.13	1.197905458	33.96250558	0.010630415	0.000620262	1.023145416	0.030541072
940	0.652778	0.3077	0.01389	-0.026387	0.004090695	94.47	1.168899413	33.38910578	0.010598512	0.000695452	0.911850986	0.066073894
960	0.666667	0.281313	0.01389	-0.145208	0.002898968	93.79	1.060967466	23.49165971	0.009824564	0.000718802	0.810009497	0.062979902
1080	0.75	0.136105	0.01389	-0.083862	0.001308077	94.47	0.517039501	10.67679541	0.005386259	0.000664513	0.374992966	0.020177218

1220	0.847222	0.052243	0.01389	-0.030836	0.000511499	87.13	0.183042336	3.850582722	0.002154026	0.000409661	0.137762425	0.00205027
1340	0.930556	0.021407	0.01389	-0.014318	0.000197905	85.84	0.073892651	1.467775397	0.000955094	0.00024117	0.054634192	0.000370888
1480	1.027778	0.007089	0.01389	-0.003585	7.35684E-05	91.09	0.02596638	0.578996138	0.000370692	0.000122153	0.017491829	7.1818E-05
1500	1.041667	0.003504			0	91.76	0.012929247	0	0	0	0.01479911	3.49639E-06
							Sum	**1597.6121**	**0.4458144**	**0.0132317**		
								M_o	M_1	M_2		

Bromide background = <LOD
Tracer added (NaBr)= 2.35 kg
Br = 1.83 kg
Tracer recovery (Br) = 87.27%

Tracer flow modelling parameters:

ALPHA α	5.033916	MEAN	0.294701	MEAN (delayed)	0.461367	d	e_{RTD}	0.801347
BETA β	0.058543	VAR	0.017253	dVAR	0.198653		e_v	1.077038
ERROR	1.75771	MODE	0.236158	MODE (delayed)	0.402824	d	e_λ	0.863082
RMS error	0.212296							

Hydraulic parameters: e_{RTD}, e_v, e_λ as listed above.

Lambley July 2008 (NaCl)

Time elapsed (min)	t (day)	Cond. (mS/cm)	Cond. – b/c (mS/cm)	NaCl (mg/L)	Δt (day)	ΔC (ug/L)	Area, CΔt (mg/L.day)	Flow, Q (L/s)	RTD (d^{-1})	M_o QCΔt (g)	M_1 tRTDΔt (d)	M_2 $(t-\tau_m)^2$RTDΔt (d^2)	Gammadist	Error
0	0	0.432	-0.001	-0.51	0.01389	2.04	-0.00354195	78.3	-0.149629355	-23.96171678	0	-0.000583701		
20	0.0138889	0.436	0.003	1.53	0.01389	-1.02	0.0141678	75.28	0.431574629	92.15009142	8.3258E-05	0.001596474		
40	0.0277778	0.434	0.001	0.51	0.01389	-1.02	0	71.18	0.136023212	0	5.24823E-05	0.000476455		
60	0.0416667	0.432	-0.001	-0.51	0.01389	-1.02	-0.0141678	74.1	-0.141603259	-90.70565587	-8.1953E-05	-0.000468944		
80	0.0555556	0.43	-0.003	-1.53	0.01389	2.55	-0.00354195	70.6	-0.404744538	-21.60532829	-0.000312328	-0.001265214		
100	0.0694444	0.435	0.002	1.02	0.01389	-1.02	0.0070839	71.76	0.274263154	43.92063337	0.000264549	0.000807869		
120	0.0833333	0.433	0	0	0.01389	0	0	74.1	0	0	0	0		
140	0.0972222	0.433	0	0	0.01389	-0.51	-0.00354195	71.18	0	-21.78282249	0	0		
160	0.1111111	0.432	-0.001	-0.51	0.01389	1.02	0	75.28	-0.14385821	0	-0.000222021	-0.000350536		
180	0.125	0.434	0.001	0.51	0.01389	0.51	0.01062585	77.69	0.14846366	71.32512555	0.00025777	0.000338164		
200	0.1388889	0.435	0.002	1.02	0.01389	-1.02	0.0070839	70.03	0.26765118	42.86178867	0.000516344	0.000568542		
220	0.1527778	0.433	0	0	0.01389	-0.51	-0.00354195	70.03	0	-21.43089433	0	0		
240	0.1666667	0.432	-0.001	-0.51	0.01389	0.51	-0.00354195	74.1	-0.141603259	-22.67641397	-0.000327812	-0.000259578	0	0.020051483
260	0.1805556	0.433	0	0	0.01389	0.51	0.00354195	82.02	0	25.10012785	0	0	0.002777403	7.71397E-06
280	0.1944444	0.434	0.001	0.51	0.01389	0	0.0070839	80.77	0.154349463	49.4351945	0.000416872	0.000241329	0.025002279	0.016730694
300	0.2083333	0.434	0.001	0.51	0.01389	0.51	0.01062585	83.28	0.159146011	76.45715608	0.000460529	0.000228653	0.083959124	0.005653068
320	0.2222222	0.435	0.002	1.02	0.01389	0	0.0141678	82.65	0.315884193	101.1716931	0.000975029	0.000415495	0.188285634	0.016281392
340	0.2361111	0.435	0.002	1.02	0.01389	0	0.0141678	78.3	0.299258709	95.84686714	0.000981444	0.000358897	0.338446962	0.001535719
360	0.25	0.435	0.002	1.02	0.01389	2.04	0.0283356	72.34	0.276479886	177.1024871	0.000960076	0.000300974	0.528924972	0.063728522
380	0.2638889	0.439	0.006	3.06	0.01389	0	0.0425034	75.28	0.863149258	276.4502743	0.003163802	0.000848699	0.750517369	0.012685943
400	0.2777778	0.439	0.006	3.06	0.01389	0.51	0.04604535	74.69	0.856384406	297.1405893	0.003304217	0.000756429	0.992275766	0.018466462
420	0.2916667	0.44	0.007	3.57	0.01389	1.02	0.0566712	79.53	1.063858979	389.4100303	0.004309959	0.000839028	1.24296853	0.032080231
440	0.3055556	0.442	0.009	4.59	0.01389	0	0.0637551	77.69	1.336172939	427.9507533	0.005670941	0.000934528	1.492090015	0.024310135

460	0.3194444	0.442	0.009	4.59	0.01389	1.02	0.070839	77.69	1.336172939	475.500837	0.00592871	0.000822424	1.730485678	0.155482536
480	0.3333333	0.444	0.011	5.61	0.01389	1.02	0.0850068	80.77	1.697844097	593.222334	0.007861017	0.000911685	1.950686301	0.06392918
500	0.3472222	0.446	0.013	6.63	0.01389	1.02	0.0991746	83.91	2.084549029	718.9983953	0.010053606	0.00096678	2.14700423	0.003900652
520	0.3611111	0.448	0.015	7.65	0.01389	0.51	0.10980045	72.34	2.073599142	686.2721374	0.010400827	0.000821063	2.315493582	0.05851292
540	0.375	0.449	0.016	8.16	0.01389	0.51	0.11688435	85.19	2.604735577	860.3174399	0.013567416	0.000868668	2.453802671	0.022780742
560	0.3888889	0.45	0.017	8.67	0.01389	-0.51	0.11688435	85.19	2.76753155	860.3174399	0.014949283	0.000764917	2.56097118	0.042667186
580	0.4027778	0.449	0.016	8.16	0.01389	1.02	0.1204263	86.48	2.644178104	899.809899	0.014793076	0.000593995	2.637201397	4.86744E-05
600	0.4166667	0.451	0.018	9.18	0.01389	-1.02	0.1204263	95.15	3.27292715	990.0197952	0.018942067	0.000583414	2.683625511	0.347276421
620	0.4305556	0.449	0.016	8.16	0.01389	-0.51	0.10980045	85.19	2.604735577	808.176989	0.015577406	0.000357435	2.702083742	0.009476665
640	0.4444444	0.448	0.015	7.65	0.01389	0.51	0.10980045	86.48	2.478916972	820.4149079	0.015303179	0.000251746	2.694922603	0.046658432
660	0.4583333	0.449	0.016	8.16	0.01389	-0.51	0.10980045	97.92	2.993962996	928.9434295	0.019060316	0.000213298	2.664817636	0.108336668
680	0.4722222	0.448	0.015	7.65	0.01389	0	0.1062585	85.19	2.441939603	782.1067635	0.016017088	0.000113037	2.614623856	0.029819851
700	0.4861111	0.448	0.015	7.65	0.01389	0	0.1062585	84.55	2.423594242	776.2310935	0.01636431	6.46991E-05	2.547252674	0.015291408
720	0.5	0.448	0.015	7.65	0.01389	-1.53	0.09563265	89.1	2.554018296	736.2030915	0.017737657	3.18232E-05	2.465574194	0.007822359
740	0.5138889	0.445	0.012	6.12	0.01389	0	0.0850068	89.76	2.05834956	659.2501758	0.014692328	7.37595E-06	2.372342593	0.098591625
760	0.5277778	0.445	0.012	6.12	0.01389	-0.51	0.08146485	83.28	1.909752132	586.17153	0.014000075	1.25262E-07	2.270141769	0.129880691
780	0.5416667	0.444	0.011	5.61	0.01389	0.51	0.08146485	81.39	1.710876947	572.8686458	0.012872211	3.26189E-06	2.161348348	0.202924483
800	0.5555556	0.445	0.012	6.12	0.01389	0	0.0850068	85.19	1.953551682	625.6854108	0.015074908	1.77897E-05	2.048109178	0.00894112
820	0.5694444	0.445	0.012	6.12	0.01389	1.02	0.0920907	85.84	1.968457289	682.9976754	0.015569676	4.26462E-05	1.932331438	0.001305077
840	0.5833333	0.447	0.014	7.14	0.01389	-1.53	0.08854875	89.1	2.38375041	681.6695292	0.019314337	9.43539E-05	1.815677888	0.32270639
860	0.5972222	0.444	0.011	5.61	0.01389	0	0.0779229	84.55	1.777302444	569.2361352	0.014743464	0.000111718	1.699577633	0.006041146
880	0.6111111	0.444	0.011	5.61	0.01389	-2.04	0.0637551	85.19	1.790755709	469.2640581	0.015200531	0.000163842	1.585233834	0.042239241
900	0.625	0.44	0.007	3.57	0.01389	-0.51	0.04604535	91.09	1.218495089	362.3850085	0.01057806	0.000152905	1.473639259	0.065098548
920	0.6388889	0.439	0.006	3.06	0.01389	0	0.0425034	87.13	0.999019592	319.9669553	0.008865467	0.000164678	1.365593406	0.134376361
940	0.6527778	0.439	0.006	3.06	0.01389	-1.02	0.0354195	94.47	1.083178938	289.1013263	0.009821274	0.000226981	1.261720959	0.031877253
960	0.6666667	0.437	0.004	2.04	0.01389	0.51	0.03187755	93.79	0.71692144	258.3183238	0.006638693	0.000186128	1.162490729	0.198531992
980	0.6805556	0.438	0.005	2.55	0.01389	0.51	0.03896145	94.47	0.902649115	318.0114589	0.008532667	0.00028438	1.068234453	0.027418504

1000	0.6944444	0.439	0.006	3.06	0.01389	-1.53	0.03187755	78.3	0.897776128	215.6554511	0.008659798	0.000337418	0.97916558	0.006624243
1020	0.7083333	0.436	0.003	1.53	0.01389	0.51	0.02479365	75.28	0.431574629	161.26266	0.004246155	0.000190749	0.895393929	0.215128343
1040	0.7222222	0.437	0.004	2.04	0.01389	-0.51	0.02479365	71.18	0.544092846	152.4797574	0.005458158	0.000279386	0.81694552	0.074448581
1060	0.7361111	0.436	0.003	1.53	0.01389	0.51	0.02479365	74.1	0.424809777	158.7348978	0.004343503	0.000250788	0.743774602	0.10173856
1080	0.75	0.437	0.004	2.04	0.01389	-1.02	0.0212517	70.6	0.539659384	129.6319697	0.005621902	0.000362962	0.675777537	0.018528152
1100	0.7638889	0.435	0.002	1.02	0.01389	1.02	0.0212517	71.76	0.274263154	131.7619001	0.002910046	0.000208483	0.612804592	0.114610305
1120	0.7777778	0.437	0.004	2.04	0.01389	-1.53	0.01770975	74.1	0.566413036	113.3820698	0.006119149	0.000483206	0.554670333	0.000137891
1140	0.7916667	0.434	0.001	0.51	0.01389	1.53	0.01770975	71.18	0.136023212	108.9141124	0.001495745	0.000129412	0.501162691	0.133326839
1160	0.8055556	0.437	0.004	2.04	0.01389	0	0.0283356	75.28	0.575432839	184.3001828	0.006438614	0.000607114	0.452050763	0.015223137
1180	0.8194444	0.437	0.004	2.04	0.01389	-1.02	0.0212517	77.69	0.593854639	142.6502511	0.006759303	0.00069129	0.407091769	0.03488037
1200	0.8333333	0.435	0.002	1.02	0.01389	0	0.0141678	70.03	0.26765118	85.72357734	0.003098062	0.000342178	0.36603537	0.009679449
1220	0.8472222	0.435	0.002	1.02	0.01389	0.51	0.01770975	70.03	0.26765118	107.1544717	0.003149697	0.000374225	0.328630242	0.003718446
1240	0.8611111	0.436	0.003	1.53	0.01389	0.51	0.02479365	74.1	0.424809777	158.7348978	0.005081079	0.000647103	0.294626533	0.016947677
1260	0.875	0.437	0.004	2.04	0.01389	-0.51	0.02479365	82.02	0.626952729	175.7008949	0.007619827	0.00103681	0.263779234	0.131894987
1280	0.8888889	0.436	0.003	1.53	0.01389	-0.51	0.01770975	80.77	0.46304839	123.5879862	0.005717104	0.000828643	0.235850554	0.051618857
1300	0.9027778	0.435	0.002	1.02	0.01389	0	0.0141678	83.28	0.318292022	101.9428748	0.003991249	0.000614529	0.210611732	0.011595045
1320	0.9166667	0.435	0.002	1.02	0.01389	1.53	0.02479365	82.65	0.315884193	177.0504629	0.004021996	0.000656167	0.187844361	0.016394199
1340	0.9305556	0.438	0.005	2.55	0.01389	-0.51	0.03187755	78.3	0.748146774	215.6554511	0.009670109	0.001667713	0.16734131	0.337334986
1360	0.9444444	0.437	0.004	2.04	0.01389	-0.51	0.02479365	72.34	0.552959771	154.9646762	0.00725391	0.001319567	0.148907419	0.163258303
1380	0.9583333	0.436	0.003	1.53	0.01389	0	0.0212517	75.28	0.431574629	138.2251371	0.005744798	0.001100073	0.132359272	0.08952983
1400	0.9722222	0.436	0.003	1.53	0.01389	-0.51	0.01770975	74.69	0.428192203	114.2848421	0.005782379	0.001163372	0.117526051	0.096513458
1420	0.9861111	0.435	0.002	1.02	0.01389	0	0.0141678	79.53	0.303959708	97.35250758	0.004163361	0.000878523	0.104248862	0.039884422
1460	1.0138889	0.435	0.002	1.02	0.01389	0	0.0141678	77.69	0.29692732	95.1001674	0.004181603	0.0009659	0.081785571	0.046285972
1480	1.0277778	0.435	0.002	1.02	0.01389	0	0.0141678	77.69	0.29692732	95.1001674	0.004238885	0.001022137	0.072338994	0.050439916
1500	1.0416667	0.435	0.002	1.02	0.01389	-0.51	0.01062585	80.77	0.308698927	74.15279175	0.004466488	0.001122781	0.063926499	0.059913542
1520	1.0555556	0.434	0.001	0.51	0.01389	0	0.0070839	83.91	0.160349925	51.35702823	0.002350997	0.000615304	0.056443541	0.010796537
1540	1.0694444	0.434	0.001	0.51	0.01389	1.02	0.0141678	72.34	0.138239943	88.55124353	0.002053497	0.000558867	0.049794858	0.007822533

1560	1.0833333	0.436	0.003	1.53	0.01389	-1.02	0.0141678	85.19	0.488387921	104.2809018	0.007349017	0.002077389	0.043893677	0.197575132
1580	1.0972222	0.434	0.001	0.51	0.01389	0	0.0070839	85.19	0.162795974	52.1404509	0.002481078	0.000727659	0.038661406	0.015409391
1600	1.1111111	0.434	0.001	0.51	0.01389	0	0.0070839	86.48	0.165261131	52.92999406	0.00255053	0.000775291	0.034026844	0.017222438
1620	1.125	0.434	0.001	0.51				95.15	0.181829286	0	0	0	0.029925658	0.023074712
									Sum	**19484.385**	**0.5299508**	**0.0366398**		
										M_o	***M_1***	***M_2***		

NaCl background = 0.433 mS/cm
Tracer added = 20 kg
Tracer recovery = 97.42%

Tracer flow modelling parameters:

ALPHA α	4.772402	MEAN	0.354286	MEAN (delayed)	0.507064	d
BETA β	0.074236	VAR	0.026301	dVAR	0.209538	
ERROR	3.809526	MODE	0.28005	MODE (delayed)	0.432827	d
RMS error	0.234969					

Hydraulic parameters:

e_{RTD}	0.790462
e_v	1.184566
e_λ	0.936354

APPENDIX F

Actual tracer RTDs for the investigated wetlands and lagoons

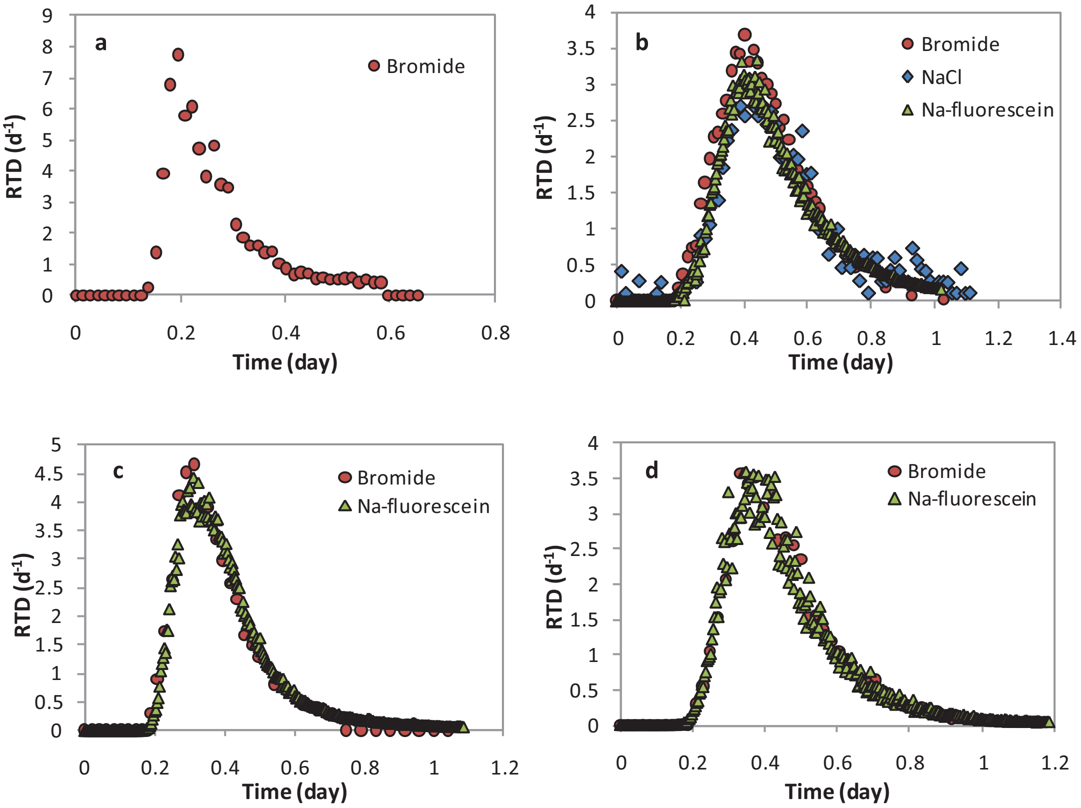


Figure F.1 Tracer RTDs for Lambley wetland showing actual tracer responses for the wetland from 2007 to 2010 **(a)** bromide tracer RTD on February 2007 (data from Kruse et al., 2007) **(b)** RTDs for bromide, NaCl and Na-fluorescein tracer on July 2008 **(c)** RTDs for bromide and Na-fluorescein on November 2009 (d) RTDs for bromide and Na-fluorescein tracer on April 2010

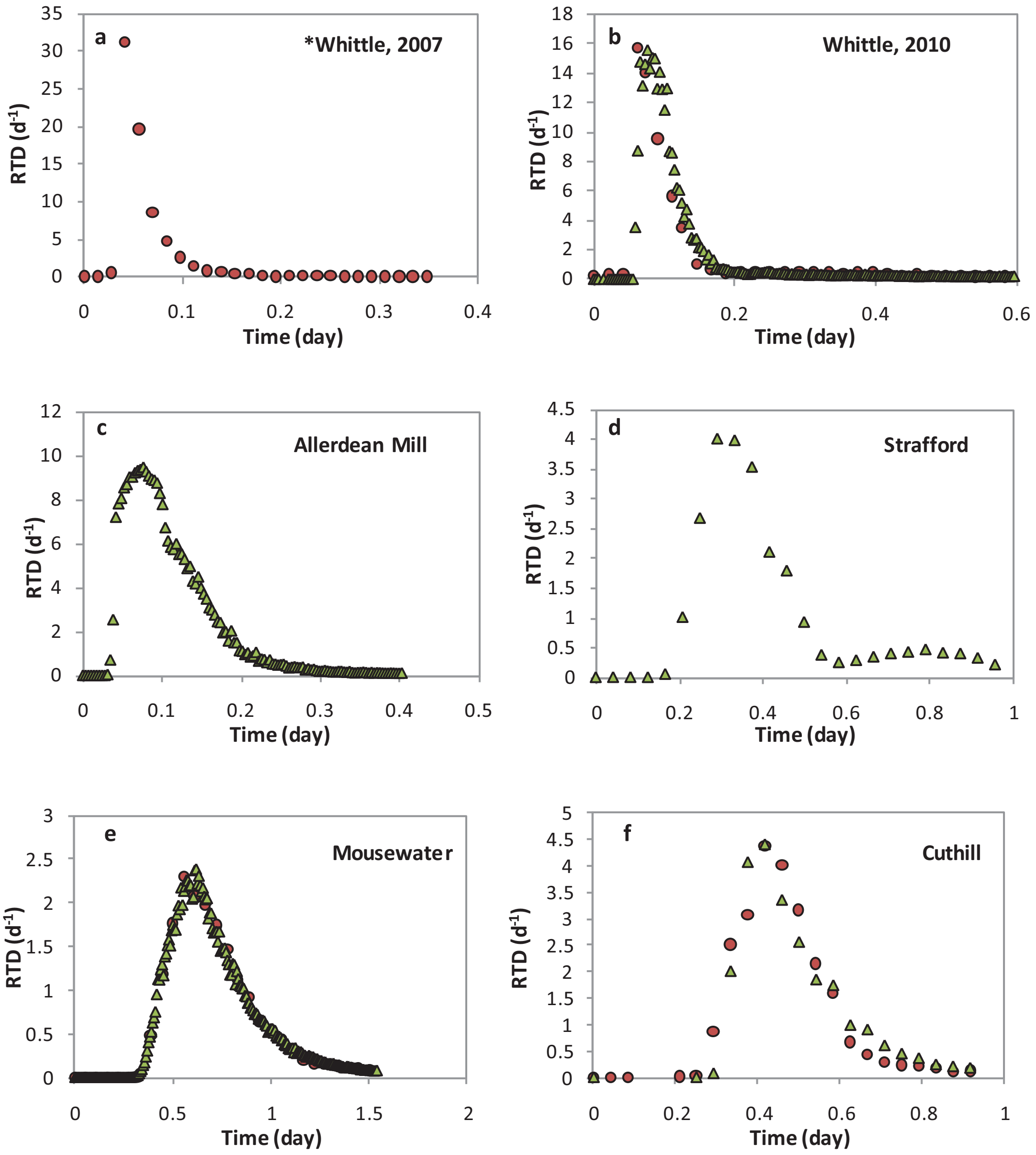
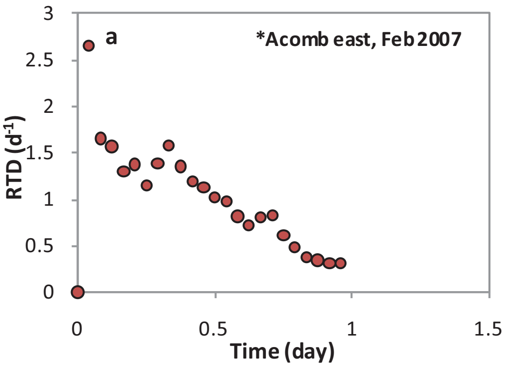
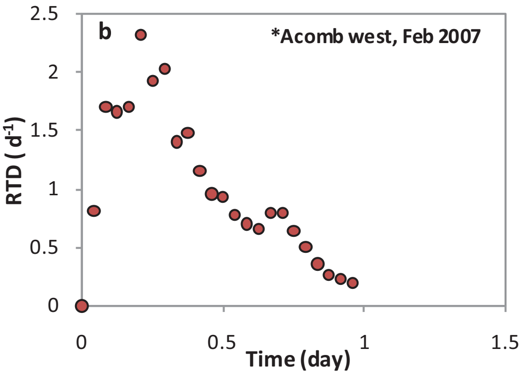
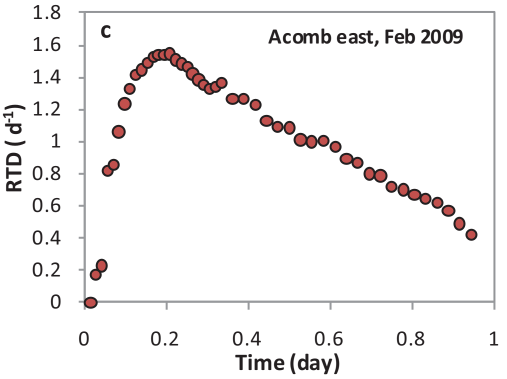


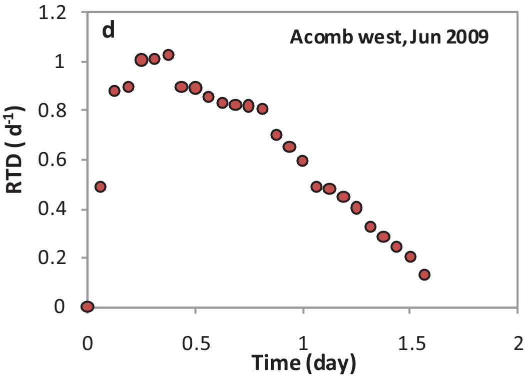
Figure F.2 Actual tracer RTDs for the investigated wetland systems within the UK Coal Authority mine water treatment sites. Red circles denote bromide tracer, green triangle denote Na-fluorescein tracer. *Data from Kruse et al. (2007).

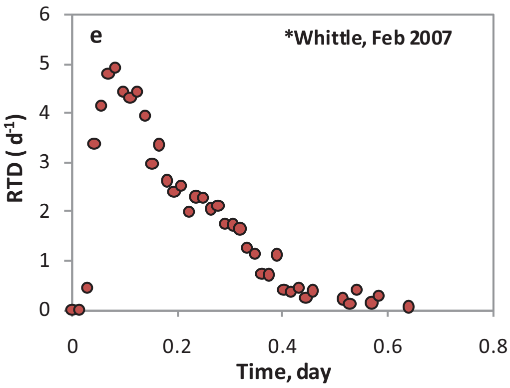
APPENDIX G

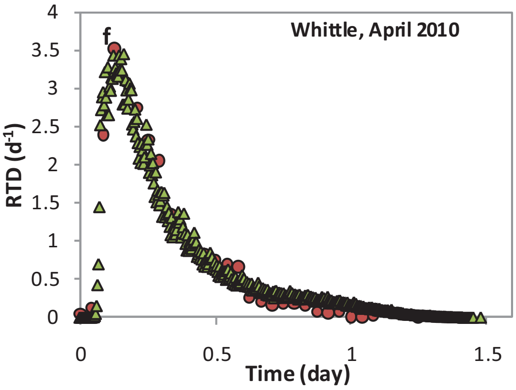

a
*Acomb east, Feb 2007
RTD (d^{-1})
0
0.5
1
1.5
2
2.5
3
Time (day)
0
0.5
1
1.5

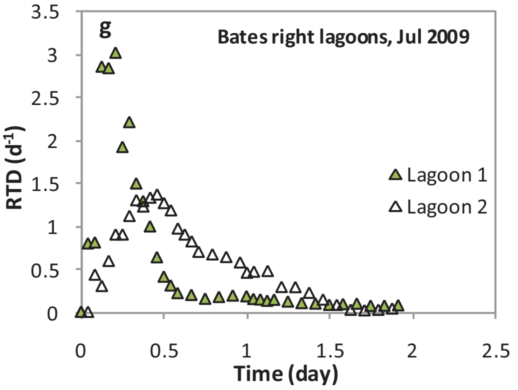

b
*Acomb west, Feb 2007
RTD (d^{-1})
0
0.5
1
1.5
2
2.5
Time (day)
0
0.5
1
1.5

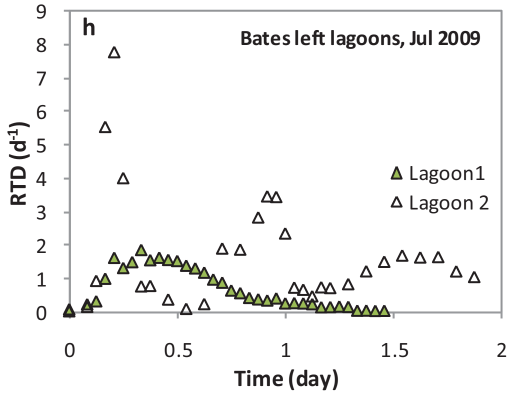

c
Acomb east, Feb 2009
RTD (d^{-1})
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
Time (day)
0
0.2
0.4
0.6
0.8
1


d
Acomb west, Jun 2009
RTD (d^{-1})
0
0.2
0.4
0.6
0.8
1
1.2
Time (day)
0
0.5
1
1.5
2


e
*Whittle, Feb 2007
RTD (d^{-1})
0
1
2
3
4
5
6
Time, day
0
0.2
0.4
0.6
0.8


f
Whittle, April 2010
RTD (d^{-1})
0
0.5
1
1.5
2
2.5
3
3.5
4
Time (day)
0
0.5
1
1.5


g
Bates right lagoons, Jul 2009
RTD (d^{-1})
0
0.5
1
1.5
2
2.5
3
3.5
Lagoon 1
Lagoon 2
Time (day)
0
0.5
1
1.5
2
2.5


h
Bates left lagoons, Jul 2009
RTD (d^{-1})
0
1
2
3
4
5
6
7
8
9
Lagoon1
Lagoon 2
Time (day)
0
0.5
1
1.5
2

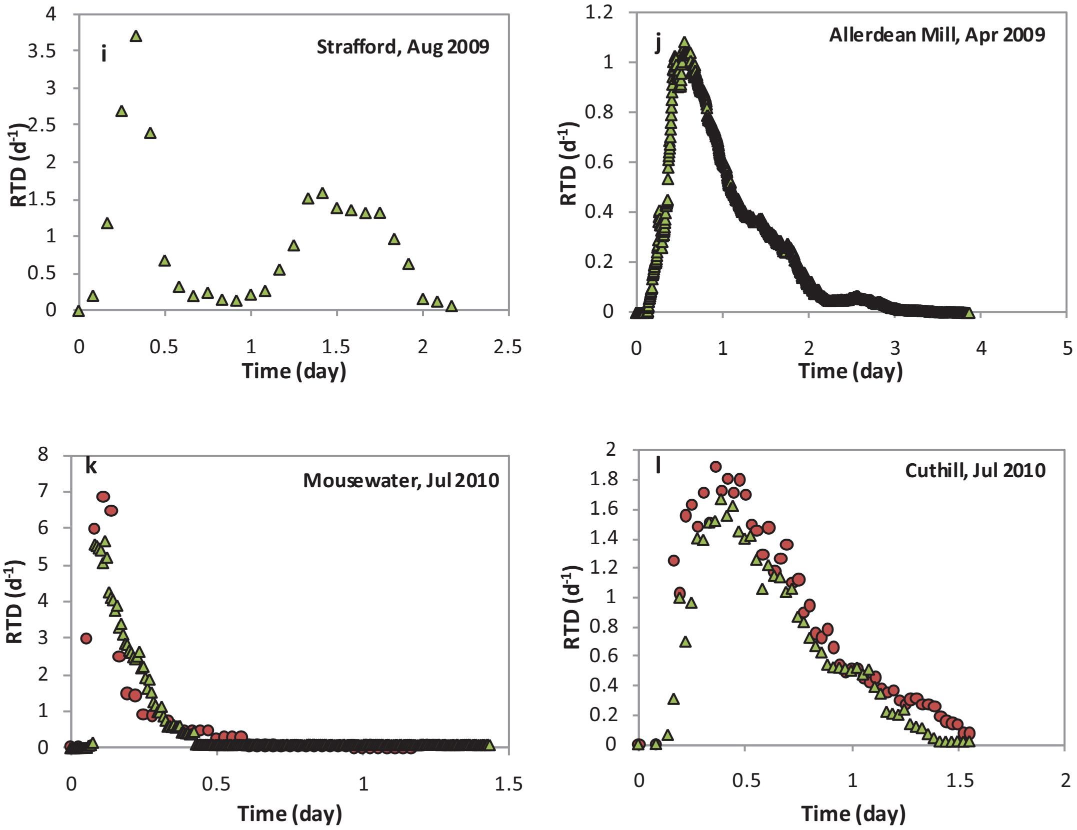


Figure G.1 Actual tracer RTDs for the investigated lagoon systems within the UK Coal Authority mine water treatment sites. Red circles denote bromide tracer, green triangle denote Na-fluorescein tracer. * Data from Kruse et al. (2007).

APPENDIX H

Correlation between particulate iron and turbidity measurement

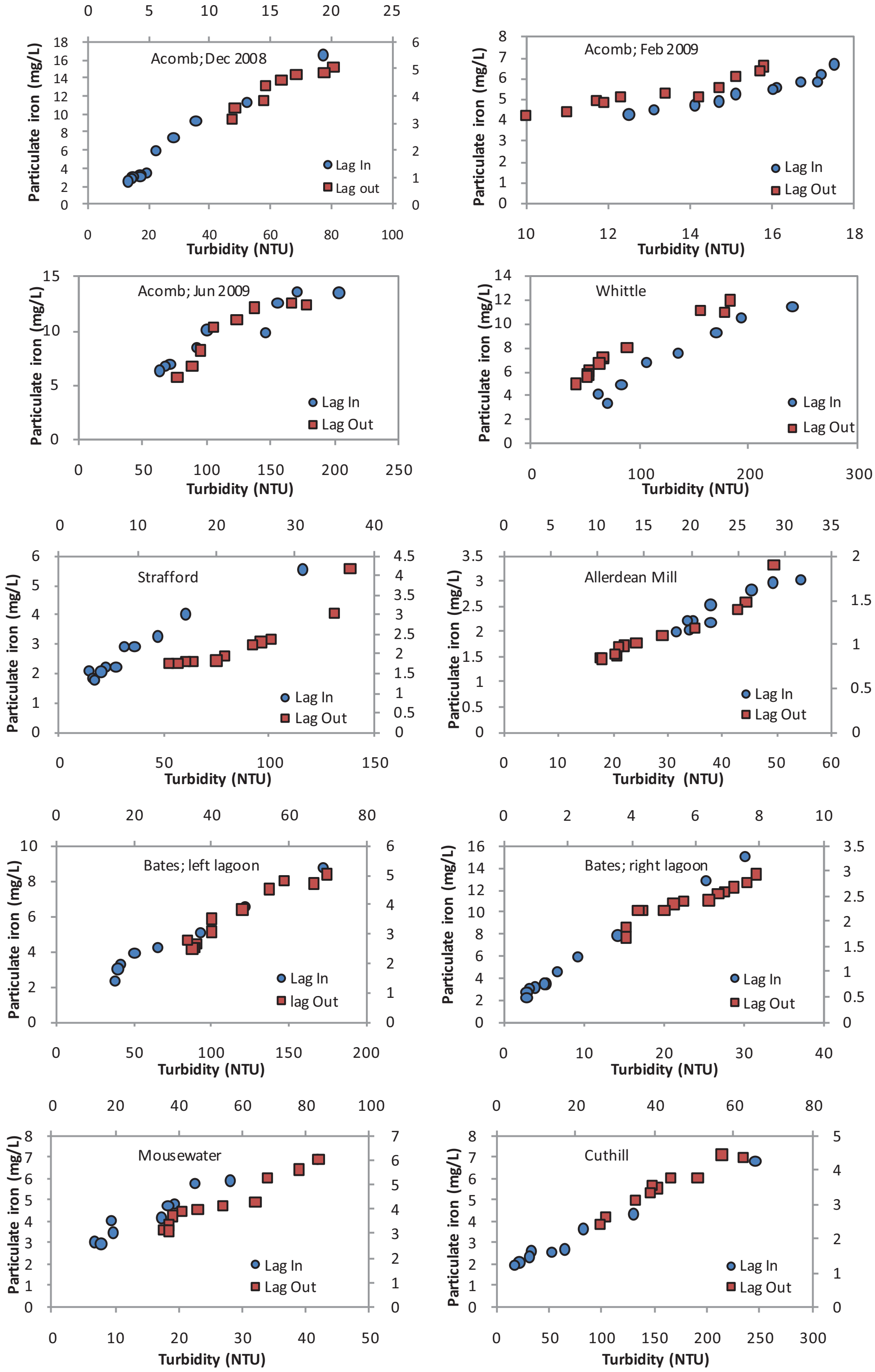


Figure H.1 Correlations between particulate iron and turbidity in each sample of inlet (in) and outlet (out) of treatment lagoons (lag). Primary axes: inlet samples; secondary axes: outlet samples

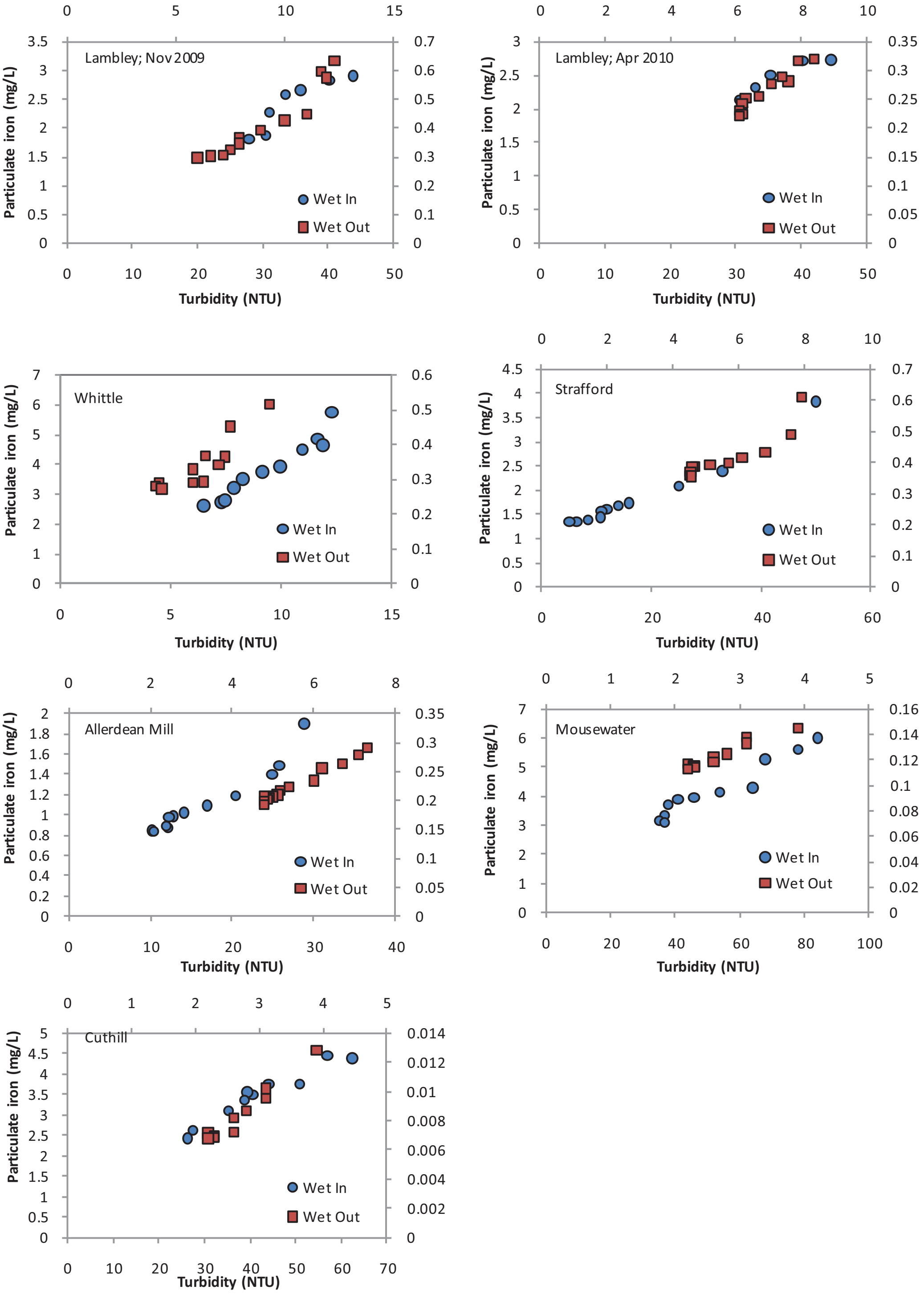


Figure H.2 Correlations between particulate iron and turbidity in each inlet (in) and outlet (out) samples of mine treatment wetlands (wet). Primary axes: inlet samples; secondary axes: outlet samples

APPENDIX I

Determination of ferrous iron oxidation rates

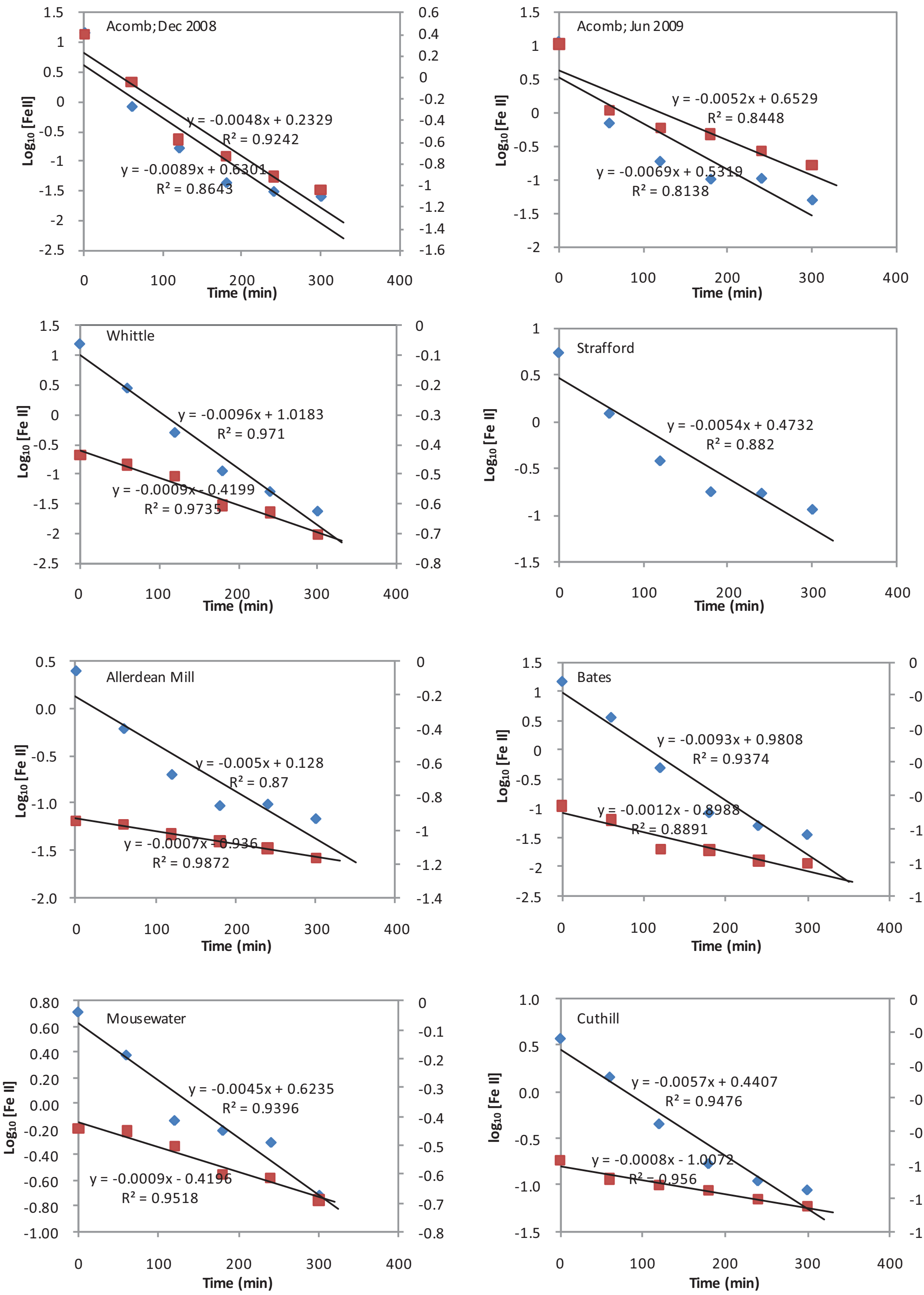


Figure I.1 Ferrous iron oxidation rates in lagoon systems. Blue diamonds denote inlet samples; pH~6.5, DO~8.5 mg/L, temperature=20°C. Red squares denote outlet samples; pH~7.0, DO~8.5 mg/L, temperature=20°C. Primary axes: inlet samples; secondary axes: outlet samples.

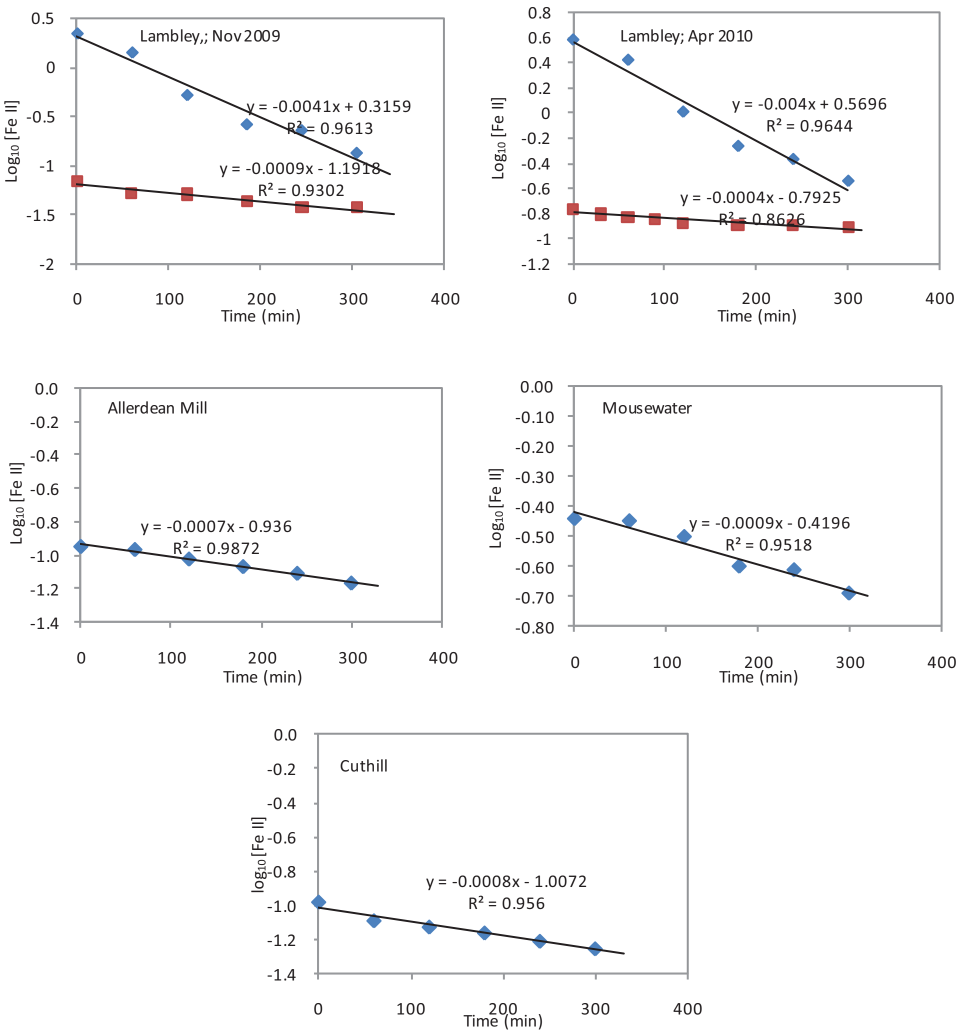


Figure I.2 Ferrous iron oxidation rates in wetland systems. Blue diamonds denote inlet samples; pH~7.0, DO~8.5 mg/L, temperature=20°C. Red squares denote outlet samples; pH~7.5, DO~8.5 mg/L, temperature=20°C. Primary axes: inlet samples; secondary axes: outlet sample

APPENDIX J

Determination of iron settlement rates

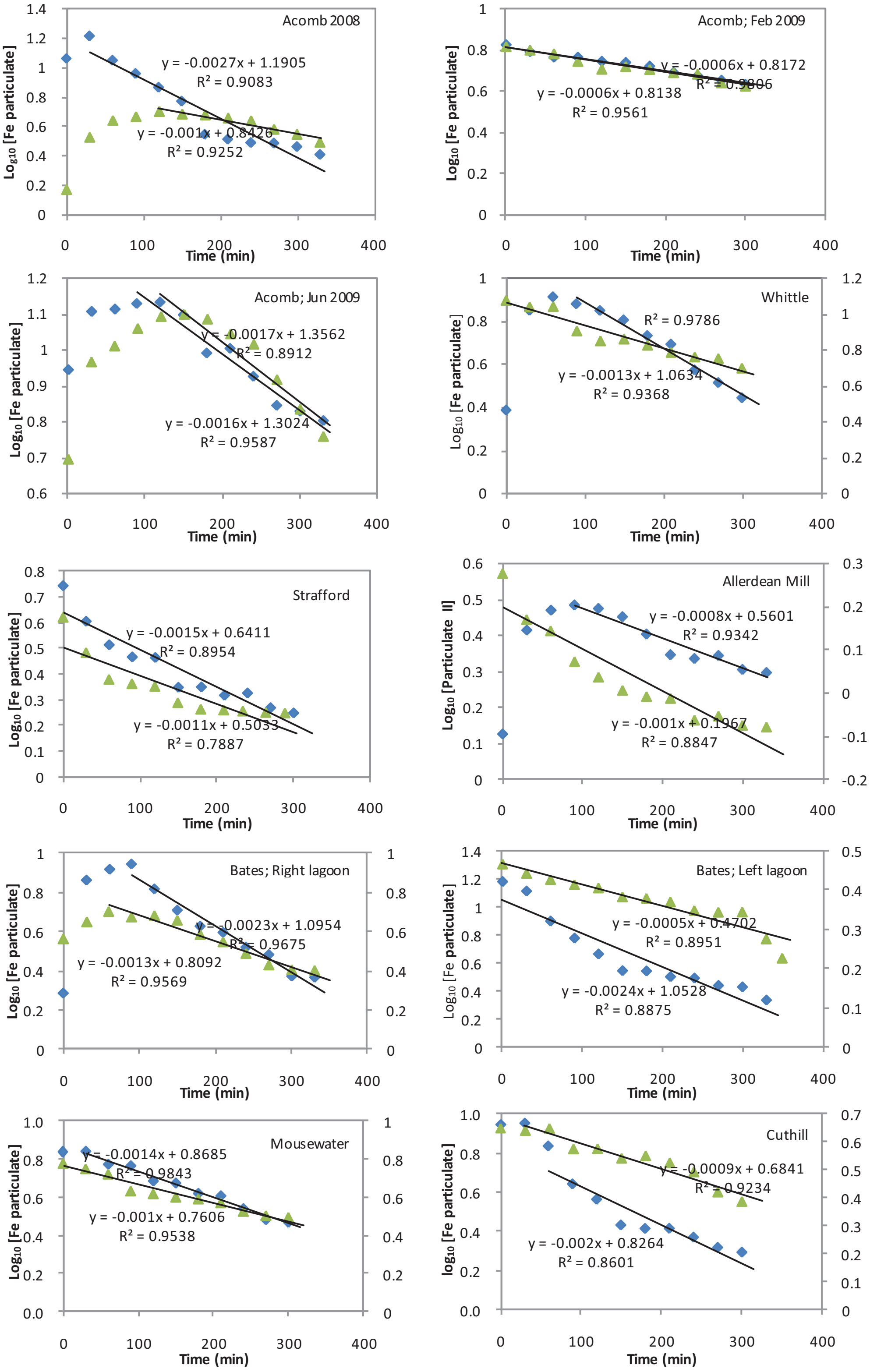


Figure J.1 Fe settlement rates in lagoon systems. Blue diamonds denote inlet samples; pH~6.5, DO~8.5 mg/L, temperature=20°C. Green triangles denote outlet samples; pH~7.0, DO~8.5 mg/L, temperature=20°C. Primary axes: inlet samples; secondary axes: outlet samples

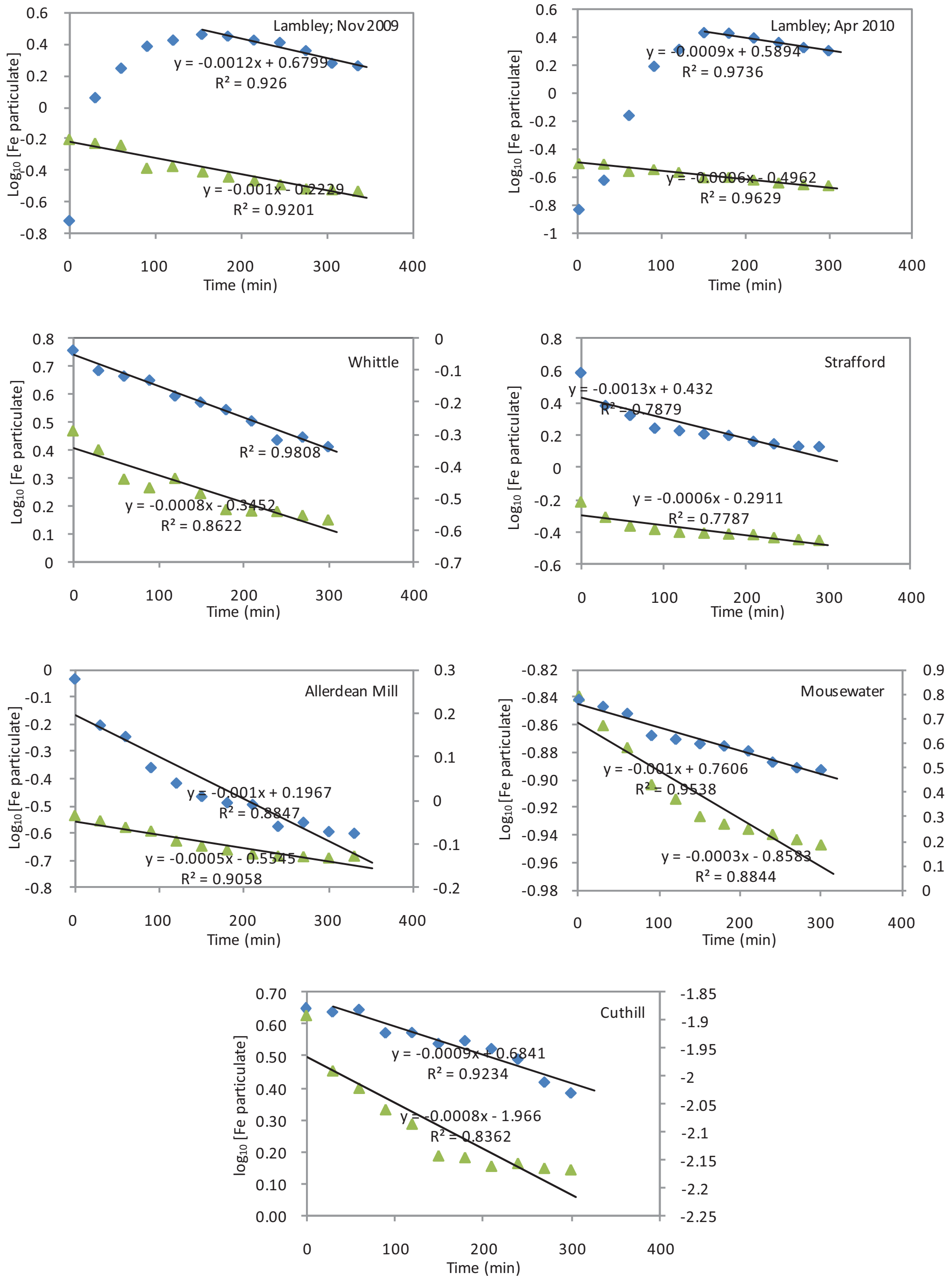


Figure J.2 Fe settlement rates in wetland systems. Blue diamonds denote inlet samples; pH~7.0, DO~8.5 mg/L, temperature=20°C. Green triangles denote outlet samples; pH~7.5, DO~8.5 mg/L, temperature=20°C. Primary axes: inlet samples; secondary axes: outlet samples

APPENDIX K

Table K1. Summary wetlands performance data and iron removal in the systems

	In/Out	Fe total (mg/L)	Flow (L/s)	Actual residence time (day)	Fe loading rate (kg/d)	Fe removal efficiency (%)	Fe load removal (%)	Area-adjusted removal ($g/m^2/d$)	Residence time adjusted removal (g/m^2)	First-order removal, k_1 (m/d)	TIS removal rate, k_{TIS} (m/d)
Lambley 2007	In	3.841	81.86	0.248	27.17	57.67	56.13	2.29	9.23	0.89	1.02
	Out	1.626	84.83								
Lambley 2008	In	6.810	81.45	0.486	47.92	85.11	85.07	5.96	12.93	1.96	2.38
	Out	1.014	81.66								
Lambley 2009	In	6.580	76.89	0.382	43.71	83.28	82.97	5.32	13.92	1.74	2.16
	Out	1.1	78.34								
Lambley 2010	In	6.070	78.91	0.436	41.38	85.01	85.45	5.14	11.79	1.89	2.35
	Out	0.91	76.57								
Allerdean Mill	In	3.014	7.91	0.107	2.06	66.36	64.87	1.28	11.98	0.70	0.93
	Out	1.014	8.26								
Strafford	In	5.111	14.04	0.362	6.20	73.74	47.67	2.71	7.47	0.96	1.08
	Out	1.342	27.97								
Whittle 2007	In	20.800	25	0.053	44.93	91.82	92.46	17.19	324.34	2.25	5.28
	Out	1.7	25								
Whittle 2010	In	7.435	23.07	0.088	14.82	88.90	89.49	5.49	53.82	1.83	3.36
	Out	0.825	21.85								
Mousewater	In	8.408	31.9	0.698	23.17	97.82	97.65	2.70	3.86	1.26	2.04
	Out	0.183	34.47								
Cuthill	In	7.869	10.61	0.468	7.21	98.60	99.01	2.59	5.54	1.43	2.47
	Out	0.100	7.48								

Table K2. Summary lagoons performance data and iron removal in the systems

	In/ Out	Fe total	Flow	Actual residence time	Fe loading rate	Fe removal efficiency	Fe load removal	Area-adjusted removal	Residence time adjusted removal	First-order removal, k_1	TIS removal rate, k_{TIS}	HLR
		(mg/L)	(L/s)	(day)	(kg/d)	(%)	(%)	(g/m^2/d)	(g/m^2)	m/d	m/d	m/d
Allerdean Mill	In	10.003	9.67	0.952	8.35	69.86	79.65	6.61	6.95	1.14	1.44	0.79
	Out	3.014	6.53									
Acomb 2007 West		34.100	5.85	0.382	17.23	85.19	85.19	39.15	102.50	2.57	4.31	1.35
		5.05	5.85									
Acomb 2007 East		34.100	6.25	0.939	18.41	71.70	71.70	35.20	37.50	1.82	3.00	1.44
		9.65	6.25									
Acomb 2009 West		32.000	6.5	0.734	17.97	22.25	22.25	10.66	14.53	0.38	0.40	1.25
		24.88	6.5									
Acomb 2009 East		6.990	6.25	0.505	3.77	13.87	13.88	1.39	2.77	0.22	0.22	1.39
		6.02	6.25									
Bates Lag (R)1		18.967	78.69	0.281	128.95	49.35	46.38	22.33	79.48	1.62	1.82	2.39
		9.605	83.32									
Lag (R) 2		9.605*	78.69	0.656	65.30	42.42	39.03	9.72	14.82	1.32	1.48	2.39
		5.53	83.32									
Lag (L) 1		18.828	58.55	0.516	95.24	76.83	67.04	25.67	49.77	2.60	3.36	1.77
		4.361	83.32									
Lag (L) 2		4.361*	58.55	1.144	22.06	70.25	57.67	5.43	23.96	2.15	2.45	1.77
		1.297	83.32									
Strafford		6.601	14.04	0.821	8.00	22.57	22.57	2.12	6.04	0.37	0.37	1.65
		5.111	14.04									
Whittle 2007		28.600	23.07	0.179	61.77	24.47	30.31	16.8	3.21	0.67	0.72	2.4
		21.6	28.6									

Whittle 2010	19.573	23.07	0.278	42.27	16.52	22.97	7.764	93.85	0.43	0.46	1.94
	16.338	19.57									
Mousewater	14.578	36.72	0.211	46.25	55.74	61.56	8.49	40.25	0.85	1.16	0.89
	6.451	31.9									
Cuthill	17.413	10.71	0.622	16.12	53.45	53.93	11.87	19.09	0.98	1.17	1.60
	8.105	10.61									

[a] Unfiltered iron concentration at system's influent and effluent, respectively

[b] Filtered iron concentration at system's influent and effluent, respectively

[†] No available data for ferrous Fe (Fe iron assumed the same as dissolved Fe because dissolved Fe is predominantly of ferrous Fe at circum-neutral pH)

[c] Calculated as Fe total – Fe dissolved

[d] Calculated as the difference of dissolved ferrous iron at system's influent and effluent (Ferrous Fe_{in} – Ferrous Fe_{out})*

[e] Calculated as (Fe $particulate_{in}$ + $Fe_{oxidised}$)*

[f] Calculated as the difference of total iron at system's influent and effluent (Fe_{total} in – Fe_{total} out)*

[*] Calculated after Hedin (2008)

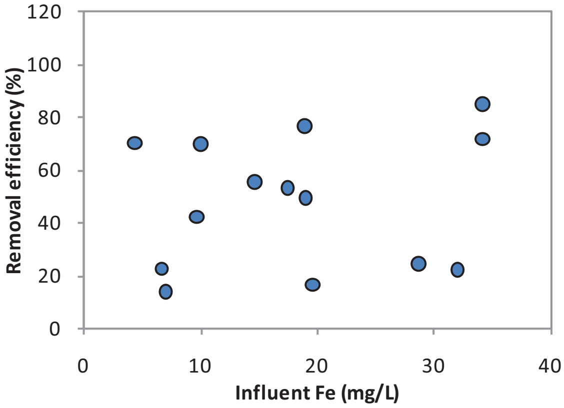
Table K3. Iron oxidation and settlement rates in wetlands (field data)

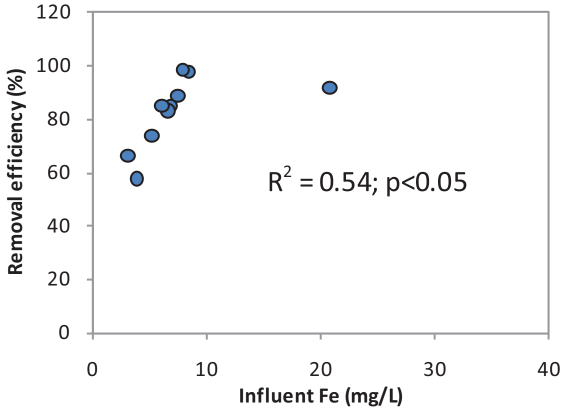
	In/Out	Fe total (mg/L)	Fe dissolved (mg/L)	Ferrous Fe (mg/L)	Ferric iron (mg/L)	Fe particulate (mg/L)	Fe oxidised (mg/L)	Total particulate Fe (mg/L)	Fe settle (mg/L)	Fe oxidised ($g/m^2/d$)	Fe settled ($g/m^2/d$)
Lambley 2007	In	3.841	3.65	3.65[†]	<LOD	0.19	2.4	2.59	2.21	2.48	2.29
	Out	1.626	1.25	1.25[†]	<LOD	0.38					
Lambley 2008	In	6.810	5.85	5.14	0.71	0.96	5.03	5.99	5.8	5.17	5.96
	Out	1.014	0.82	0.11	0.71	0.19					
Lambley 2009	In	6.580	6.31	5.55	0.76	0.27	5.5	5.77	5.48	5.34	5.32
	Out	1.1	0.38	0.05	0.33	0.72					
Lambley 2010	In	6.070	5.90	4.78	1.12	0.17	4.71	4.88	5.16	4.69	5.14
	Out	0.91	0.49	0.07	0.42	0.42					
Allerdean Mill	In	3.014	0.89	0.72	0.17	2.12	0.72	2.84	2.00	0.46	1.28
	Out	1.014	<LOD	<LOD	<LOD	1.014					
Strafford	In	5.111	<LOD	<LOD	<LOD	5.111	0	5.11	3.77	0	2.71
	Out	1.342	<LOD	<LOD	<LOD	1.342					
Whittle 2007	In	20.800	1.56	1.56	<LOD	19.24	1.56	20.80	19.10	1.40	17.19
	Out	1.7	<LOD	<LOD	<LOD	1.7					
Whittle 2010	In	7.435	<LOD	<LOD	<LOD	7.435	0	7.435	6.61	0	5.49
	Out	0.825	<LOD	<LOD	<LOD	0.825					
Mousewater	In	8.408	1.399	1.37	0.029	7.009	1.37	8.379	8.225	0.45	2.70
	Out	0.183	<LOD	<LOD	<LOD	0.183					
Cuthill	In	7.869	0.15	0.01	0.14	7.719	0.01	7.729	7.759	0.003	2.59
	Out	0.100	<LOD	<LOD	<LOD	0.100					

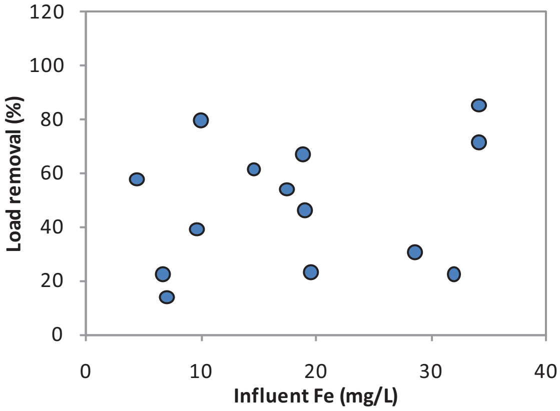
Table K4. Iron oxidation and settlement rates in wetlands (field data)

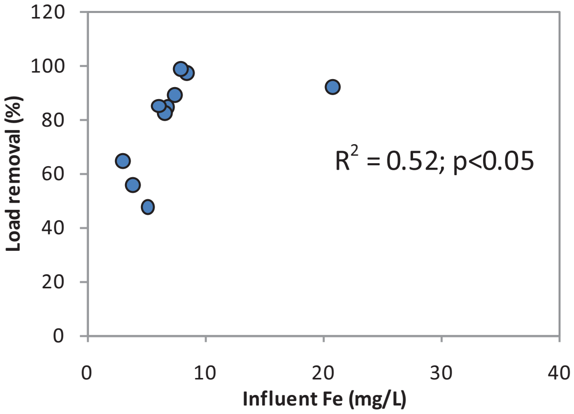
	In/ Out	Fe total (mg/L)	Fe dissolved (mg/L)	Ferrous Fe (mg/L)	Ferric Fe (mg/L)	Particulate Fe (mg/L)	Fe oxidised (mg/L)	Total particulate Fe (mg/L)	Fe settle (mg/L)	Fe oxidised (g/m^2/d)	Fe settled (g/m^2/d)
Allerdean Mill	In	10.003	3.37	3.19	2.13	3.23	3.37	6.601	1.49	4.84	2.13
	Out	3.014	<LOD	<LOD	<LOD	3.014					
Acomb 2007 West		34.100	20.6	20.6	<LOD	13.5	18.92	32.42	29.05	25.50	39.15
		5.05	1.68	1.68	<LOD	3.37					
Acomb 2007 East		34.100	20.6	20.6	<LOD	13.5	18.92	32.42	24.45	27.24	35.21
		9.65	1.68	1.68	<LOD	7.97					
Acomb 2009 West		32.000	30.32	30.19	0.13	1.68	29.33	31.01	7.12	43.92	10.66
		24.88	15.99	13.64	0.14	8.89					
Acomb 2009 East		6.990	<LOD	<LOD	<LOD	6.99	0	6.99	0.97	0	1.39
		6.02	<LOD	<LOD	<LOD	6.02					
Bates Lag 1		18.967	16.871	15.44	1.43	2.096	12.72	14.816	9.362	30.34	22.33
		9.605	4.151	3.33	0.82	5.454					
Lag 2		9.605*	5.151	3.33	1.82	4.454	4.31	8.763	4.075	10.28	9.72
		5.53	0.842	0.53	0.31	4.688					
Lag 3		18.828	16.23	15.23	1	2.60	15.02	17.62	14.47	37.94	36.54
		4.361	1.21	1.12	0.09	3.15					
Lag 4		4.361*	<LOD	<LOD	<LOD	4.361	0	4.361	3.064	0	5.43
		1.297	<LOD	<LOD	<LOD	1.297					
Strafford		6.601	3.37	3.19	0.18	3.231	3.37	6.601	1.49	4.81	2.13
		5.111	<LOD	<LOD	<LOD	5.111					
Whittle 2007		28.600	23.91	23.91	<LOD	4.69	19.60	23.75	7	45.74	16.8
		21.6	4.85	4.85	<LOD	16.75					
Whittle 2010		19.573	17.03	17.00	0.03	2.543	14.14	16.68	3.235	33.93	7.76

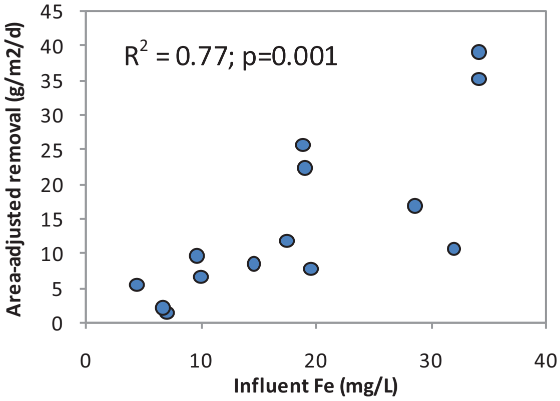
	16.338	2.89	0.41	2.48	13.448					
Mousewater	14.578	10.41	7.86	2.55	4.168	9.79	13.958	8.127	10.23	8.13
	6.451	0.62	0.24	0.38	5.831					
Cuthill	17.413	15.19	13.38	1.81	2.22	14.85	17.07	9.31	18.95	11.87
	8.105	0.34	0.07	0.27	7.765					

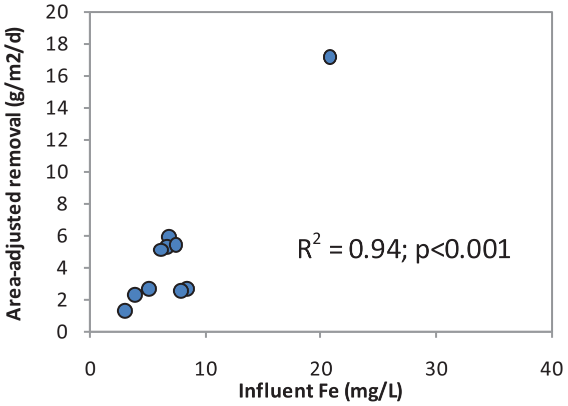

Removal efficiency (%)
0
20
40
60
80
100
120
0
10
20
30
40
Influent Fe (mg/L)

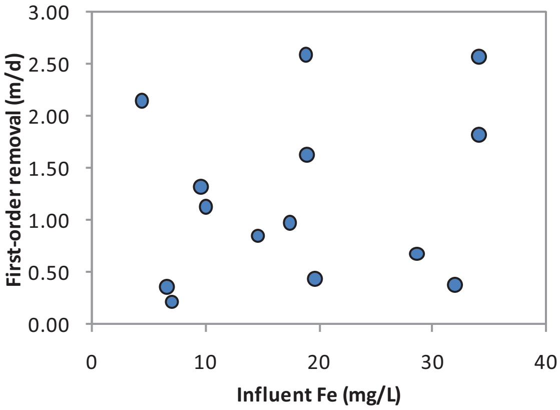

Removal efficiency (%)
0
20
40
60
80
100
120
$R^2 = 0.54; p<0.05$
0
10
20
30
40
Influent Fe (mg/L)

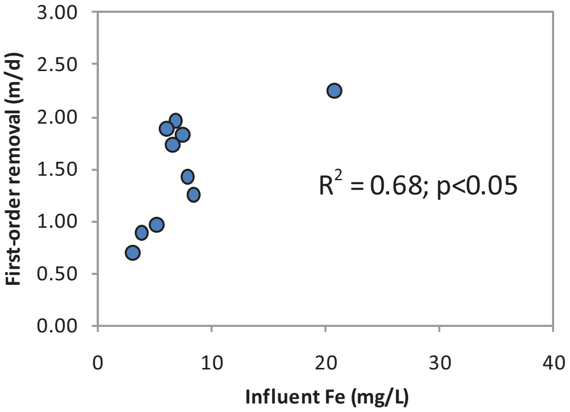

Load removal (%)
0
20
40
60
80
100
120
0
10
20
30
40
Influent Fe (mg/L)


Load removal (%)
0
20
40
60
80
100
120
$R^2 = 0.52; p<0.05$
0
10
20
30
40
Influent Fe (mg/L)


Area-adjusted removal (g/m2/d)
0
5
10
15
20
25
30
35
40
45
$R^2 = 0.77; p=0.001$
0
10
20
30
40
Influent Fe (mg/L)


Area-adjusted removal (g/m2/d)
0
2
4
6
8
10
12
14
16
18
20
$R^2 = 0.94; p<0.001$
0
10
20
30
40
Influent Fe (mg/L)


First-order removal (m/d)
0.00
0.50
1.00
1.50
2.00
2.50
3.00
0
10
20
30
40
Influent Fe (mg/L)


First-order removal (m/d)
0.00
0.50
1.00
1.50
2.00
2.50
3.00
$R^2 = 0.68; p<0.05$
0
10
20
30
40
Influent Fe (mg/L)

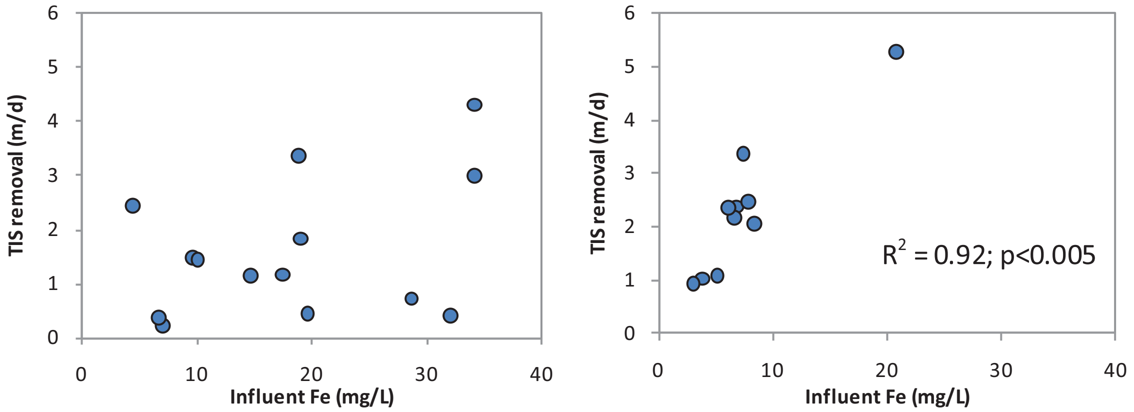
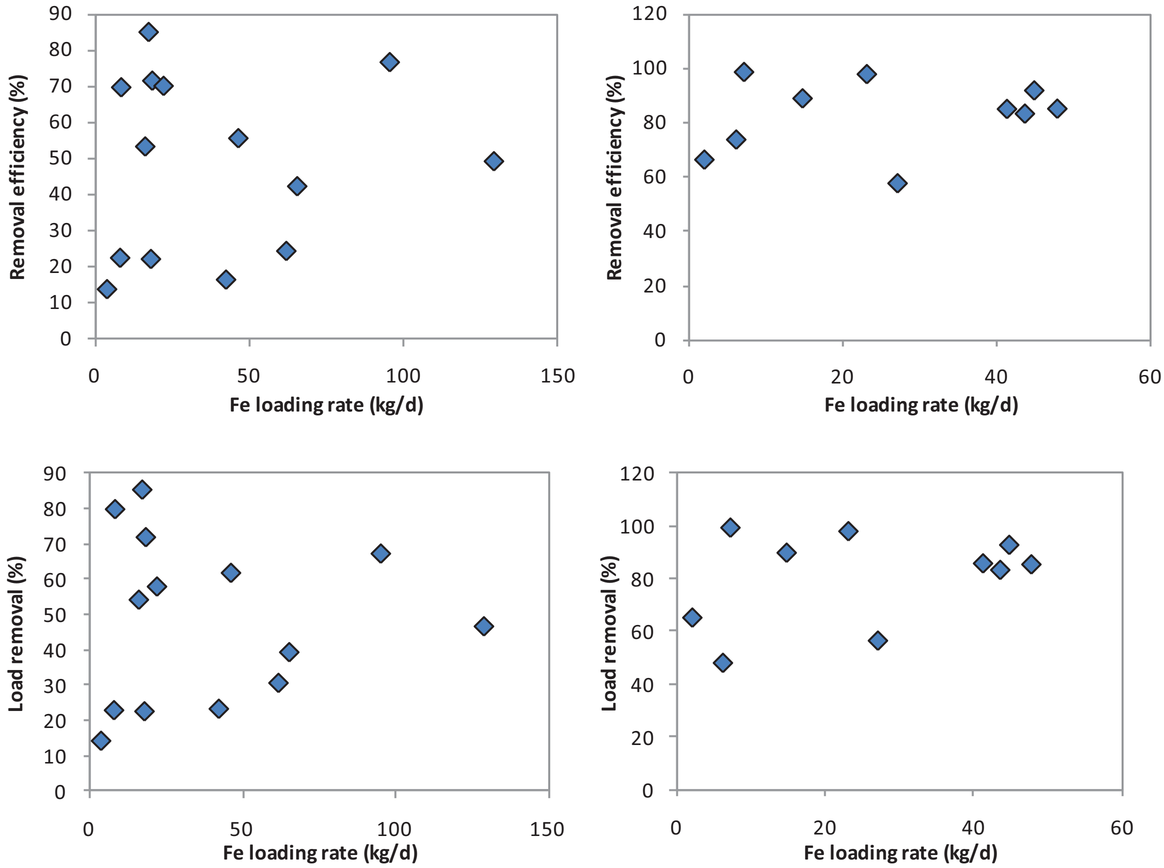


Figure K.1 Scatter plots of iron removal metrics as a function of influent Fe concentration (a) iron removal efficiency (b) iron load removal (c) area-adjusted removal rate (d) first-order removal rate and (e) TIS removal rate



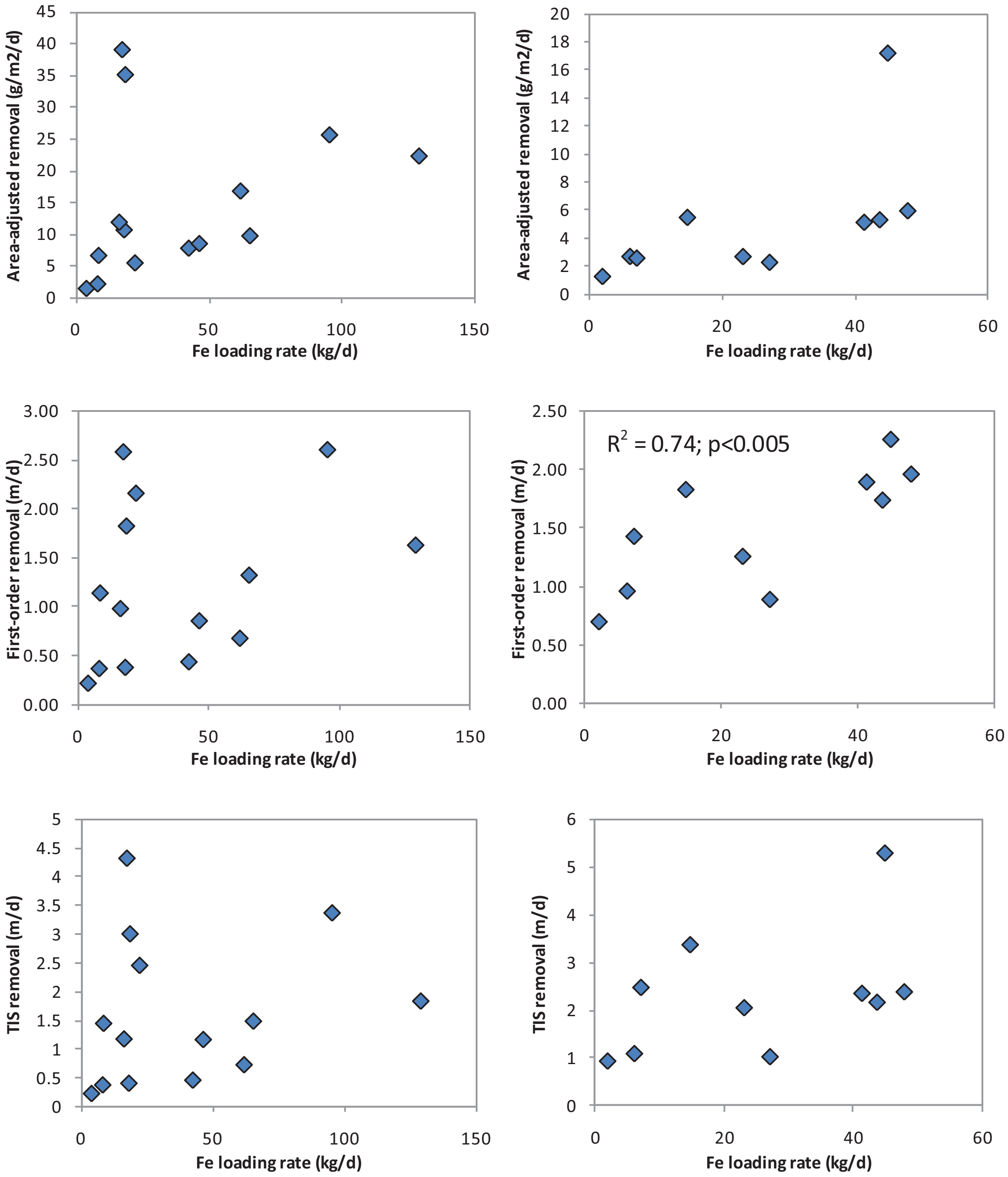


Figure K.2 Scatter plots of iron removal metrics as a function of Fe loading rate (a) iron removal efficiency (b) iron load removal (c) area-adjusted removal rate (d) first-order removal rate and (e) TIS removal rate

APPENDIX L

Table L1. Iron oxidation and settlement rates in settlement lagoons (column tests)

Site		Inlet/ Outlet	Fe Total In (mg/L)	Fe Dissolved (mg/L)	Ferrous iron (mg/L)	Particulate iron (mg/L)	Fe oxidised (mg/L)	Fe particulate total (mg/L)	Fe oxidation rate (min^{-1})	Fe settlement rate (min^{-1})
Acomb	Dec-08	In	31.11	19.6	14.2	11.51	11.68	23.19	0.0204	0.0062
		Out	5.71	4.22	2.52	1.49	2.52	4.01	0.0113	0.0017
	Feb-09	In	6.69	<LOD	<LOD	6.69	-	6.69	-	0.0014
		Out	6.61	<LOD	<LOD	6.61	-	6.61	-	0.0014
	Jun-09	In	23.88	15.04	11.58	8.84	0.71	9.55	0.0158	0.0036
		Out	19.1	14.13	10.87	4.97	10.87	15.84	0.014	0.0038
Whittle	Feb-10	In	18.72	16.29	16.12	2.43	15.75	18.18	0.022	0.006
		Out	14.62	2.63	0.37	11.99	0.37	12.36	0.0021	0.0029
Strafford	Aug-09	In	11.33	5.78	5.6	5.55	5.6	11.15	0.0124	0.0034
		Out	4.19	<LOD	<LOD	4.19	-	4.19	-	0.0025
Allerdean	Apr-09	In	5.13	3.8	2.47	1.33	2.36	3.69	0.0115	0.0019
		Out	2.92	1.02	0.11	1.9	0.11	2.01	0.0017	0.0022
Bates	Jul-09	In	17.28	15.36	14.6	1.92	14.46	16.38	0.0213	0.0054
		Out	6.38	2.76	0.14	3.62	0.14	3.76	0.0027	0.003
		In	15.05	<LOD	<LOD	15.05	-	15.05	-	0.0055
		Out	2.94	<LOD	<LOD	2.94	-	2.94	-	0.0013
Mousewater	Jul-10	In	12.23	5.37	5.26	6.86	4.9	11.76	0.0103	0.0031
		Out	6.68	0.67	0.36	6.01	0.36	6.37	0.002	0.0022
Cuthill	Jul-10	In	12.54	3.76	3.65	8.78	3.54	12.32	0.0131	0.0045
		Out	4.69	0.23	0.11	4.46	0.11	4.57	0.0019	0.0021

Table L2. Iron oxidation and settlement rate in wetlands (column tests)

Site	Inlet/ Outlet	Fe Total In	Fe Dissolved	Ferrous iron	Particulate iron	Fe oxidised ferrous	Fe particulate total (ferrous)	Fe oxidation rate (min^{-1})	Fe settlement rate (min^{-1})
i.Lambley									
Nov-09	In	4.69	4.49	2.24	0.20	2.17	2.37	0.0101	0.0028
	Out	0.84	0.21	0.07	0.63	0.07	0.70	0.002	0.0024
Apr-10	In	4.94	4.79	3.87	0.15	3.70	3.85	0.0093	0.0018
	Out	0.7	0.38	0.17	0.32	0.17	0.49	0.001	0.0013
ii.Whittle									
Feb-10	In	5.74	<LOD	<LOD	5.74	-	5.74	-	0.0026
	Out	0.52	<LOD	<LOD	0.52	-	0.52	-	0.0019
iii.Strafford									
Aug-09	In	3.83	<LOD	<LOD	3.83	-	3.83	-	0.0029
	Out	0.61	<LOD	<LOD	0.61	-	0.61	-	0.0014
iv.Allerdean Mill									
Apr-09	In	2.92	0.84	0.11	2.08	0.11	2.19	0.0017	0.0022
	Out	0.291	<LOD	<LOD	0.29	-	0.29	-	0.0011
v.Mousewater									
Jul-10	In	6.68	0.67	0.36	6.01	0.36	6.37	0.002	0.0022
	Out	0.15	<LOD	<LOD	0.15	-	0.15	-	0.0008
vi.Cuthill									
Jul-10	In	4.69	0.23	0.11	4.46	0.11	4.57	0.0019	0.0021
	Out	0.013	<LOD	<LOD	0.013	-	0.013	-	*

*Reaction rate below the detection limit (0.01 mg/L

APPENDIX M

Saturation Index (SI)

Table M1. Saturation Index (SI) for selected species in Lambley wetland

	26/02/2007		29/07/2008		17/11/2009		27/04/2010	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Aragonite(CaCO3)	-0.07	-0.87	-1.09	-1.35	-1.77	-1.23	-1.47	-1.20
Calcite(CaCO3)	0.09	-0.72	-0.94	-1.20	-1.61	-1.08	-1.31	-1.04
Dolomite(CaMg(CO3)2	-0.06	-1.70	-2.00	-2.52	-3.46	-2.41	-2.85	-2.31
Gypsum(CaSO4:2H2O)	-2.02	-2.10	-2.07	-2.07	-1.85	-1.87	-1.97	-1.99
Fe(OH)3(a)	-0.60	-3.01	-2.79	-3.43	-2.79	-2.04	-3.65	-3.41
Geothite(FeOOH)	4.72	2.26	2.83	2.17	2.58	3.26	1.75	2.00
Hematite(Fe2O3)	11.38	6.44	7.63	6.31	7.10	8.44	5.43	5.94
Melanterite(FeSO4:7H2O)	-5.39	-5.72	-5.48	-6.32	-5.14	-5.91	-5.31	-6.15
Siderite(FeCO3)	1.28	0.20	0.33	-0.78	-0.32	-0.57	-0.06	-0.61
Hausmannite(Mn3O4)	-21.11	-26.99	-25.86	-26.47	-28.34	-24.78	-29.45	-27.18
Manganite(MnOOH)	-8.56	-10.58	-10.91	-10.82	-10.77	-9.24	-11.63	-10.74
Pyrochroite(Mn(OH)2	-4.88	-6.34	-7.00	-7.64	-8.08	-7.02	-7.56	-7.16
Pyrolusite(MnO2)	-20.70	-23.53	-21.94	-21.22	-21.67	-20.03	-23.80	-22.41
Rhodochrosite(MnCO3)	0.65	-0.07	-0.28	-0.68	-0.93	-0.45	-0.67	-0.56

Table M2. Saturation Index (SI) for selected species in Acomb lagoons on 26/02/2007

	Acomb East		**Acomb West**	
	Inlet	Outlet	Inlet	Outlet
Aragonite(CaCO3)	-0.09	-0.25	-0.09	-0.14
Calcite(CaCO3)	0.07	-0.10	0.07	0.02
Dolomite(CaMg(CO3)2	-0.32	-0.65	-0.32	-0.44
Gypsum(CaSO4:2H2O)	-0.57	-0.58	-0.57	-0.56
Fe(OH)3(a)*	3.90	0.14	3.90	1.62
Geothite(FeOOH)	9.27	5.51	9.27	6.96
Hematite(Fe2O3)	20.49	12.96	20.49	15.87
Melanterite(FeSO4:7H2O)	-3.88	-4.43	-3.88	-4.10
Siderite(FeCO3)	1.33	0.63	1.33	1.05
Hausmannite(Mn3O4)	-14.74	-21.54	-14.74	-19.09
Manganite(MnOOH)	-4.84	-8.06	-4.84	-6.87
Pyrochroite(Mn(OH)2	-6.34	-6.65	-6.34	-6.43
Pyrolusite(MnO2)	-11.54	-17.71	-11.54	-15.65
Rhodochrosite(MnCO3)	-0.04	-0.21	-0.04	-0.09

Table M3. Saturation Index (SI) for selected species in Acomb lagoons on 17/02/2008

	Acomb East		**Acomb West**	
	Inlet	Outlet	Inlet	Outlet
Aragonite(CaCO3)	-0.10	-0.05	-0.63	-0.18
Calcite(CaCO3)	0.05	0.10	-0.48	-0.02
Dolomite(CaMg(CO3)2	-0.35	-0.25	-1.40	-0.50
Gypsum(CaSO4:2H2O)	-0.64	-0.65	-0.64	-0.65
Fe(OH)3(a)	0.42	0.91	-2.79	-1.71
Geothite(FeOOH)	5.79	6.26	2.59	3.64
Hematite(Fe2O3)	13.52	14.46	7.12	9.22
Melanterite(FeSO4:7H2O)	-4.53	-4.61	-3.91	-4.25
Siderite(FeCO3)	0.75	0.72	0.85	0.95
Hausmannite(Mn3O4)	-20.47	-19.34	-29.00	-25.50
Manganite(MnOOH)	-7.72	-7.16	-11.53	-10.12
Pyrochroite(Mn(OH)2	-6.25	-6.14	-7.26	-6.37
Pyrolusite(MnO2)	-17.44	-16.50	-23.99	-22.18
Rhodochrosite(MnCO3)	-0.04	0.00	-0.53	-0.10

Table M4. Saturation Index (SI) for selected species in Acomb lagoons on 02/06/2009

	Acomb East		**Acomb West**	
	Inlet	Outlet	Inlet	Outlet
Aragonite(CaCO3)	-0.67	-0.13	-0.12	-0.10
Calcite(CaCO3)	-0.51	0.02	0.03	0.05
Dolomite(CaMg(CO3)2	-1.44	-0.33	-0.30	-0.27
Gypsum(CaSO4:2H2O)	-0.64	-0.65	-0.63	-0.64
Fe(OH)3(a)*	-3.11	-2.47	-2.59	-2.50
Geothite(FeOOH)	2.34	3.10	3.00	3.06
Hematite(Fe2O3)	6.64	8.17	7.97	8.09
Melanterite(FeSO4:7H2O)	-3.93	-4.10	-4.10	-4.07
Siderite(FeCO3)	0.81	1.23	1.23	1.28
Hausmannite(Mn3O4)	-29.75	-26.66	-26.77	-26.80
Manganite(MnOOH)	-11.93	-11.28	-11.39	-11.35
Pyrochroite(Mn(OH)2	-7.70	-6.74	-6.72	-6.70
Pyrolusite(MnO2)	-24.04	-23.16	-23.33	-23.36
Rhodochrosite(MnCO3)	-0.60	-0.10	-0.09	-0.09

Table M5. Saturation Index (SI) for selected species in Whittle on 26/02/2007

	Lagoon		**Wetland**	
	Inlet	Outlet	Inlet	Outlet
Aragonite(CaCO3)	0.25	0.21	0.30	0.67
Calcite(CaCO3)	0.40	0.37	0.45	0.83
Dolomite(CaMg(CO3)2	0.66	0.70	0.87	1.59
Gypsum(CaSO4:2H2O)	-0.19	-0.23	-0.23	-0.30
Fe(OH)3(a)	-2.22	-3.74	-1.62	3.94
Geothite(FeOOH)	2.88	1.60	3.73	9.24
Hematite(Fe2O3)	7.66	5.14	9.40	20.42
Melanterite(FeSO4:7H2O)	-3.48	-3.73	-3.75	-5.08
Siderite(FeCO3)	1.59	1.43	1.51	0.60
Hausmannite(Mn3O4)	-27.85	-29.44	-25.06	-11.28
Manganite(MnOOH)	-10.69	-12.22	-10.12	-3.44
Pyrochroite(Mn(OH)2	-5.82	-6.03	-5.89	-5.16
Pyrolusite(MnO2)	-25.01	-26.78	-22.70	-10.27
Rhodochrosite(MnCO3)	0.32	0.29	0.35	0.54

Table M6. Saturation Index (SI) for selected species in Whittle on 23/02/2010

	Lagoon		**Wetland**	
	Inlet	Outlet	Inlet	Outlet
Aragonite(CaCO3)	-0.16	0.07	0.48	0.78
Calcite(CaCO3)	-0.01	0.22	0.64	0.94
Dolomite(CaMg(CO3)2	-0.05	0.39	1.18	1.75
Gypsum(CaSO4:2H2O)	-0.35	-0.37	-0.39	-0.38
Fe(OH)3(a)	-2.21	-1.39	1.40	0.89
Geothite(FeOOH)	3.21	3.97	6.68	6.10
Hematite(Fe2O3)	8.36	9.88	15.29	14.11
Melanterite(FeSO4:7H2O)	-3.84	-3.91	-4.25	-5.19
Siderite(FeCO3)	1.12	1.26	1.32	0.64
Hausmannite(Mn3O4)	-26.80	-24.81	-18.55	-18.32
Manganite(MnOOH)	-10.86	-9.92	-6.88	-6.68
Pyrochroite(Mn(OH)2	-6.65	-6.10	-5.39	-5.01
Pyrolusite(MnO2)	-23.09	-22.05	-17.02	-17.35
Rhodochrosite(MnCO3)	-0.14	0.07	0.34	0.32

Table M7. Saturation Index (SI) for selected species in Allerdean Mill on 9/10/2008

	Lag inf	Lag eff north	Lag eff south	Pond	Wet eff north	Wet eff south
Aragonite(CaCO3)	-0.90	-0.27	-0.26	-0.89	0.12	-0.16
Calcite(CaCO3)	-0.75	-0.12	-0.09	-0.74	0.27	-0.01
Dolomite(CaMg(CO3)2	-1.89	-0.64	-0.76	-1.63	0.14	-0.35
Gypsum(CaSO4:2H2O)	-0.75	-0.74	-0.70	-1.33	-0.76	-0.96
Fe(OH)3(a)	-3.58	-1.55	-1.54	-2.12	-0.45	-1.50
Geothite(FeOOH)	1.80	3.81	3.46	3.23	4.92	3.85
Hematite(Fe2O3)	5.54	9.56	8.81	8.41	11.78	9.65
Melanterite(FeSO4:7H2O)	-4.42	-4.90	-4.85	-4.94	-5.82	-6.48
Siderite(FeCO3)	0.34	0.30	0.18	0.24	-0.22	-0.96
Hausmannite(Mn3O4)	-30.17	-23.54	-25.37	-24.66	-	-
Manganite(MnOOH)	-11.93	-9.34	-8.99	-9.90	-	-
Pyrochroite(Mn(OH)2	-7.61	-6.05	-6.05	-6.00	-	-
Pyrolusite(MnO2)	-24.46	-20.89	-21.83	-22.10	-	-
Rhodochrosite(MnCO3)	-0.64	-0.12	-0.13	-0.19	-	-

Table M8. Saturation Index (SI) for selected species in Allerdean Mill on 20/04/2009

	Lag inf	Lag eff north	Lag eff south	Pond	Wet eff north	Wet eff south
Aragonite(CaCO3)	-0.62	0.07	0.13	-0.46	0.12	0.14
Calcite(CaCO3)	-0.47	0.22	0.28	-0.31	0.28	0.29
Dolomite(CaMg(CO3)2	-1.27	0.08	0.20	-0.76	0.22	0.28
Gypsum(CaSO4:2H2O)	-0.82	-0.81	-0.81	-1.27	-0.82	-0.89
Fe(OH)3(a)	-1.48	0.03	0.54	-2.80	1.59	1.03
Geothite(FeOOH)	4.04	5.48	5.97	2.73	7.11	6.52
Hematite(Fe2O3)	10.04	12.92	13.88	7.41	16.18	15.00
Melanterite(FeSO4:7H2O)	-4.52	-4.97	-4.99	-4.96	-5.56	-5.52
Siderite(FeCO3)	0.47	0.67	0.71	0.63	0.17	0.29
Hausmannite(Mn3O4)	-24.44	-19.66	-18.79	-24.70	-15.48	-16.84
Manganite(MnOOH)	-9.84	-7.87	-7.36	-10.73	-5.96	-6.57
Pyrochroite(Mn(OH)2	-7.06	-5.76	-5.72	-5.54	-5.79	-5.78
Pyrolusite(MnO2)	-20.18	-17.83	-16.97	-23.47	-13.72	-15.05
Rhodochrosite(MnCO3)	-0.43	0.19	0.21	0.15	0.07	0.12

Table M10. Saturation Index (SI) for selected species in Allerdean Mill on 23/04/2009

	Lag inf	Lag eff north	Lag eff south	Pond	Wet eff north	Wet eff south
Aragonite(CaCO3)	-0.76	-0.15	-0.05	-0.46	-0.01	-0.42
Calcite(CaCO3)	-0.60	0.01	0.10	-0.31	0.14	-0.26
Dolomite(CaMg(CO3)2	-1.61	-0.37	-0.18	-1.21	-0.10	-0.86
Gypsum(CaSO4:2H2O)	-0.87	-0.87	-0.87	-0.82	-0.91	-1.17
Fe(OH)3(a)	-1.94	0.22	0.71	-1.35	1.05	-1.06
Geothite(FeOOH)	3.39	5.61	6.10	4.03	6.45	4.35
Hematite(Fe2O3)	8.72	13.16	14.15	9.99	14.84	10.64
Melanterite(FeSO4:7H2O)	-4.41	-4.94	-4.96	-4.57	-5.49	-5.62
Siderite(FeCO3)	0.42	0.53	0.60	0.53	0.16	-0.12
Hausmannite(Mn3O4)	-26.59	-19.71	-18.81	-23.38	-17.46	-21.76
Manganite(MnOOH)	-10.18	-7.59	-7.14	-9.30	-6.48	-8.61
Pyrochroite(Mn(OH)2	-7.20	-5.89	-5.91	-6.05	-5.96	-6.02
Pyrolusite(MnO2)	-21.56	-17.44	-16.52	-20.76	-15.10	-19.29
Rhodochrosite(MnCO3)	-0.48	0.09	0.12	-0.06	0.01	-0.30

Table M9. Saturation Index (SI) for selected species in Bates on 13/07/2009

	Lag right inf	Lag right eff 1	Lag right eff 2	Lag left inf	Lag left eff 1	Lag left eff 2	Wet out
Aragonite(CaCO3)	0.11	0.26	0.53	-0.04	0.51	0.73	0.83
Calcite(CaCO3)	0.26	0.41	0.68	0.11	0.66	0.73	0.98
Dolomite(CaMg(CO3)2	0.83	1.16	1.70	0.56	1.66	1.84	2.41
Gypsum(CaSO4:2H2O)	-0.21	-0.25	-0.24	-0.25	-0.28	-0.28	-0.28
Fe(OH)3(a)	-2.76	-2.18	-1.53	-0.50	-0.49	-0.09	0.04
Geothite(FeOOH)	2.88	3.39	4.11	5.07	5.10	5.55	5.73
Hematite(Fe2O3)	7.74	8.74	10.19	12.10	12.17	13.08	13.43
Melanterite(FeSO4:7H2O)	-4.14	-4.40	-4.68	-4.12	-4.82	-5.31	-6.84
Siderite(FeCO3)	1.03	0.93	0.94	0.91	0.80	0.40	-0.86
Hausmannite(Mn3O4)	-24.91	-23.15	-20.68	-20.94	-18.96	-16.33	-17.21
Manganite(MnOOH)	-10.68	-9.79	-8.99	-8.39	-7.80	-6.93	-7.03
Pyrochroite(Mn(OH)2	-6.63	-6.16	-5.78	-6.78	-6.10	-5.58	-6.60
Pyrolusite(MnO2)	-21.79	-20.78	-19.25	-17.35	-16.77	-15.30	-14.26
Rhodochrosite(MnCO3)	0.61	0.80	0.99	0.50	0.97	1.09	-0.38

Table M11. Saturation Index (SI) for selected species in Strafford on 11/08/2009

	Lag inf	Lag eff	Wet eff
Aragonite(CaCO3)	-0.58	0.05	0.38
Calcite(CaCO3)	-0.42	0.20	0.53
Dolomite(CaMg(CO3)2	-0.84	0.42	1.12
Gypsum(CaSO4:2H2O)	-1.29	-1.21	-1.19
Fe(OH)3(a)	-2.88	-1.15	-0.75
Geothite(FeOOH)	2.66	4.45	4.91
Hematite(Fe2O3)	7.29	10.86	11.80
Melanterite(FeSO4:7H2O)	-4.80	-4.89	-5.48
Siderite(FeCO3)	0.72	1.19	0.93
Hausmannite(Mn3O4)	-18.17	-21.55	-19.50
Manganite(MnOOH)	-8.28	-9.24	-8.58
Pyrochroite(Mn(OH)2	-4.06	-5.87	-5.57

Table M12. Saturation Index (SI) for selected species in Mousewater on 6/07/2009

	Lag inf	Lag eff	Wet eff
Aragonite(CaCO3)	-0.58	0.05	0.38
Calcite(CaCO3)	-0.42	0.20	0.53
Dolomite(CaMg(CO3)2	-0.84	0.42	1.12
Gypsum(CaSO4:2H2O)	-1.29	-1.21	-1.19
Fe(OH)3(a)	-2.88	-1.15	-0.75
Geothite(FeOOH)	2.66	4.45	4.91
Hematite(Fe2O3)	7.29	10.86	11.80
Melanterite(FeSO4:7H2O)	-4.80	-4.89	-5.48
Siderite(FeCO3)	0.72	1.19	0.93
Hausmannite(Mn3O4)	-18.17	-21.55	-19.50
Manganite(MnOOH)	-8.28	-9.24	-8.58
Pyrochroite(Mn(OH)2	-4.06	-5.87	-5.57
Pyrolusite(MnO2)	-19.95	-19.84	-18.54
Rhodochrosite(MnCO3)	2.79	0.59	0.63

Table I13. Saturation Index (SI) for selected species in Cuthill on 6/07/2010

	Lag inf	Lag eff	Wet eff
Aragonite(CaCO3)	-0.58	0.05	0.38
Calcite(CaCO3)	-0.42	0.20	0.53
Dolomite(CaMg(CO3)2	-0.84	0.42	1.12
Gypsum(CaSO4:2H2O)	-1.29	-1.21	-1.19
Fe(OH)3(a)	-2.88	-1.15	-0.75
Geothite(FeOOH)	2.66	4.45	4.91
Hematite(Fe2O3)	7.29	10.86	11.80
Melanterite(FeSO4:7H2O)	-4.80	-4.89	-5.48
Siderite(FeCO3)	0.72	1.19	0.93
Hausmannite(Mn3O4)	-18.17	-21.55	-19.50
Manganite(MnOOH)	-8.28	-9.24	-8.58
Pyrochroite(Mn(OH)2	-4.06	-5.87	-5.57
Pyrolusite(MnO2)	-19.95	-19.84	-18.54
Rhodochrosite(MnCO3)	2.79	0.59	0.63

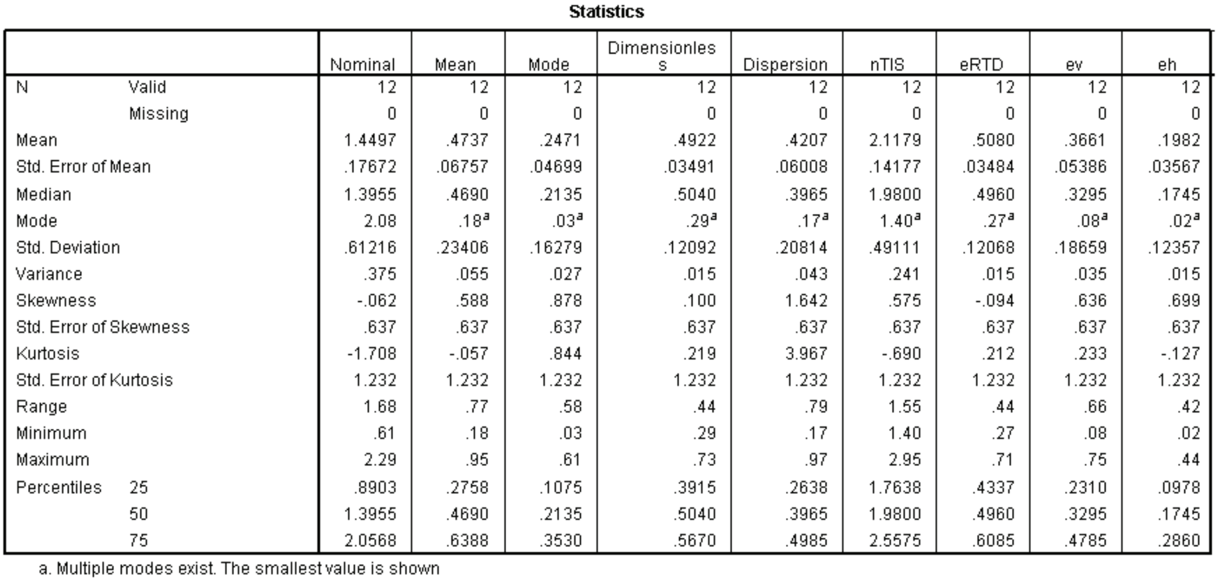
APPENDIX N

Statistical analysis

Comparison of wetland and lagoon hydraulic performance (parametric and non-parametric independent t-test)

Descriptive statistics

Lagoon

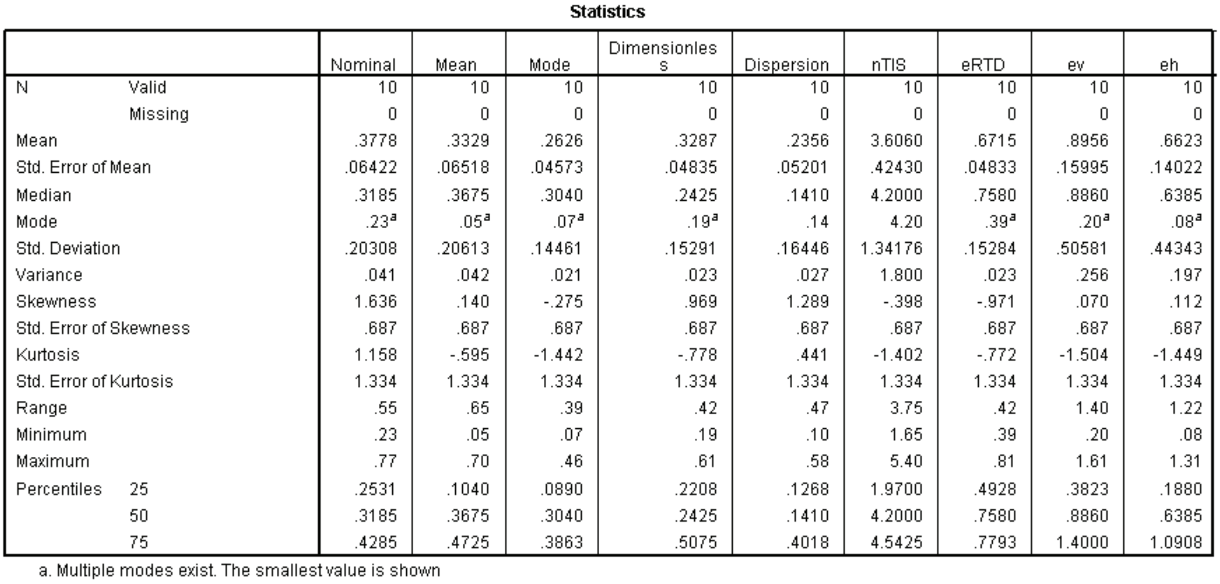


Statistics

		Nominal	Mean	Mode	Dimensionless	Dispersion	nTIS	eRTD	ev	eh
N	Valid	12	12	12	12	12	12	12	12	12
	Missing	0	0	0	0	0	0	0	0	0
Mean		1.4497	.4737	.2471	.4922	.4207	2.1179	.5080	.3661	.1982
Std. Error of Mean		.17672	.06757	.04699	.03491	.06008	.14177	.03484	.05386	.03567
Median		1.3955	.4690	.2135	.5040	.3965	1.9800	.4960	.3295	.1745
Mode		2.08	.18[a]	.03[a]	.29[a]	.17[a]	1.40[a]	.27[a]	.08[a]	.02[a]
Std. Deviation		.61216	.23406	.16279	.12092	.20814	.49111	.12068	.18659	.12357
Variance		.375	.055	.027	.015	.043	.241	.015	.035	.015
Skewness		-.062	.588	.878	.100	1.642	.575	-.094	.636	.699
Std. Error of Skewness		.637	.637	.637	.637	.637	.637	.637	.637	.637
Kurtosis		-1.708	-.057	.844	.219	3.967	-.690	.212	.233	-.127
Std. Error of Kurtosis		1.232	1.232	1.232	1.232	1.232	1.232	1.232	1.232	1.232
Range		1.68	.77	.58	.44	.79	1.55	.44	.66	.42
Minimum		.61	.18	.03	.29	.17	1.40	.27	.08	.02
Maximum		2.29	.95	.61	.73	.97	2.95	.71	.75	.44
Percentiles	25	.8903	.2758	.1075	.3915	.2638	1.7638	.4337	.2310	.0978
	50	1.3955	.4690	.2135	.5040	.3965	1.9800	.4960	.3295	.1745
	75	2.0568	.6388	.3530	.5670	.4985	2.5575	.6085	.4785	.2860

a. Multiple modes exist. The smallest value is shown

Wetland



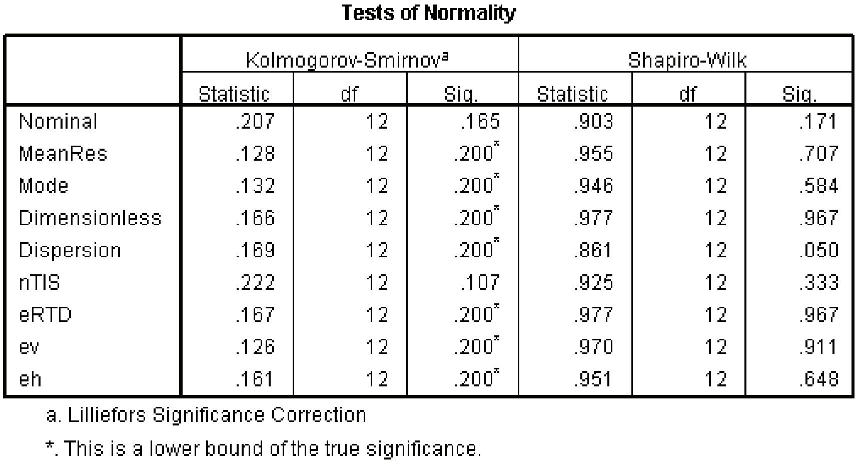
Statistics

		Nominal	Mean	Mode	Dimensionless	Dispersion	nTIS	eRTD	ev	eh
N	Valid	10	10	10	10	10	10	10	10	10
	Missing	0	0	0	0	0	0	0	0	0
Mean		.3778	.3329	.2626	.3287	.2356	3.6060	.6715	.8956	.6623
Std. Error of Mean		.06422	.06518	.04573	.04835	.05201	.42430	.04833	.15995	.14022
Median		.3185	.3675	.3040	.2425	.1410	4.2000	.7580	.8860	.6385
Mode		.23[a]	.05[a]	.07[a]	.19[a]	.14	4.20	.39[a]	.20[a]	.08[a]
Std. Deviation		.20308	.20613	.14461	.15291	.16446	1.34176	.15284	.50581	.44343
Variance		.041	.042	.021	.023	.027	1.800	.023	.256	.197
Skewness		1.636	.140	-.275	.969	1.289	-.398	-.971	.070	.112
Std. Error of Skewness		.687	.687	.687	.687	.687	.687	.687	.687	.687
Kurtosis		1.158	-.595	-1.442	-.778	.441	-1.402	-.772	-1.504	-1.449
Std. Error of Kurtosis		1.334	1.334	1.334	1.334	1.334	1.334	1.334	1.334	1.334
Range		.55	.65	.39	.42	.47	3.75	.42	1.40	1.22
Minimum		.23	.05	.07	.19	.10	1.65	.39	.20	.08
Maximum		.77	.70	.46	.61	.58	5.40	.81	1.61	1.31
Percentiles	25	.2531	.1040	.0890	.2208	.1268	1.9700	.4928	.3823	.1880
	50	.3185	.3675	.3040	.2425	.1410	4.2000	.7580	.8860	.6385
	75	.4285	.4725	.3863	.5075	.4018	4.5425	.7793	1.4000	1.0908

a. Multiple modes exist. The smallest value is shown

Test of normality

Lagoon



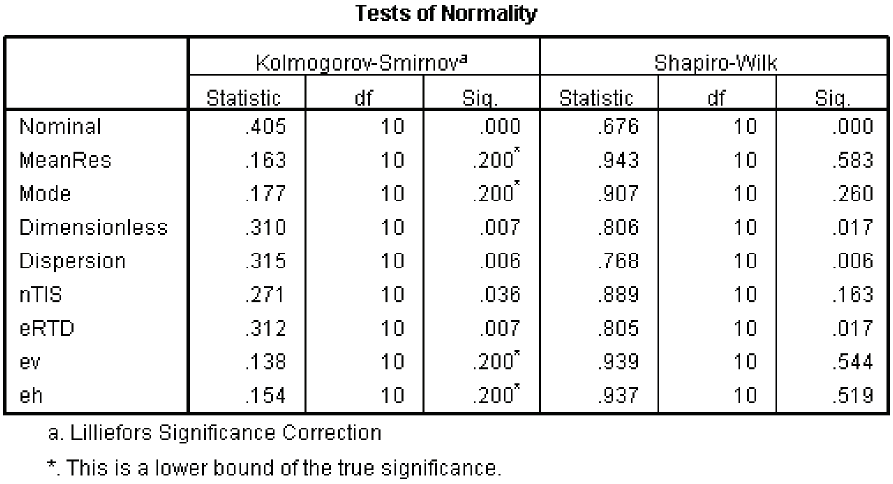
Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
Nominal	.207	12	.165	.903	12	.171
MeanRes	.128	12	.200*	.955	12	.707
Mode	.132	12	.200*	.946	12	.584
Dimensionless	.166	12	.200*	.977	12	.967
Dispersion	.169	12	.200*	.861	12	.050
nTIS	.222	12	.107	.925	12	.333
eRTD	.167	12	.200*	.977	12	.967
ev	.126	12	.200*	.970	12	.911
eh	.161	12	.200*	.951	12	.648

a. Lilliefors Significance Correction

*. This is a lower bound of the true significance.

Wetland



Tests of Normality

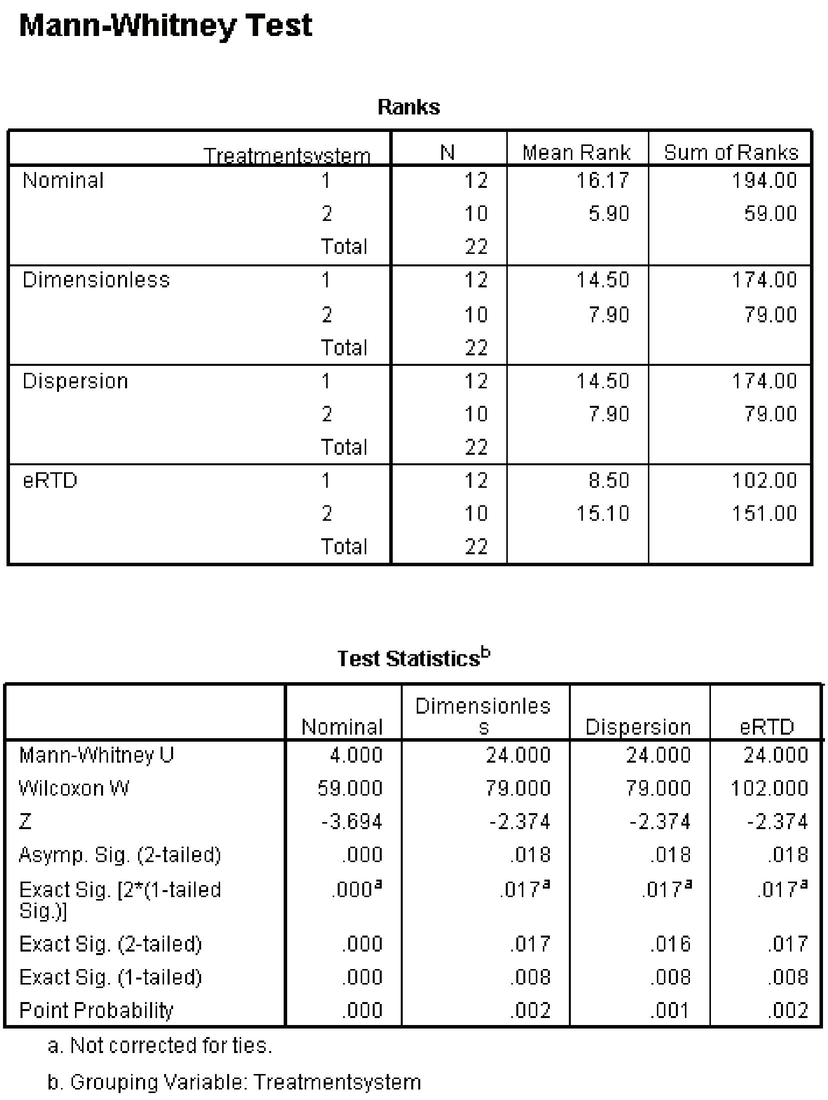
	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
Nominal	.405	10	.000	.676	10	.000
MeanRes	.163	10	.200*	.943	10	.583
Mode	.177	10	.200*	.907	10	.260
Dimensionless	.310	10	.007	.806	10	.017
Dispersion	.315	10	.006	.768	10	.006
nTIS	.271	10	.036	.889	10	.163
eRTD	.312	10	.007	.805	10	.017
ev	.138	10	.200*	.939	10	.544
eh	.154	10	.200*	.937	10	.519

a. Lilliefors Significance Correction

*. This is a lower bound of the true significance.

Independent t-test (non-parametric)

1 denotes lagoon; 2 denotes wetland



Mann-Whitney Test

Ranks

	Treatmentsystem	N	Mean Rank	Sum of Ranks
Nominal	1	12	16.17	194.00
	2	10	5.90	59.00
	Total	22		
Dimensionless	1	12	14.50	174.00
	2	10	7.90	79.00
	Total	22		
Dispersion	1	12	14.50	174.00
	2	10	7.90	79.00
	Total	22		
eRTD	1	12	8.50	102.00
	2	10	15.10	151.00
	Total	22		

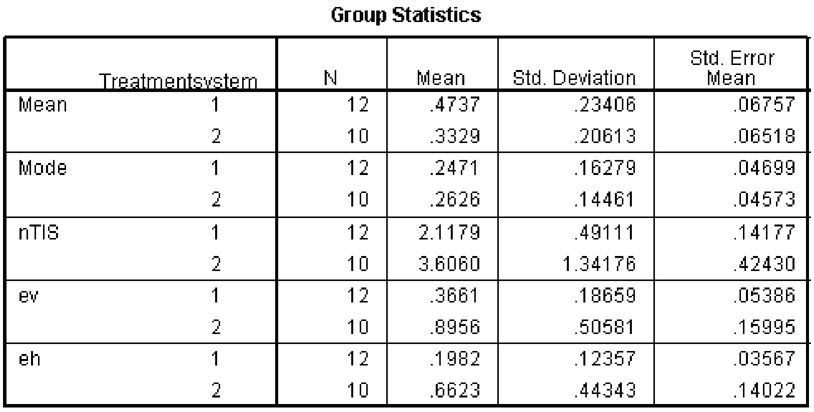
Test Statistics[b]

	Nominal	Dimensionless	Dispersion	eRTD
Mann-Whitney U	4.000	24.000	24.000	24.000
Wilcoxon W	59.000	79.000	79.000	102.000
Z	-3.694	-2.374	-2.374	-2.374
Asymp. Sig. (2-tailed)	.000	.018	.018	.018
Exact Sig. [2*(1-tailed Sig.)]	.000[a]	.017[a]	.017[a]	.017[a]
Exact Sig. (2-tailed)	.000	.017	.016	.017
Exact Sig. (1-tailed)	.000	.008	.008	.008
Point Probability	.000	.002	.001	.002

a. Not corrected for ties.

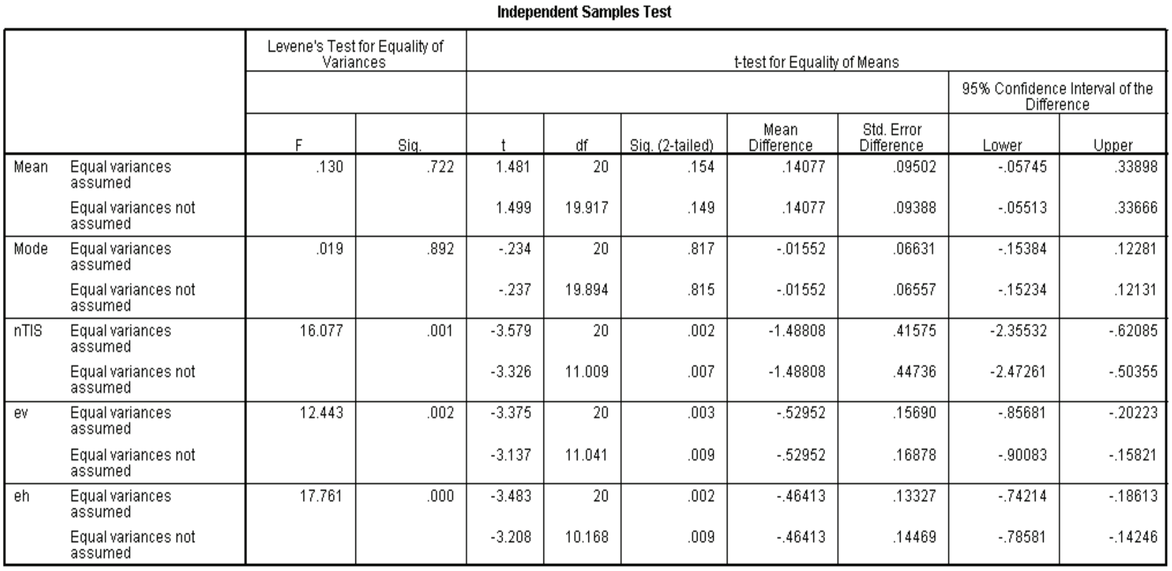
b. Grouping Variable: Treatmentsystem

Independent t-test (parametric)



Group Statistics

	Treatmentsystem	N	Mean	Std. Deviation	Std. Error Mean
Mean	1	12	.4737	.23406	.06757
	2	10	.3329	.20613	.06518
Mode	1	12	.2471	.16279	.04699
	2	10	.2626	.14461	.04573
nTIS	1	12	2.1179	.49111	.14177
	2	10	3.6060	1.34176	.42430
ev	1	12	.3661	.18659	.05386
	2	10	.8956	.50581	.15995
eh	1	12	.1982	.12357	.03567
	2	10	.6623	.44343	.14022



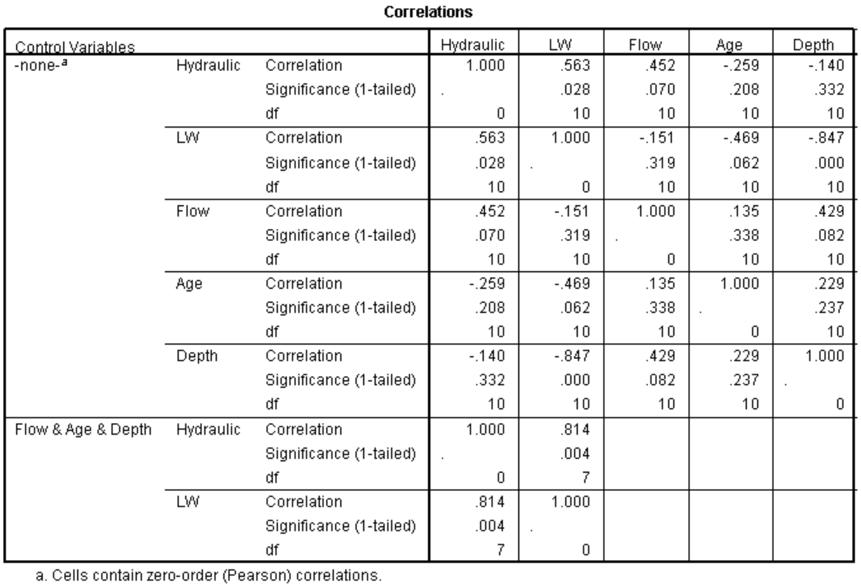
Independent Samples Test

		Levene's Test for Equality of Variances		t-test for Equality of Means						
									95% Confidence Interval of the Difference	
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	Lower	Upper
Mean	Equal variances assumed	.130	.722	1.481	20	.154	.14077	.09502	-.05745	.33898
	Equal variances not assumed			1.499	19.917	.149	.14077	.09388	-.05513	.33666
Mode	Equal variances assumed	.019	.892	-.234	20	.817	-.01552	.06631	-.15384	.12281
	Equal variances not assumed			-.237	19.894	.815	-.01552	.06557	-.15234	.12131
nTIS	Equal variances assumed	16.077	.001	-3.579	20	.002	-1.48808	.41575	-2.35532	-.62085
	Equal variances not assumed			-3.326	11.009	.007	-1.48808	.44736	-2.47261	-.50355
ev	Equal variances assumed	12.443	.002	-3.375	20	.003	-.52952	.15690	-.85681	-.20223
	Equal variances not assumed			-3.137	11.041	.009	-.52952	.16878	-.90083	-.15821
eh	Equal variances assumed	17.761	.000	-3.483	20	.002	-.46413	.13327	-.74214	-.18613
	Equal variances not assumed			-3.208	10.168	.009	-.46413	.14469	-.78581	-.14246

Physical influences on RTDs (Partial correlation analysis)

Lagoons

i) Hydraulic efficiency and Length to width ratio (L/W)

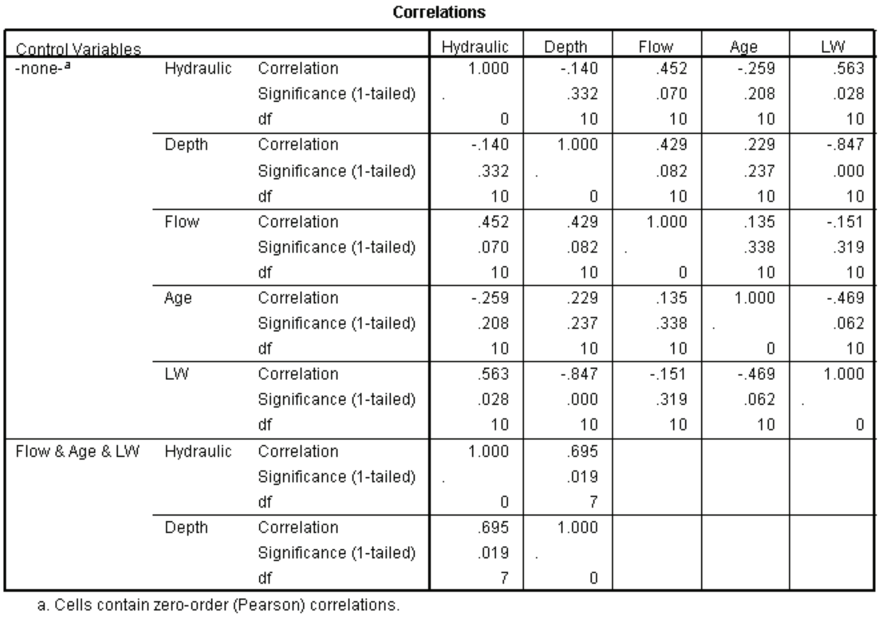


Correlations

Control Variables			Hydraulic	LW	Flow	Age	Depth
-none-[a]	Hydraulic	Correlation	1.000	.563	.452	-.259	-.140
		Significance (1-tailed)	.	.028	.070	.208	.332
		df	0	10	10	10	10
	LW	Correlation	.563	1.000	-.151	-.469	-.847
		Significance (1-tailed)	.028	.	.319	.062	.000
		df	10	0	10	10	10
	Flow	Correlation	.452	-.151	1.000	.135	.429
		Significance (1-tailed)	.070	.319	.	.338	.082
		df	10	10	0	10	10
	Age	Correlation	-.259	-.469	.135	1.000	.229
		Significance (1-tailed)	.208	.062	.338	.	.237
		df	10	10	10	0	10
	Depth	Correlation	-.140	-.847	.429	.229	1.000
		Significance (1-tailed)	.332	.000	.082	.237	.
		df	10	10	10	10	0
Flow & Age & Depth	Hydraulic	Correlation	1.000	.814			
		Significance (1-tailed)	.	.004			
		df	0	7			
	LW	Correlation	.814	1.000			
		Significance (1-tailed)	.004	.			
		df	7	0			

a. Cells contain zero-order (Pearson) correlations.

ii) Hydraulic efficiency and depth

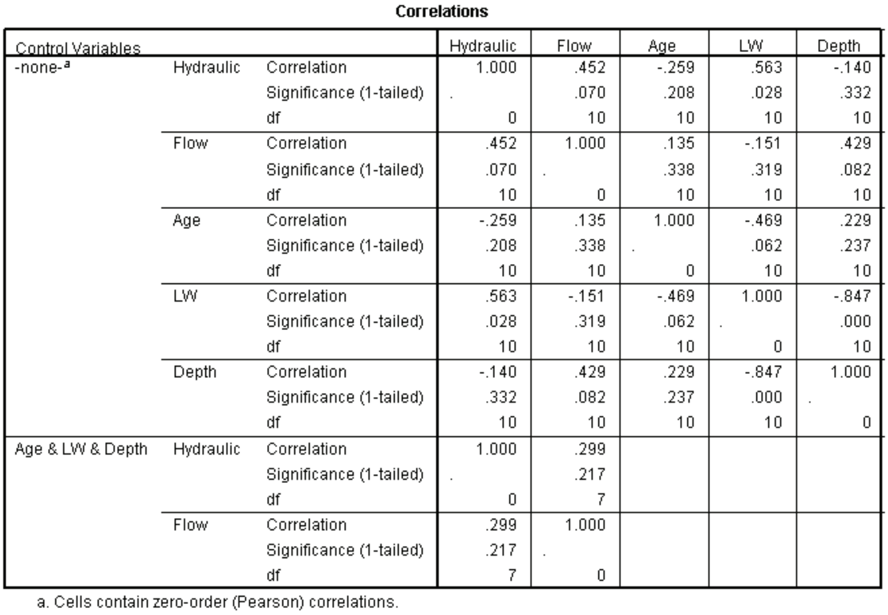


Correlations

Control Variables			Hydraulic	Depth	Flow	Age	LW
-none-[a]	Hydraulic	Correlation	1.000	-.140	.452	-.259	.563
		Significance (1-tailed)	.	.332	.070	.208	.028
		df	0	10	10	10	10
	Depth	Correlation	-.140	1.000	.429	.229	-.847
		Significance (1-tailed)	.332	.	.082	.237	.000
		df	10	0	10	10	10
	Flow	Correlation	.452	.429	1.000	.135	-.151
		Significance (1-tailed)	.070	.082	.	.338	.319
		df	10	10	0	10	10
	Age	Correlation	-.259	.229	.135	1.000	-.469
		Significance (1-tailed)	.208	.237	.338	.	.062
		df	10	10	10	0	10
	LW	Correlation	.563	-.847	-.151	-.469	1.000
		Significance (1-tailed)	.028	.000	.319	.062	.
		df	10	10	10	10	0
Flow & Age & LW	Hydraulic	Correlation	1.000	.695			
		Significance (1-tailed)	.	.019			
		df	0	7			
	Depth	Correlation	.695	1.000			
		Significance (1-tailed)	.019	.			
		df	7	0			

a. Cells contain zero-order (Pearson) correlations.

iii) Hydraulic efficiency and flow

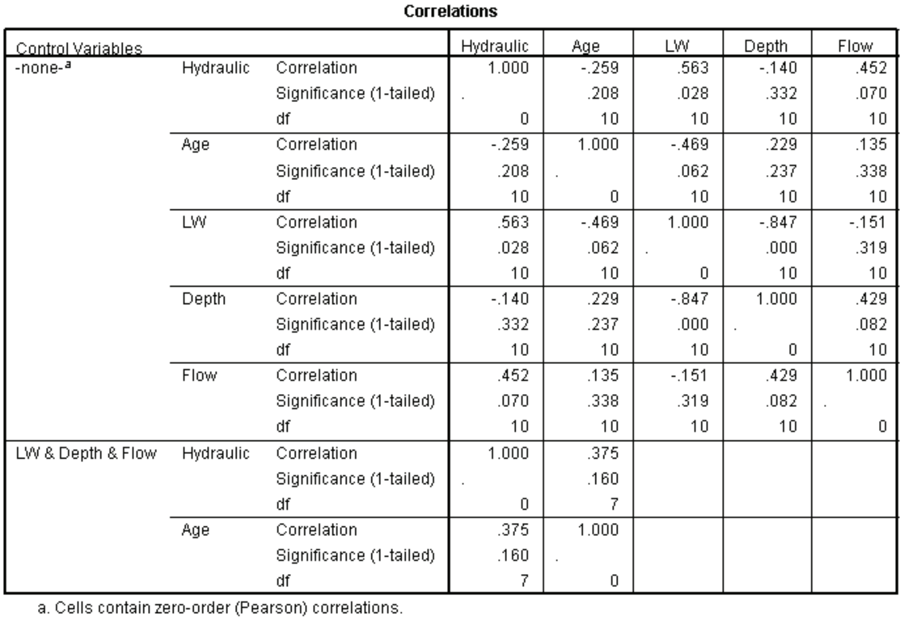


Correlations

Control Variables			Hydraulic	Flow	Age	LW	Depth
-none-[a]	Hydraulic	Correlation	1.000	.452	-.259	.563	-.140
		Significance (1-tailed)	.	.070	.208	.028	.332
		df	0	10	10	10	10
	Flow	Correlation	.452	1.000	.135	-.151	.429
		Significance (1-tailed)	.070	.	.338	.319	.082
		df	10	0	10	10	10
	Age	Correlation	-.259	.135	1.000	-.469	.229
		Significance (1-tailed)	.208	.338	.	.062	.237
		df	10	10	0	10	10
	LW	Correlation	.563	-.151	-.469	1.000	-.847
		Significance (1-tailed)	.028	.319	.062	.	.000
		df	10	10	10	0	10
	Depth	Correlation	-.140	.429	.229	-.847	1.000
		Significance (1-tailed)	.332	.082	.237	.000	.
		df	10	10	10	10	0
Age & LW & Depth	Hydraulic	Correlation	1.000	.299			
		Significance (1-tailed)	.	.217			
		df	0	7			
	Flow	Correlation	.299	1.000			
		Significance (1-tailed)	.217	.			
		df	7	0			

a. Cells contain zero-order (Pearson) correlations.

iv) Hydraulic efficiency and age

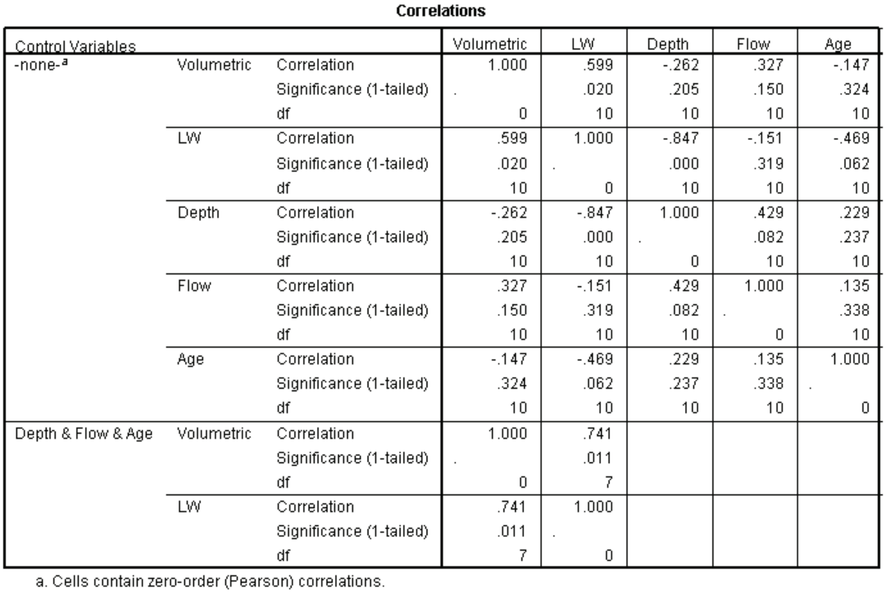


Correlations

Control Variables			Hydraulic	Age	LW	Depth	Flow
-none-[a]	Hydraulic	Correlation	1.000	-.259	.563	-.140	.452
		Significance (1-tailed)	.	.208	.028	.332	.070
		df	0	10	10	10	10
	Age	Correlation	-.259	1.000	-.469	.229	.135
		Significance (1-tailed)	.208	.	.062	.237	.338
		df	10	0	10	10	10
	LW	Correlation	.563	-.469	1.000	-.847	-.151
		Significance (1-tailed)	.028	.062	.	.000	.319
		df	10	10	0	10	10
	Depth	Correlation	-.140	.229	-.847	1.000	.429
		Significance (1-tailed)	.332	.237	.000	.	.082
		df	10	10	10	0	10
	Flow	Correlation	.452	.135	-.151	.429	1.000
		Significance (1-tailed)	.070	.338	.319	.082	.
		df	10	10	10	10	0
LW & Depth & Flow	Hydraulic	Correlation	1.000	.375			
		Significance (1-tailed)	.	.160			
		df	0	7			
	Age	Correlation	.375	1.000			
		Significance (1-tailed)	.160	.			
		df	7	0			

a. Cells contain zero-order (Pearson) correlations.

i) Volumetric efficiency and Length to width ratio (L/W)

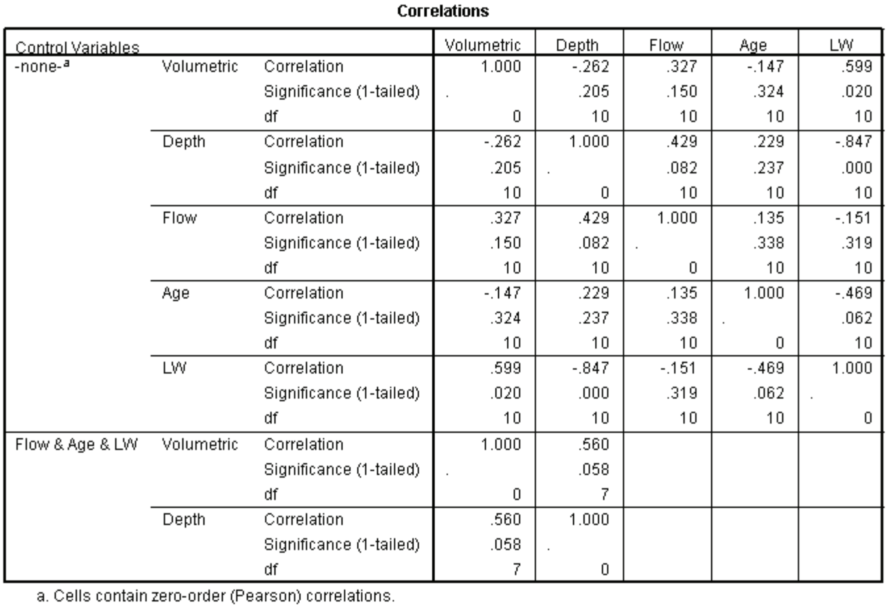


Correlations

Control Variables			Volumetric	LW	Depth	Flow	Age
-none-[a]	Volumetric	Correlation	1.000	.599	-.262	.327	-.147
		Significance (1-tailed)	.	.020	.205	.150	.324
		df	0	10	10	10	10
	LW	Correlation	.599	1.000	-.847	-.151	-.469
		Significance (1-tailed)	.020	.	.000	.319	.062
		df	10	0	10	10	10
	Depth	Correlation	-.262	-.847	1.000	.429	.229
		Significance (1-tailed)	.205	.000	.	.082	.237
		df	10	10	0	10	10
	Flow	Correlation	.327	-.151	.429	1.000	.135
		Significance (1-tailed)	.150	.319	.082	.	.338
		df	10	10	10	0	10
	Age	Correlation	-.147	-.469	.229	.135	1.000
		Significance (1-tailed)	.324	.062	.237	.338	.
		df	10	10	10	10	0
Depth & Flow & Age	Volumetric	Correlation	1.000	.741			
		Significance (1-tailed)	.	.011			
		df	0	7			
	LW	Correlation	.741	1.000			
		Significance (1-tailed)	.011	.			
		df	7	0			

a. Cells contain zero-order (Pearson) correlations.

ii) Volumetric efficiency and depth

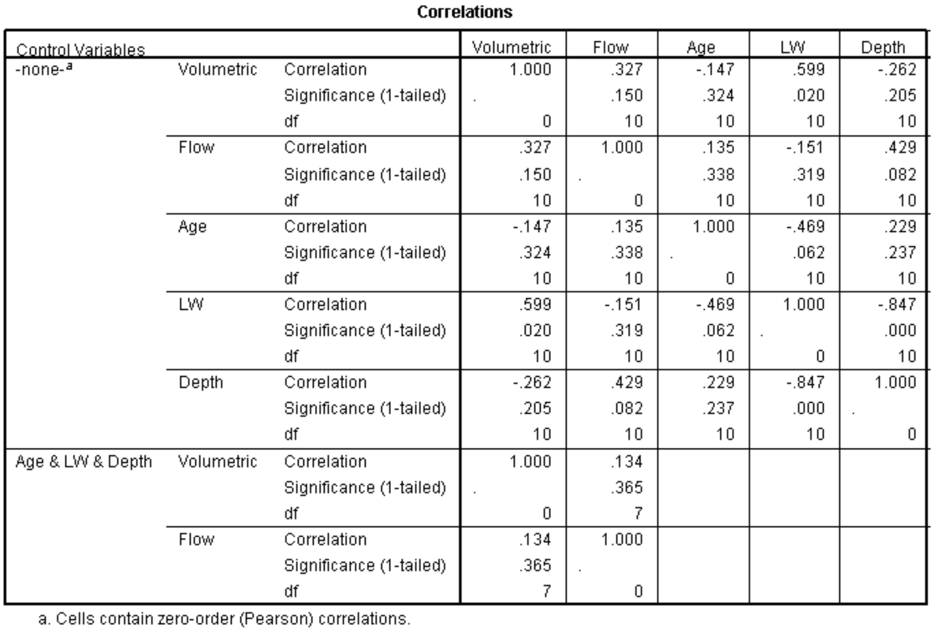


Correlations

Control Variables			Volumetric	Depth	Flow	Age	LW
-none-[a]	Volumetric	Correlation	1.000	-.262	.327	-.147	.599
		Significance (1-tailed)	.	.205	.150	.324	.020
		df	0	10	10	10	10
	Depth	Correlation	-.262	1.000	.429	.229	-.847
		Significance (1-tailed)	.205	.	.082	.237	.000
		df	10	0	10	10	10
	Flow	Correlation	.327	.429	1.000	.135	-.151
		Significance (1-tailed)	.150	.082	.	.338	.319
		df	10	10	0	10	10
	Age	Correlation	-.147	.229	.135	1.000	-.469
		Significance (1-tailed)	.324	.237	.338	.	.062
		df	10	10	10	0	10
	LW	Correlation	.599	-.847	-.151	-.469	1.000
		Significance (1-tailed)	.020	.000	.319	.062	.
		df	10	10	10	10	0
Flow & Age & LW	Volumetric	Correlation	1.000	.560			
		Significance (1-tailed)	.	.058			
		df	0	7			
	Depth	Correlation	.560	1.000			
		Significance (1-tailed)	.058	.			
		df	7	0			

a. Cells contain zero-order (Pearson) correlations.

iii) Volumetric efficiency and flow

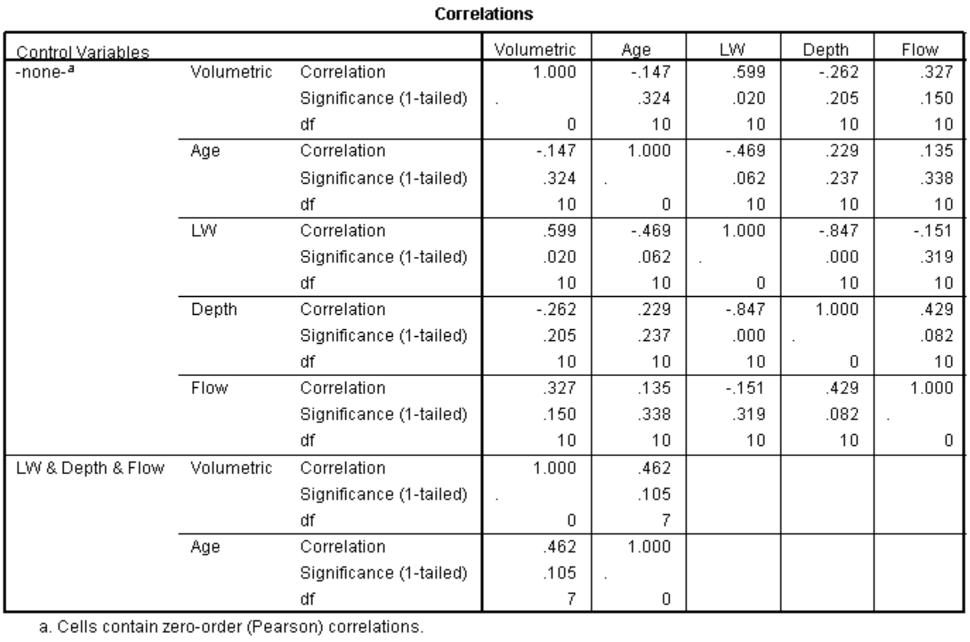


Correlations

Control Variables			Volumetric	Flow	Age	LW	Depth
-none-[a]	Volumetric	Correlation	1.000	.327	-.147	.599	-.262
		Significance (1-tailed)	.	.150	.324	.020	.205
		df	0	10	10	10	10
	Flow	Correlation	.327	1.000	.135	-.151	.429
		Significance (1-tailed)	.150	.	.338	.319	.082
		df	10	0	10	10	10
	Age	Correlation	-.147	.135	1.000	-.469	.229
		Significance (1-tailed)	.324	.338	.	.062	.237
		df	10	10	0	10	10
	LW	Correlation	.599	-.151	-.469	1.000	-.847
		Significance (1-tailed)	.020	.319	.062	.	.000
		df	10	10	10	0	10
	Depth	Correlation	-.262	.429	.229	-.847	1.000
		Significance (1-tailed)	.205	.082	.237	.000	.
		df	10	10	10	10	0
Age & LW & Depth	Volumetric	Correlation	1.000	.134			
		Significance (1-tailed)	.	.365			
		df	0	7			
	Flow	Correlation	.134	1.000			
		Significance (1-tailed)	.365	.			
		df	7	0			

a. Cells contain zero-order (Pearson) correlations.

iv) Volumetric efficiency and age

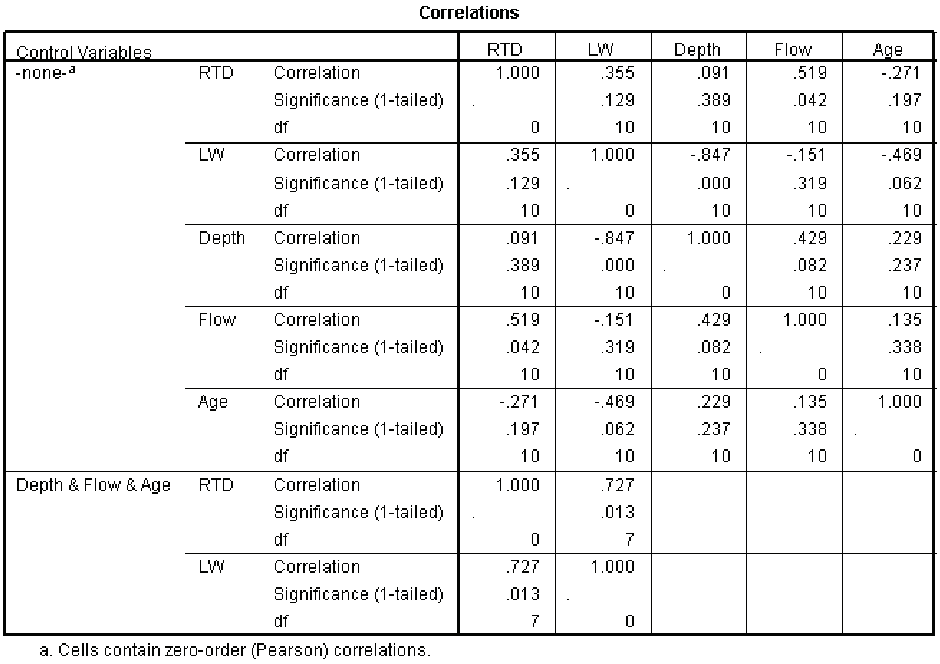


Correlations

Control Variables			Volumetric	Age	LW	Depth	Flow
-none-[a]	Volumetric	Correlation	1.000	-.147	.599	-.262	.327
		Significance (1-tailed)	.	.324	.020	.205	.150
		df	0	10	10	10	10
	Age	Correlation	-.147	1.000	-.469	.229	.135
		Significance (1-tailed)	.324	.	.062	.237	.338
		df	10	0	10	10	10
	LW	Correlation	.599	-.469	1.000	-.847	-.151
		Significance (1-tailed)	.020	.062	.	.000	.319
		df	10	10	0	10	10
	Depth	Correlation	-.262	.229	-.847	1.000	.429
		Significance (1-tailed)	.205	.237	.000	.	.082
		df	10	10	10	0	10
	Flow	Correlation	.327	.135	-.151	.429	1.000
		Significance (1-tailed)	.150	.338	.319	.082	.
		df	10	10	10	10	0
LW & Depth & Flow	Volumetric	Correlation	1.000	.462			
		Significance (1-tailed)	.	.105			
		df	0	7			
	Age	Correlation	.462	1.000			
		Significance (1-tailed)	.105	.			
		df	7	0			

a. Cells contain zero-order (Pearson) correlations.

i) RTD efficiency and Length to width ratio (L/W)

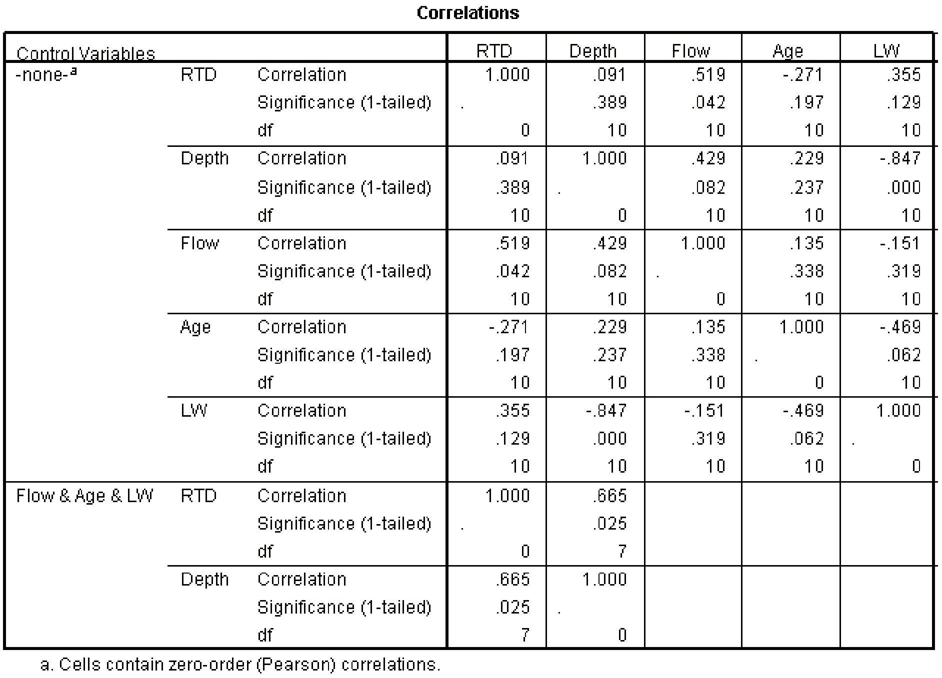


Correlations

Control Variables			RTD	LW	Depth	Flow	Age
-none-[a]	RTD	Correlation	1.000	.355	.091	.519	-.271
		Significance (1-tailed)	.	.129	.389	.042	.197
		df	0	10	10	10	10
	LW	Correlation	.355	1.000	-.847	-.151	-.469
		Significance (1-tailed)	.129	.	.000	.319	.062
		df	10	0	10	10	10
	Depth	Correlation	.091	-.847	1.000	.429	.229
		Significance (1-tailed)	.389	.000	.	.082	.237
		df	10	10	0	10	10
	Flow	Correlation	.519	-.151	.429	1.000	.135
		Significance (1-tailed)	.042	.319	.082	.	.338
		df	10	10	10	0	10
	Age	Correlation	-.271	-.469	.229	.135	1.000
		Significance (1-tailed)	.197	.062	.237	.338	.
		df	10	10	10	10	0
Depth & Flow & Age	RTD	Correlation	1.000	.727			
		Significance (1-tailed)	.	.013			
		df	0	7			
	LW	Correlation	.727	1.000			
		Significance (1-tailed)	.013	.			
		df	7	0			

a. Cells contain zero-order (Pearson) correlations.

ii) RTD efficiency and depth



Correlations

Control Variables			RTD	Depth	Flow	Age	LW
-none-[a]	RTD	Correlation	1.000	.091	.519	-.271	.355
		Significance (1-tailed)	.	.389	.042	.197	.129
		df	0	10	10	10	10
	Depth	Correlation	.091	1.000	.429	.229	-.847
		Significance (1-tailed)	.389	.	.082	.237	.000
		df	10	0	10	10	10
	Flow	Correlation	.519	.429	1.000	.135	-.151
		Significance (1-tailed)	.042	.082	.	.338	.319
		df	10	10	0	10	10
	Age	Correlation	-.271	.229	.135	1.000	-.469
		Significance (1-tailed)	.197	.237	.338	.	.062
		df	10	10	10	0	10
	LW	Correlation	.355	-.847	-.151	-.469	1.000
		Significance (1-tailed)	.129	.000	.319	.062	.
		df	10	10	10	10	0
Flow & Age & LW	RTD	Correlation	1.000	.665			
		Significance (1-tailed)	.	.025			
		df	0	7			
	Depth	Correlation	.665	1.000			
		Significance (1-tailed)	.025	.			
		df	7	0			

a. Cells contain zero-order (Pearson) correlations.

iii) RTD efficiency and flow

Correlations

Control Variables			RTD	Flow	Age	LW	Depth
-none-[a]	RTD	Correlation	1.000	.519	-.271	.355	.091
		Significance (1-tailed)	.	.042	.197	.129	.389
		df	0	10	10	10	10
	Flow	Correlation	.519	1.000	.135	-.151	.429
		Significance (1-tailed)	.042	.	.338	.319	.082
		df	10	0	10	10	10
	Age	Correlation	-.271	.135	1.000	-.469	.229
		Significance (1-tailed)	.197	.338	.	.062	.237
		df	10	10	0	10	10
	LW	Correlation	.355	-.151	-.469	1.000	-.847
		Significance (1-tailed)	.129	.319	.062	.	.000
		df	10	10	10	0	10
	Depth	Correlation	.091	.429	.229	-.847	1.000
		Significance (1-tailed)	.389	.082	.237	.000	.
		df	10	10	10	10	0
Age & LW & Depth	RTD	Correlation	1.000	.262			
		Significance (1-tailed)	.	.248			
		df	0	7			
	Flow	Correlation	.262	1.000			
		Significance (1-tailed)	.248	.			
		df	7	0			

a. Cells contain zero-order (Pearson) correlations.

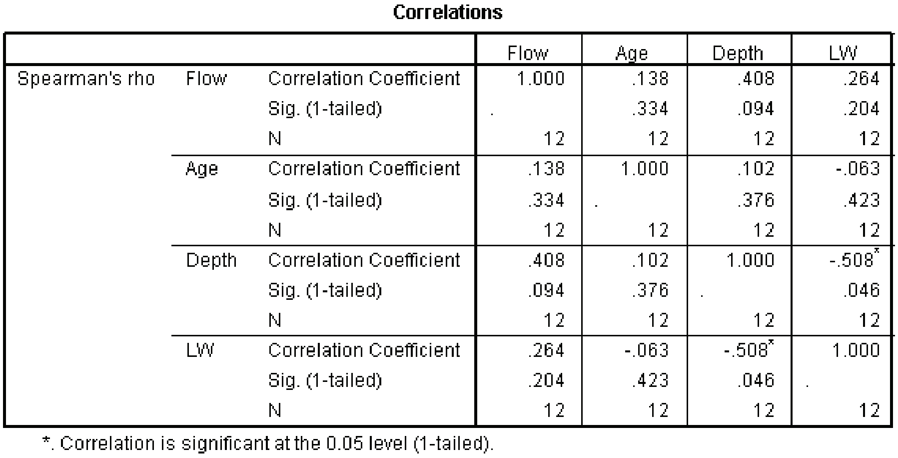
iv) RTD efficiency and age

Correlations

Control Variables			RTD	Age	LW	Depth	Flow
-none-[a]	RTD	Correlation	1.000	-.271	.355	.091	.519
		Significance (1-tailed)	.	.197	.129	.389	.042
		df	0	10	10	10	10
	Age	Correlation	-.271	1.000	-.469	.229	.135
		Significance (1-tailed)	.197	.	.062	.237	.338
		df	10	0	10	10	10
	LW	Correlation	.355	-.469	1.000	-.847	-.151
		Significance (1-tailed)	.129	.062	.	.000	.319
		df	10	10	0	10	10
	Depth	Correlation	.091	.229	-.847	1.000	.429
		Significance (1-tailed)	.389	.237	.000	.	.082
		df	10	10	10	0	10
	Flow	Correlation	.519	.135	-.151	.429	1.000
		Significance (1-tailed)	.042	.338	.319	.082	.
		df	10	10	10	10	0
LW & Depth & Flow	RTD	Correlation	1.000	.171			
		Significance (1-tailed)	.	.330			
		df	0	7			
	Age	Correlation	.171	1.000			
		Significance (1-tailed)	.330	.			
		df	7	0			

a. Cells contain zero-order (Pearson) correlations.

L/W, depth, age and flow

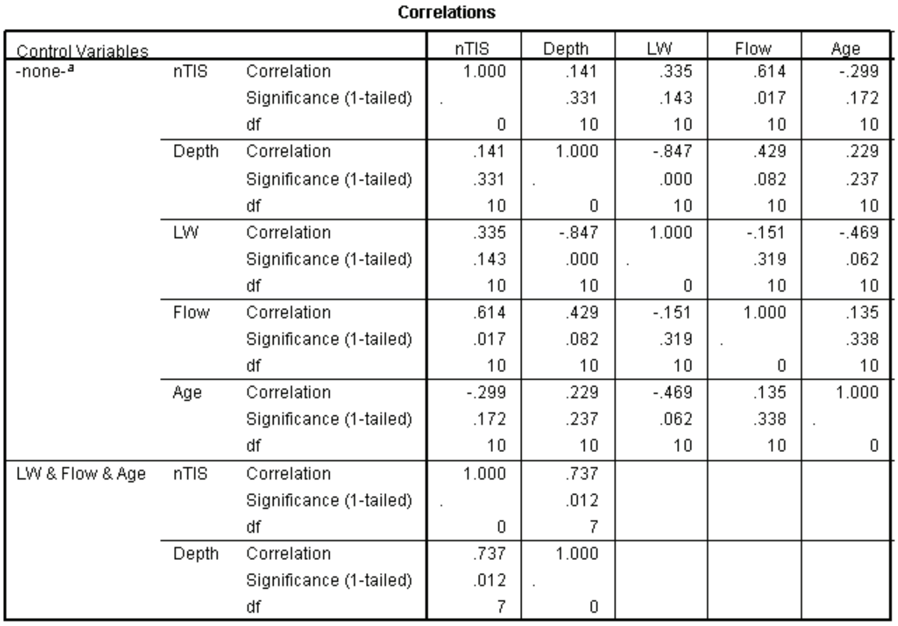


Correlations

			Flow	Age	Depth	LW
Spearman's rho	Flow	Correlation Coefficient	1.000	.138	.408	.264
		Sig. (1-tailed)	.	.334	.094	.204
		N	12	12	12	12
	Age	Correlation Coefficient	.138	1.000	.102	-.063
		Sig. (1-tailed)	.334	.	.376	.423
		N	12	12	12	12
	Depth	Correlation Coefficient	.408	.102	1.000	-.508*
		Sig. (1-tailed)	.094	.376	.	.046
		N	12	12	12	12
	LW	Correlation Coefficient	.264	-.063	-.508*	1.000
		Sig. (1-tailed)	.204	.423	.046	.
		N	12	12	12	12

*. Correlation is significant at the 0.05 level (1-tailed).

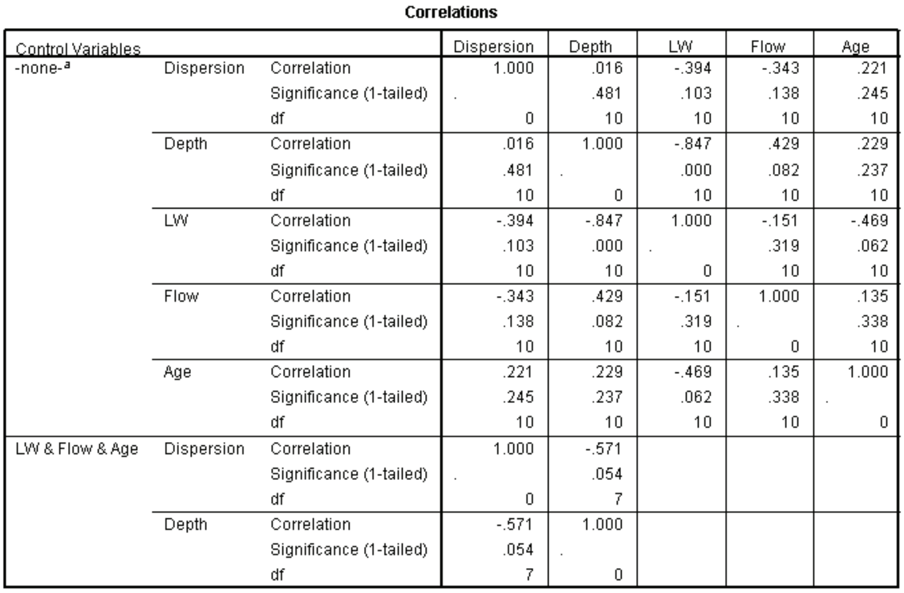
nTIS and depth (controlling for L/W, age and flow)



Correlations

Control Variables			nTIS	Depth	LW	Flow	Age
-none-[a]	nTIS	Correlation	1.000	.141	.335	.614	-.299
		Significance (1-tailed)	.	.331	.143	.017	.172
		df	0	10	10	10	10
	Depth	Correlation	.141	1.000	-.847	.429	.229
		Significance (1-tailed)	.331	.	.000	.082	.237
		df	10	0	10	10	10
	LW	Correlation	.335	-.847	1.000	-.151	-.469
		Significance (1-tailed)	.143	.000	.	.319	.062
		df	10	10	0	10	10
	Flow	Correlation	.614	.429	-.151	1.000	.135
		Significance (1-tailed)	.017	.082	.319	.	.338
		df	10	10	10	0	10
	Age	Correlation	-.299	.229	-.469	.135	1.000
		Significance (1-tailed)	.172	.237	.062	.338	.
		df	10	10	10	10	0
LW & Flow & Age	nTIS	Correlation	1.000	.737			
		Significance (1-tailed)	.	.012			
		df	0	7			
	Depth	Correlation	.737	1.000			
		Significance (1-tailed)	.012	.			
		df	7	0			

Dispersion number, D and depth (controlling for L/W, flow and age)

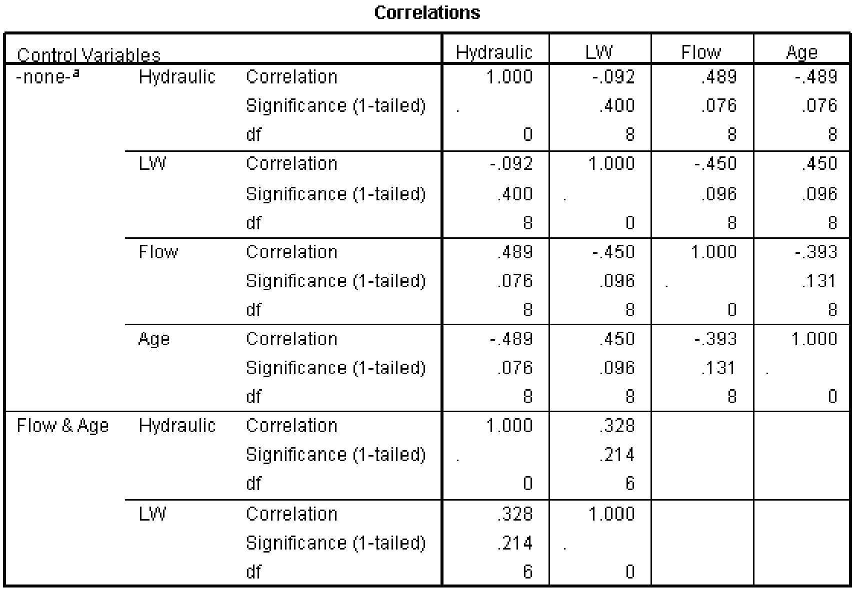


Correlations

Control Variables			Dispersion	Depth	LW	Flow	Age
-none-[a]	Dispersion	Correlation	1.000	.016	-.394	-.343	.221
		Significance (1-tailed)	.	.481	.103	.138	.245
		df	0	10	10	10	10
	Depth	Correlation	.016	1.000	-.847	.429	.229
		Significance (1-tailed)	.481	.	.000	.082	.237
		df	10	0	10	10	10
	LW	Correlation	-.394	-.847	1.000	-.151	-.469
		Significance (1-tailed)	.103	.000	.	.319	.062
		df	10	10	0	10	10
	Flow	Correlation	-.343	.429	-.151	1.000	.135
		Significance (1-tailed)	.138	.082	.319	.	.338
		df	10	10	10	0	10
	Age	Correlation	.221	.229	-.469	.135	1.000
		Significance (1-tailed)	.245	.237	.062	.338	.
		df	10	10	10	10	0
LW & Flow & Age	Dispersion	Correlation	1.000	-.571			
		Significance (1-tailed)	.	.054			
		df	0	7			
	Depth	Correlation	-.571	1.000			
		Significance (1-tailed)	.054	.			
		df	7	0			

Wetlands

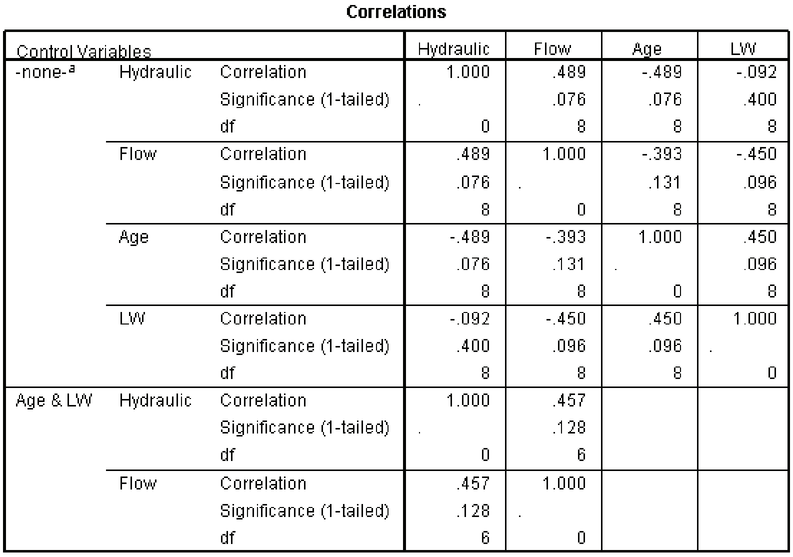
i) Hydraulic efficiency and L/W



Correlations

Control Variables			Hydraulic	LW	Flow	Age
-none-[a]	Hydraulic	Correlation	1.000	-.092	.489	-.489
		Significance (1-tailed)	.	.400	.076	.076
		df	0	8	8	8
	LW	Correlation	-.092	1.000	-.450	.450
		Significance (1-tailed)	.400	.	.096	.096
		df	8	0	8	8
	Flow	Correlation	.489	-.450	1.000	-.393
		Significance (1-tailed)	.076	.096	.	.131
		df	8	8	0	8
	Age	Correlation	-.489	.450	-.393	1.000
		Significance (1-tailed)	.076	.096	.131	.
		df	8	8	8	0
Flow & Age	Hydraulic	Correlation	1.000	.328		
		Significance (1-tailed)	.	.214		
		df	0	6		
	LW	Correlation	.328	1.000		
		Significance (1-tailed)	.214	.		
		df	6	0		

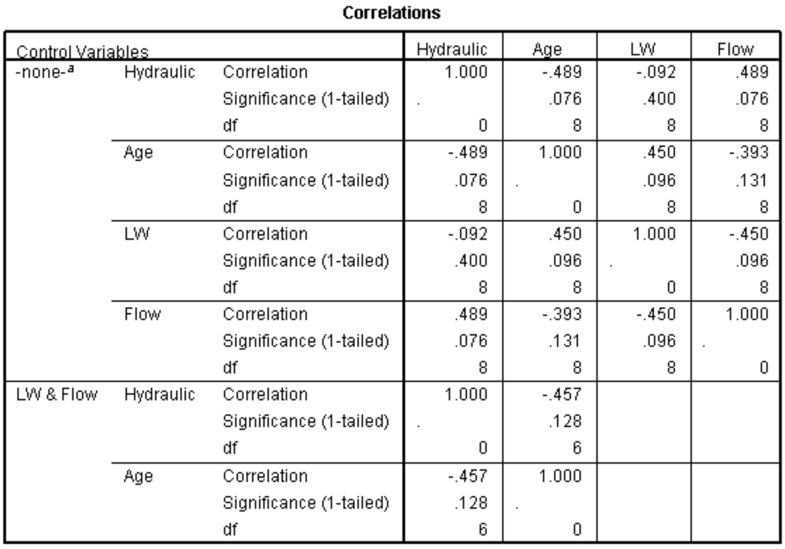
ii) Hydraulic efficiency and flow



Correlations

Control Variables			Hydraulic	Flow	Age	LW
-none-[a]	Hydraulic	Correlation	1.000	.489	-.489	-.092
		Significance (1-tailed)	.	.076	.076	.400
		df	0	8	8	8
	Flow	Correlation	.489	1.000	-.393	-.450
		Significance (1-tailed)	.076	.	.131	.096
		df	8	0	8	8
	Age	Correlation	-.489	-.393	1.000	.450
		Significance (1-tailed)	.076	.131	.	.096
		df	8	8	0	8
	LW	Correlation	-.092	-.450	.450	1.000
		Significance (1-tailed)	.400	.096	.096	.
		df	8	8	8	0
Age & LW	Hydraulic	Correlation	1.000	.457		
		Significance (1-tailed)	.	.128		
		df	0	6		
	Flow	Correlation	.457	1.000		
		Significance (1-tailed)	.128	.		
		df	6	0		

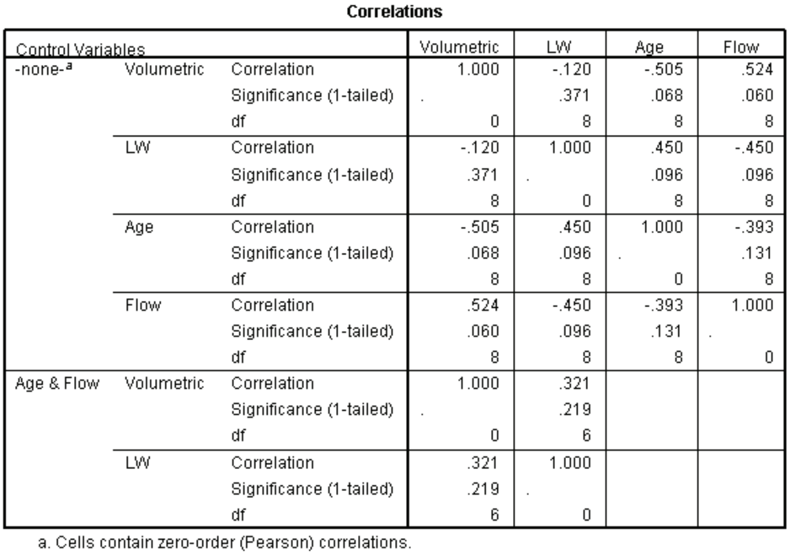
iii) Hydraulic efficiency and age



Correlations

Control Variables			Hydraulic	Age	LW	Flow
-none-[a]	Hydraulic	Correlation	1.000	-.489	-.092	.489
		Significance (1-tailed)	.	.076	.400	.076
		df	0	8	8	8
	Age	Correlation	-.489	1.000	.450	-.393
		Significance (1-tailed)	.076	.	.096	.131
		df	8	0	8	8
	LW	Correlation	-.092	.450	1.000	-.450
		Significance (1-tailed)	.400	.096	.	.096
		df	8	8	0	8
	Flow	Correlation	.489	-.393	-.450	1.000
		Significance (1-tailed)	.076	.131	.096	.
		df	8	8	8	0
LW & Flow	Hydraulic	Correlation	1.000	-.457		
		Significance (1-tailed)	.	.128		
		df	0	6		
	Age	Correlation	-.457	1.000		
		Significance (1-tailed)	.128	.		
		df	6	0		

i) Volumetric efficiency and L/W

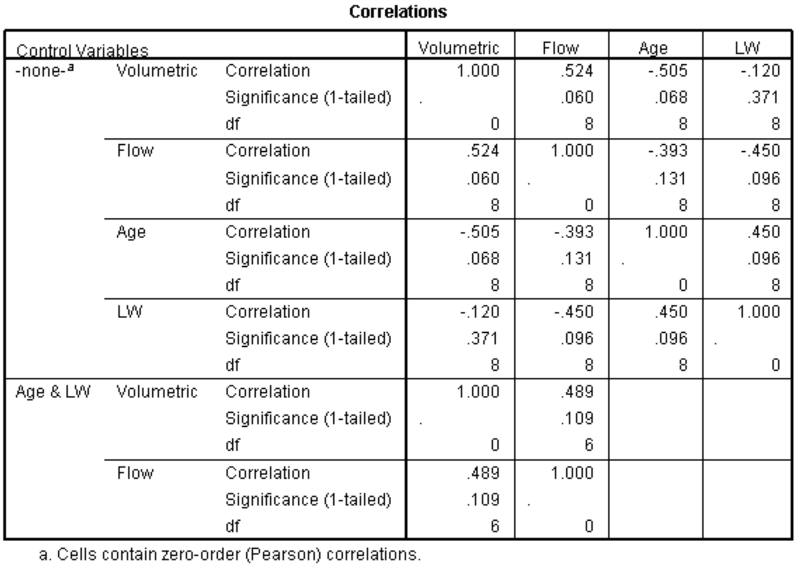


Correlations

Control Variables			Volumetric	LW	Age	Flow
-none-[a]	Volumetric	Correlation	1.000	-.120	-.505	.524
		Significance (1-tailed)	.	.371	.068	.060
		df	0	8	8	8
	LW	Correlation	-.120	1.000	.450	-.450
		Significance (1-tailed)	.371	.	.096	.096
		df	8	0	8	8
	Age	Correlation	-.505	.450	1.000	-.393
		Significance (1-tailed)	.068	.096	.	.131
		df	8	8	0	8
	Flow	Correlation	.524	-.450	-.393	1.000
		Significance (1-tailed)	.060	.096	.131	.
		df	8	8	8	0
Age & Flow	Volumetric	Correlation	1.000	.321		
		Significance (1-tailed)	.	.219		
		df	0	6		
	LW	Correlation	.321	1.000		
		Significance (1-tailed)	.219	.		
		df	6	0		

a. Cells contain zero-order (Pearson) correlations.

ii) Volumetric efficiency and flow



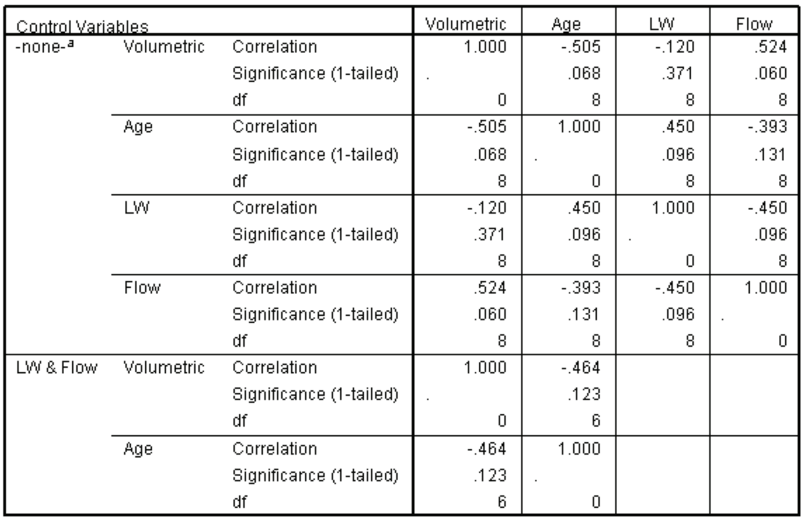
Correlations

Control Variables			Volumetric	Flow	Age	LW
-none-[a]	Volumetric	Correlation	1.000	.524	-.505	-.120
		Significance (1-tailed)	.	.060	.068	.371
		df	0	8	8	8
	Flow	Correlation	.524	1.000	-.393	-.450
		Significance (1-tailed)	.060	.	.131	.096
		df	8	0	8	8
	Age	Correlation	-.505	-.393	1.000	.450
		Significance (1-tailed)	.068	.131	.	.096
		df	8	8	0	8
	LW	Correlation	-.120	-.450	.450	1.000
		Significance (1-tailed)	.371	.096	.096	.
		df	8	8	8	0
Age & LW	Volumetric	Correlation	1.000	.489		
		Significance (1-tailed)	.	.109		
		df	0	6		
	Flow	Correlation	.489	1.000		
		Significance (1-tailed)	.109	.		
		df	6	0		

a. Cells contain zero-order (Pearson) correlations.

iii) Volumetric efficiency and age

Correlations

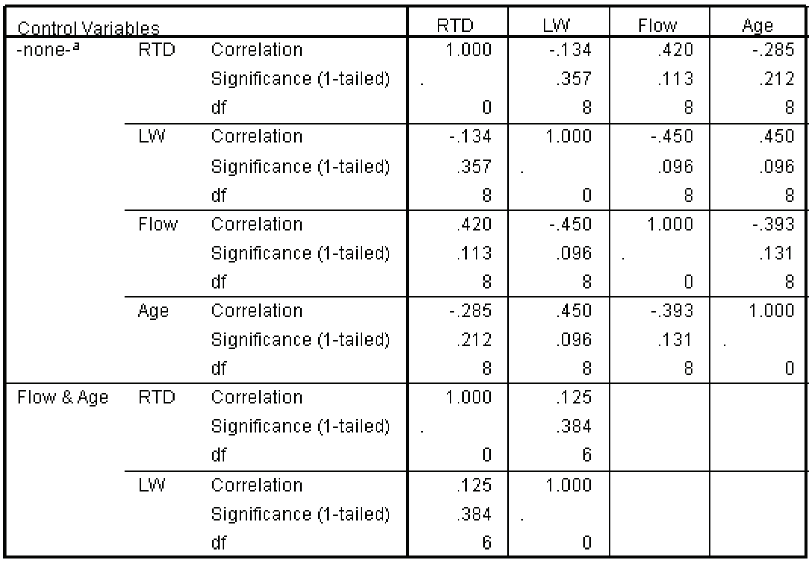


Control Variables			Volumetric	Age	LW	Flow
-none-[a]	Volumetric	Correlation	1.000	-.505	-.120	.524
		Significance (1-tailed)	.	.068	.371	.060
		df	0	8	8	8
	Age	Correlation	-.505	1.000	.450	-.393
		Significance (1-tailed)	.068	.	.096	.131
		df	8	0	8	8
	LW	Correlation	-.120	.450	1.000	-.450
		Significance (1-tailed)	.371	.096	.	.096
		df	8	8	0	8
	Flow	Correlation	.524	-.393	-.450	1.000
		Significance (1-tailed)	.060	.131	.096	.
		df	8	8	8	0
LW & Flow	Volumetric	Correlation	1.000	-.464		
		Significance (1-tailed)	.	.123		
		df	0	6		
	Age	Correlation	-.464	1.000		
		Significance (1-tailed)	.123	.		
		df	6	0		

a. Cells contain zero-order (Pearson) correlations.

i) RTD efficiency and L/W

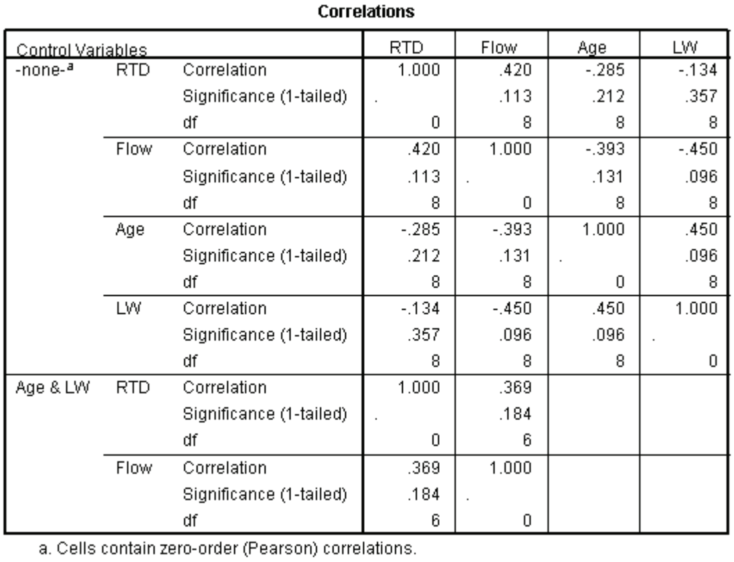
Correlations



Control Variables			RTD	LW	Flow	Age
-none-[a]	RTD	Correlation	1.000	-.134	.420	-.285
		Significance (1-tailed)	.	.357	.113	.212
		df	0	8	8	8
	LW	Correlation	-.134	1.000	-.450	.450
		Significance (1-tailed)	.357	.	.096	.096
		df	8	0	8	8
	Flow	Correlation	.420	-.450	1.000	-.393
		Significance (1-tailed)	.113	.096	.	.131
		df	8	8	0	8
	Age	Correlation	-.285	.450	-.393	1.000
		Significance (1-tailed)	.212	.096	.131	.
		df	8	8	8	0
Flow & Age	RTD	Correlation	1.000	.125		
		Significance (1-tailed)	.	.384		
		df	0	6		
	LW	Correlation	.125	1.000		
		Significance (1-tailed)	.384	.		
		df	6	0		

a. Cells contain zero-order (Pearson) correlations.

ii) RTD efficiency and flow

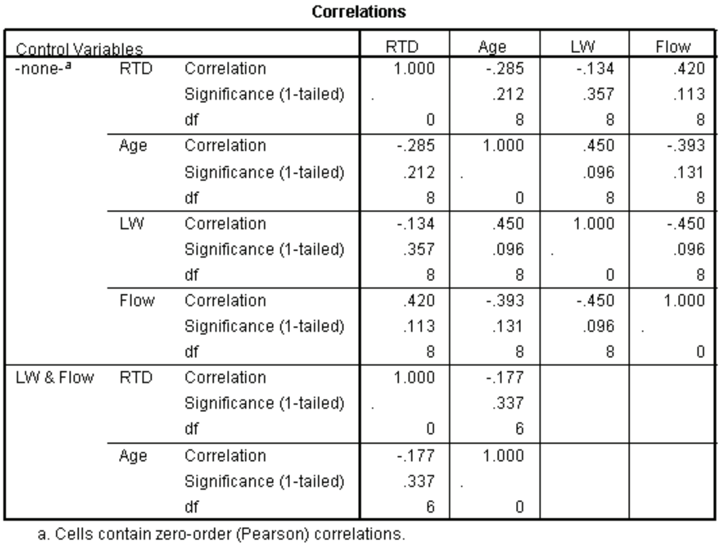


Correlations

Control Variables			RTD	Flow	Age	LW
-none-[a]	RTD	Correlation	1.000	.420	-.285	-.134
		Significance (1-tailed)	.	.113	.212	.357
		df	0	8	8	8
	Flow	Correlation	.420	1.000	-.393	-.450
		Significance (1-tailed)	.113	.	.131	.096
		df	8	0	8	8
	Age	Correlation	-.285	-.393	1.000	.450
		Significance (1-tailed)	.212	.131	.	.096
		df	8	8	0	8
	LW	Correlation	-.134	-.450	.450	1.000
		Significance (1-tailed)	.357	.096	.096	.
		df	8	8	8	0
Age & LW	RTD	Correlation	1.000	.369		
		Significance (1-tailed)	.	.184		
		df	0	6		
	Flow	Correlation	.369	1.000		
		Significance (1-tailed)	.184	.		
		df	6	0		

a. Cells contain zero-order (Pearson) correlations.

iii) RTD efficiency and age

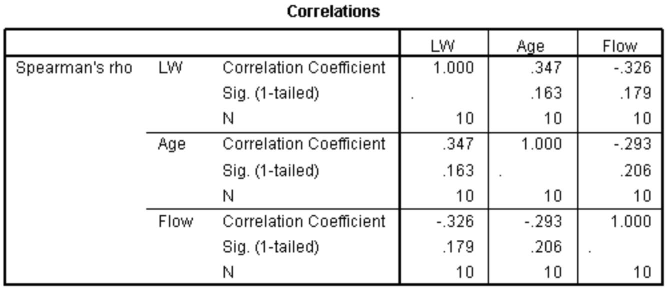


Correlations

Control Variables			RTD	Age	LW	Flow
-none-[a]	RTD	Correlation	1.000	-.285	-.134	.420
		Significance (1-tailed)	.	.212	.357	.113
		df	0	8	8	8
	Age	Correlation	-.285	1.000	.450	-.393
		Significance (1-tailed)	.212	.	.096	.131
		df	8	0	8	8
	LW	Correlation	-.134	.450	1.000	-.450
		Significance (1-tailed)	.357	.096	.	.096
		df	8	8	0	8
	Flow	Correlation	.420	-.393	-.450	1.000
		Significance (1-tailed)	.113	.131	.096	.
		df	8	8	8	0
LW & Flow	RTD	Correlation	1.000	-.177		
		Significance (1-tailed)	.	.337		
		df	0	6		
	Age	Correlation	-.177	1.000		
		Significance (1-tailed)	.337	.		
		df	6	0		

a. Cells contain zero-order (Pearson) correlations.

L/W, age and flow



Correlations

			LW	Age	Flow
Spearman's rho	LW	Correlation Coefficient	1.000	.347	-.326
		Sig. (1-tailed)	.	.163	.179
		N	10	10	10
	Age	Correlation Coefficient	.347	1.000	-.293
		Sig. (1-tailed)	.163	.	.206
		N	10	10	10
	Flow	Correlation Coefficient	-.326	-.293	1.000
		Sig. (1-tailed)	.179	.206	.
		N	10	10	10

APPENDIX O

Iron removal in lagoons and wetlands in relation to hydraulic efficiency

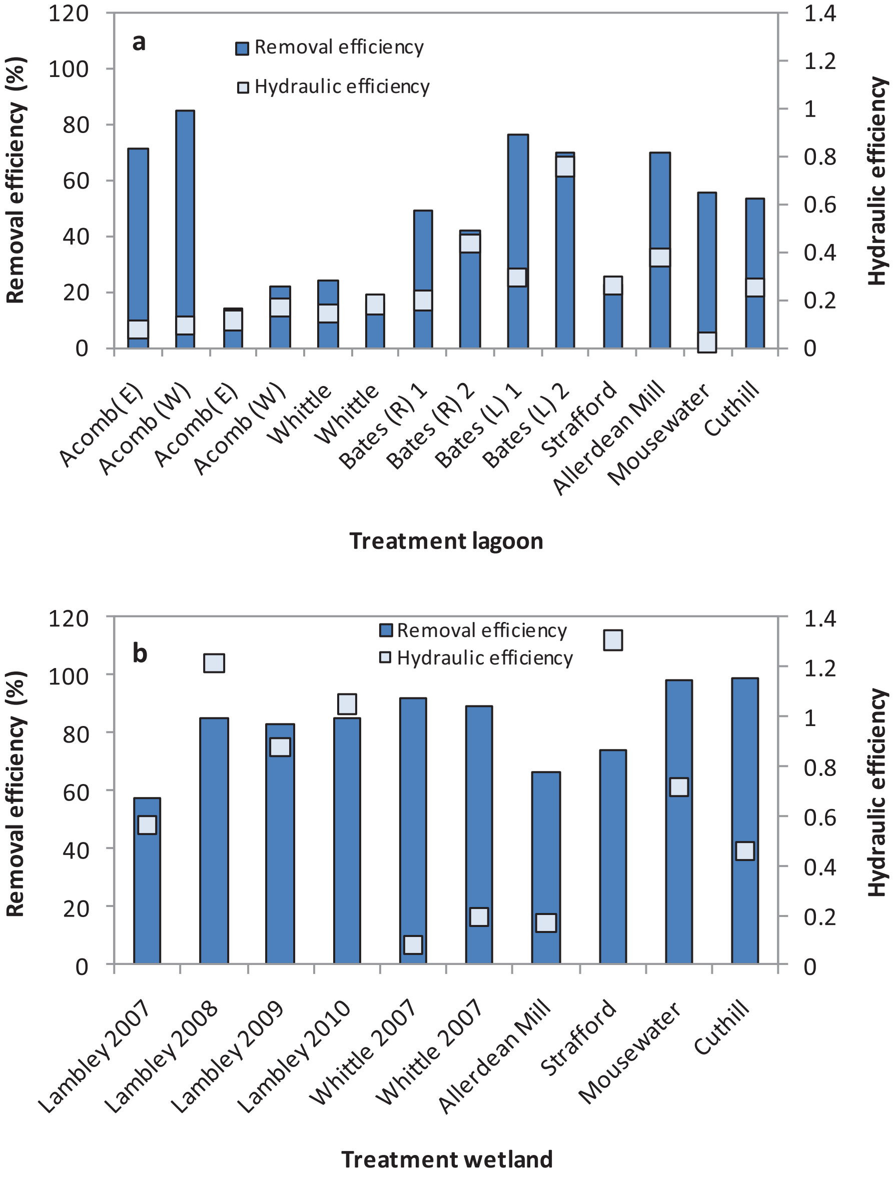


Figure O.1 Iron removal efficiency and hydraulic efficiency for individual (a) lagoon (b) wetland (plotted on the same scale)

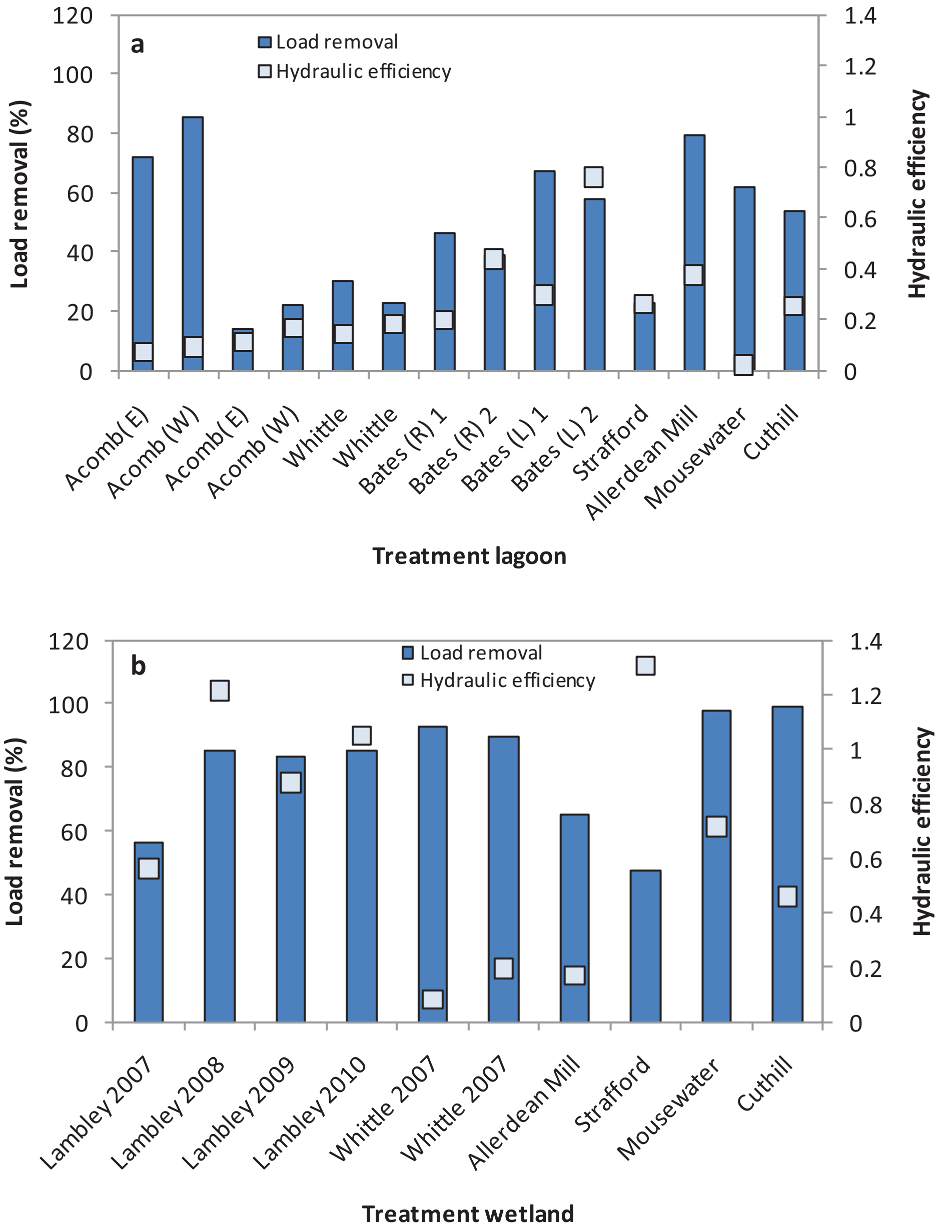


Figure O.2 Iron removal load and hydraulic efficiency for individual (a) lagoon (b) wetland (plotted on the same scale)

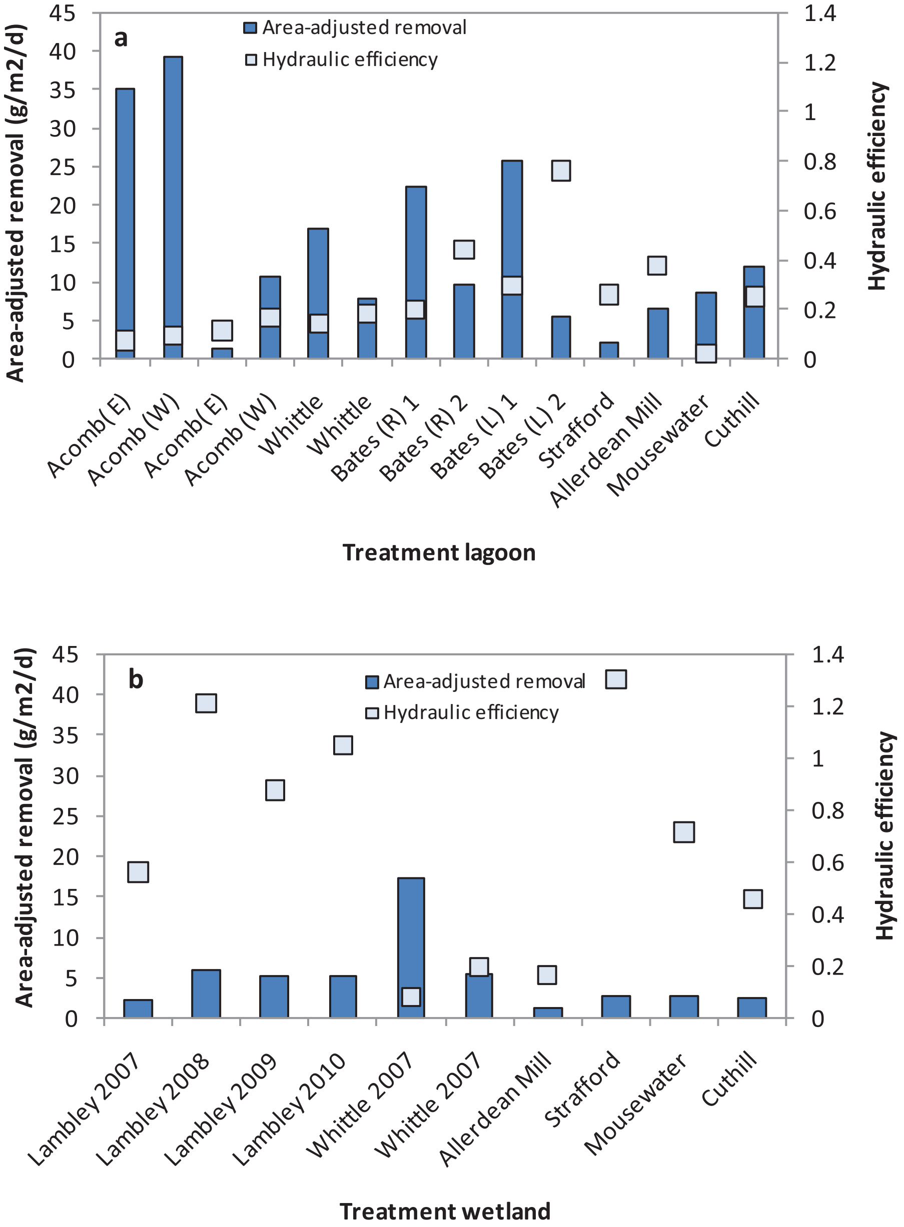


Figure O.3 Area-adjusted removal rate and hydraulic efficiency for individual (a) lagoon (b) wetland (plotted on the same scale)

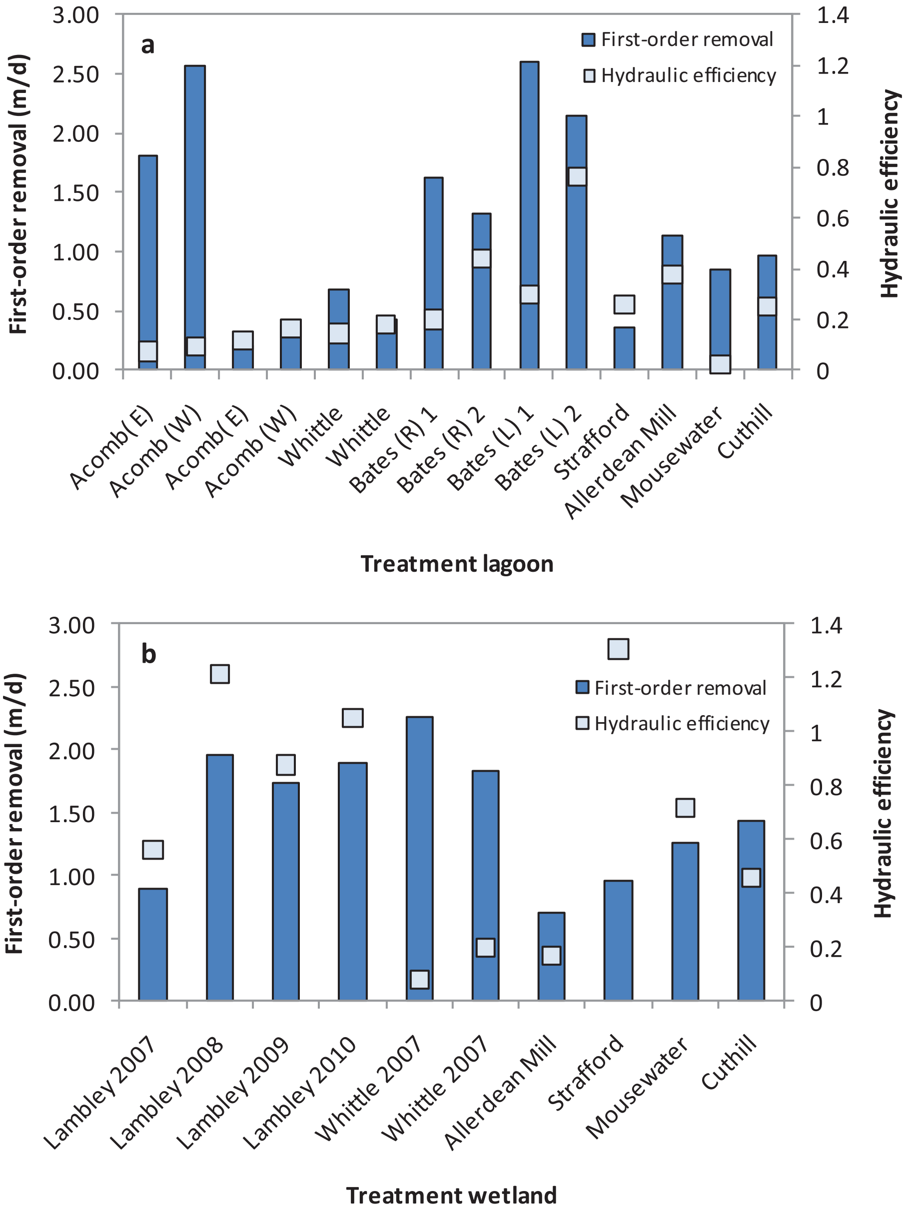


Figure O.4 First-order removal rate and hydraulic efficiency for individual (a) lagoon (b) wetland (plotted on the same scale)

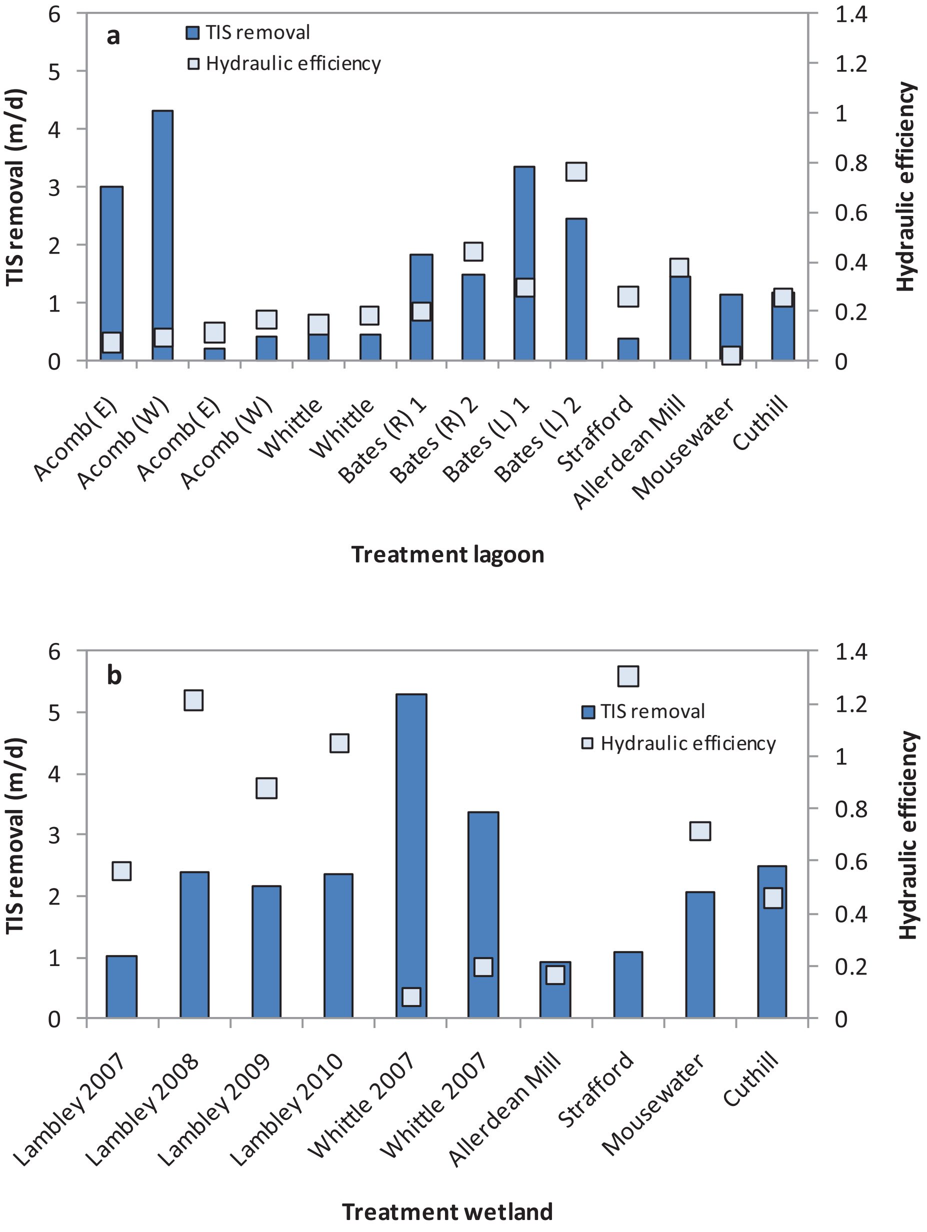


Figure O.5 TIS removal rate and hydraulic efficiency for individual (a) lagoon (b) wetland (plotted on the same scale)