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ARTICLE

Hydraulic Performance and Iron Removal in Wetlands and Lagoons Treating Ferruginous Coal Mine Waters

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Abstract A study of hydraulic residence time has been conducted for several UK Coal Authority mine water treatment systems to evaluate the impact of residence time on the overall hydraulic performance and iron removal within the systems. A series of tracer tests were conducted within the Coal Authority mine water treatment wetlands and lagoons to measure actual hydraulic residence time. The tracer residence time distributions (RTDs) were analysed based on a tanks-in-series (TIS) model to yield the mean residence time and corresponding hydraulic characteristics of the systems. The relationship between iron retention and residence time was tested against a first-order removal model. The mean hydraulic efficiency is 69 % for the wetlands compared to 24 % for the lagoons, mainly attributable to comparatively greater volumetric efficiency within the wetland systems. The mean number of TIS, *n*, is 3.9 for the wetlands and 2.1 for the lagoons, illustrating considerably different flow patterns between wetlands and lagoons. There is also a notable difference of treatment efficiency for iron; mean of 81 % and 47 % for wetlands and lagoons, respectively. Generally, it appears that system hydraulic efficiency (derived from the principle of TIS model) corresponds with iron retention in the treatment systems.

Keywords Ferruginous mine water · Hydraulic efficiency · Residence time · Settlement lagoon · Wetland · Tanks-in-series

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Introduction

The relative importance of residence time for measuring hydraulic performance of wetlands and ponds has been discussed in many studies (e.g. Thackson et al. 1987; Kadlec 1994; Persson et al. 1999; Goulet et al. 2001; Martinez and Wise 2003; Bodin et al. 2013; Kusin 2013; Qi et al. 2013). The time a fraction of water retains within a system should essentially reflect the time required for the treatment of polluted waters. Hydraulic efficiency of treatment wetlands and ponds is often associated with the ability to distribute the water evenly across the system. This would indicate how much of the fractions of water are involved in the treatment process so as to characterise the dispersion behaviour of the systems. In other words, hydraulic efficiency would indicate the extent of flow deviation from ideal systems i.e. plug-flow or completely-mixed system (Persson et al. 1999). Systems hydraulic efficiency is often limited by flow short-circuiting effects i.e. preferential flow paths and the presence of stagnant dead zones (flow re-circulation) to result in some fractions of water to quickly or slowly move towards system outlet (Thackson et al. 1987; Martinez and Wise 2003; Qi et al. 2013). Therefore, measurement of travel time the water takes to flow through a system will essentially give an indication of the hydraulic performance of the system under which polluted water is being treated. The influence of residence time during pollutant removal processes is inevitably apparent, even though clear relationship between residence time and pollutant removal efficiency (particularly for iron) has not been evidenced to date within the UK Coal Authority mine water treatment systems (e.g. Kruse et al. 2009).

The exploitation of coal may leave a series of ecological problems upon closure of the mine sites (Donggan et al. 2011) such as those encountered in the UK a few decades ago. The UK government has since initiated the development of passive treatment systems for coal mine-impacted waters across the country, mainly of wetlands and lagoons. It is the aim of the construction of such wetlands and/or lagoons to remove iron by means of oxidation of ferrous iron and subsequent hydrolysis and precipitation of ferric iron (Younger et al. 2002). Generally, these processes follow the first-order kinetics for pollutant removal, governed by the presence of oxygen, high pH and initial iron concentration. Therefore time becomes the limiting factor to effective treatment. Thus, other factors being equal, a greater removal of iron would be anticipated for a more hydraulically efficient system. Such assessment of hydraulic efficiency within the UK coal mine water treatment systems has not been widely investigated. Therefore it is the aim of this study to assess the effect of residence time on the overall system hydraulic performance and removal of iron as a consequence. This paper presents the findings of an investigation of coal mine water treatment systems (wetlands and settlement lagoons) receiving high concentration of iron (which is the primary pollutant of concern in the absence of acidity).

Site Description

The present findings are based on a series of field experiments (tracer tests) undertaken at eight UK Coal Authority mine water treatment systems within the Northern England (main study area) and part of southern Scotland. The field experiments took place between July 2008–April 2010, and included the wetland systems and settlement lagoons shown in Fig. 1. The systems receive net-alkaline (i.e. alkalinity>acidity), ferruginous mine water with flow rates ranging between 5.9 and 78 L/s, and influent iron concentration from 3 to 34 mg/L. These include a range of relatively small to very large systems, of between 375 and 4,388 m^2 treatment areas. 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. Lagoons are designed to allow 48 h of retention time. In typical applications of passive treatment within the UK coal mine water treatment systems, settlement lagoon serves as a pre-treatment unit, aimed at removing about 50 % iron by

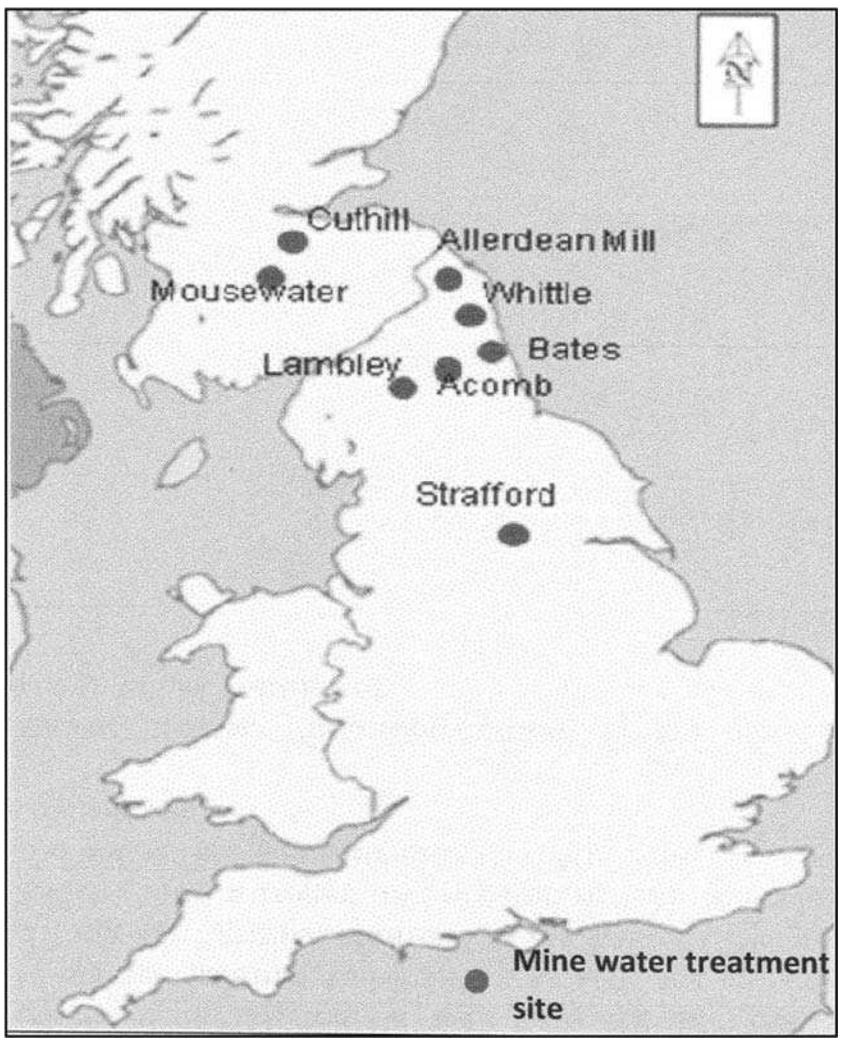

Fig. 1 Location of the investigated coal mine water treatment sites (not to scale)

means of hydrolysis and settlement of ferric hydroxides, prior to final polishing in a wetland system (or a series of wetlands) (Younger et al. 2002).

Reaction Rate Models for Pollutant Removal

Assuming that the kinetics of pollutant removal is zero-order (independent of concentration), under steady state condition, the zero-order pollutant removal is written as:

$$\frac{C_o}{C_i} = 1 - \frac{k_o t}{C_i} \tag{1}$$

where C_i = influent pollutant concentration (g/m^3); C_o = outlet pollutant concentration(g/m^3); t = time (d); k_o = zero-order rate constant (g/m^2/d). Note that the k_o is the area-adjusted removal rate as introduced by Hedin et al. (1994) and has been widely adopted for the design of coal mine water treatment systems (particularly wetlands) within the UK.

According to first-order kinetics, the rate of pollutant removal is dependent on pollutant concentration (Kadlec and Knight 1996; Tarutis et al. 1999; Macias et al. 2012). Because the iron removal process in wetlands and/or lagoons (i.e. oxidation, precipitation and settling) is believed to be first-order with respect to pollutant concentration, design based on zero-order kinetics seems to be less representative of the actual rate of pollutant removal. Thus, according to the first-order kinetics under steady-state, plug-flow conditions, the first-order pollutant removal can be written as (Levenspiel 1972):

$$\frac{C_o}{C_i} = \exp^{[-k_v t]} \tag{2}$$

where k_v = volumetric removal rate constant (d^{-1}). This approach has been widely applied for removals of biochemical oxygen demand (BOD), nutrients and total suspended solids (Kadlec and Knight 1996). It can be seen from Eq. 2 that according to the first-order kinetics, pollutant removal is closely related to residence time i.e. an increase in residence time may increase removal of the pollutant (Goulet et al. 2001). This is also evidenced by the exponential relationship of pollutant removal efficiency and the residence time from the rearrangement of Eq. 2 according to Tarutis et al. (1999) and is given as:

$$\frac{C_i - C_o}{C_i} = 1 - \exp^{[-k_v t]} \tag{3}$$

Equations 2 and 3 above are the derivation of the reaction rates for pollutant removal based on the assumption of ideal plug-flow system. Nevertheless, plug-flow is rarely the case in real systems; therefore reliance on this presumption solely may lead to inaccurate prediction of pollutant treatment. 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 satisfied in actual systems, and that the extent of treatment received differs between fast and slow moving water, suggesting the effects of non-ideal flow behaviour.

An alternative approach is to use the tanks-in-series (TIS) model, which is a commonly applied model for pollutant removal in wetlands and ponds (Persson et al. 1999; Kadlec and Wallace 2009). Principally, according to the TIS removal model, flow enters a system through a number of a series of completely-mixed tanks, each of which removes pollutant in accordance with first-order removal kinetics. This model apparently takes into account the presence of non-ideal flow behaviour within a system, and hence bridges the gaps between ideal plug-flow and completely-mixed flow conditions (Kadlec and Wallace 2009). Note that this model is still based on first-order removal kinetics which is dependent on pollutant concentration. Thus, according to this model, the first-order TIS pollutant removal can be written as:

$$\frac{C_o}{C_i} = \frac{1}{\left[1 + \frac{k_{TIS} t}{n}\right]^n} \tag{4}$$

where k_{TIS} = TIS first-order removal rate (m/d); n = number of tanks in series (unitless). Similarly, Bodin et al. (2013) have recommended that this model may be useful for quantifications of wetland pollutant removal. An advanced mathematical model may also be useful for precise estimation of iron removal in passive treatment such as the one that incorporates the hydrodynamic of pollutant reactive transport e.g. Gouin et al. (2013).

Methods

Tracer Tests

Measurement of actual residence time was undertaken by conducting tracer tests, simply by injecting a known mass of inert tracer into the inlet of the treatment system for a specified duration of time. In the first instance, a trial tracer test employing a multi-tracer approach was performed at a wetland in Lambley, Northumberland using sodium bromide (NaBr), sodium-fluorescein and sodium chloride (NaCl) (Kusin et al. 2010). The results confirmed reliability of the tracers employed, strengthening confidence in the use of such tracers in the following tests. The use of different types of tracer was mainly to ensure conservancy of the injected tracer so as to represent actual changes after addition of the tracer. Concentrations of tracer were monitored at the outlet of the systems using an Aquamatic Auto Cell P2 Autosamplers (for sodium bromide) and logging the fluorescence concentrations (for Na-fluorescein) using a Seapoint fluorimeter, whilst sodium chloride was monitored as conductivity measured by an

Eijelkamp CTD Diver. On average, 86 % of tracer masses were recovered from the system's outflow, indicating reasonably conservative behaviour of tracer during the tests. Flow-rates during the tracer tests were measured by different means depending on infrastructure available at the sites; i) using an Eijelkamp CTD Diver set behind a sharp-crested V-notch weir at the outlet from wetland, and a BaroDiver for atmospheric pressure correction, ii) using a flow impeller to measure flow depth and velocity across the width of flow channel, iii) simple 'bucket-and-stopwatch' measurement, repeated 3 times to derive a mean flow-rate. Simultaneously to the tracer tests, samples of 125 mL were collected in HDPE bottles for analysis of iron and major cations (acidified with 1 % by volume concentrated nitric acid) and anions (non-acidified), whilst, filtered samples (0.2 μm Supor membrane) were collected for analysis of dissolved cations and anions. In the laboratory, samples for cations were analysed using a calibrated Varian Vista MPX ICP-OES and Dionex IC 25 Ion Chromatography for anion analysis.

Measures of System Hydraulic Performance

The tracer test results were analysed for residence time distribution (RTD), which is typically represented by an *E* curve as a function of time (Martinez and Wise 2003; Kadlec and Wallace 2009) and is the probability density function for residence time in a system (Levenspiel 1999):

$$RTD, E(t) = \frac{Q(t)C(t)}{M_o} \tag{5}$$

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); M_o = mass of tracer recovered at system outlet (g).

$$M_o = \int_0^\infty Q(t)C(t)dt \cong \sum_{i=1}^{n} Q_i(t)C_i(t)\Delta t \tag{6}$$

where n = number of samples. Analysis of RTD is regarded as a reliable tool for interpretation of tracer test results in non-steady and/or non-ideal flow systems such as wetlands (Kadlec 1994; Levenspiel 1999), thus illustrating flow deviation from ideal conditions. Accordingly, the tracer RTD curves were modelled in accordance with TIS model that is believed to represent a good approximation of flow movement in most wetlands and ponds (Kadlec and Wallace 2009). The TIS fit for tracer RTD is represented by gamma distribution function (Levenspiel 1999; Kadlec and Wallace 2009) characterised by the number of continuously stirred tank reactors (CSTR) in series, n and mean residence time in each tank, τ_i written as:

$$g(t) = E(t) = \frac{1}{t_i^n \Gamma(n)} t^{n-1} \exp\left(-\frac{t}{\tau_i}\right) \tag{7}$$

where $g(t)$ = gamma distribution function (d^{-1}); n = number of tanks in series (unitless); t = time (d); τ_i = mean residence time in one tank (d); $\Gamma(n)$ = gamma function of n, $= \int_0^\infty t^{n-1}\exp(-t)dt$, if n is a non-integer variable, or $\Gamma(n) = (n-1)!$, if n is an integer (d^{-1}).

Accordingly, assessment of system hydraulic performance was performed based on the measurement of hydraulic residence time to account for the different flow patterns across the systems. As described earlier, residence time is an important determinand for performance measurement of wetlands and ponds. Thackson et al. (1987); Martinez and Wise (2003) and Bodin et al. (2013) expressed hydraulic efficiency, $e\lambda$ for shallow basins and treatment wetlands as:

$$e\lambda = \frac{t_m}{t_n} = \frac{V_{eff}}{V} \tag{8}$$

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 basis for this ratio of mean to volumetric nominal residence time is that there is a portion of the total 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 (Thackson et al. 1987). Consequently, the mean residence time would normally be less than the volumetric nominal residence time.

Additionally, a system with a good hydraulic performance is often associated with effective volume utilisation, which is governed by the uniformity of flow movement across the system. Therefore, according to Persson et al. (1999), hydraulic efficiency of the investigated wetlands and ponds is computed from system effective volume ratio (e_v) and the amount of mixing, to reflect system deviation from ideal plug flow expressed as $(1-\frac{1}{n})$.

$$e\lambda = e_v\left(1-\frac{1}{n}\right) = \left(\frac{t_m}{t_n}\right)\left(1-\frac{t_m-t_p}{t_m}\right) = \frac{t_p}{t_n} \tag{9}$$

where $e_v = \frac{t_m}{t_n} = \frac{V_{eff}}{V}$, an expression that is equivalent to the hydraulic efficiency as introduced by Thackson et al. (1987) and Martinez and Wise (2003); n = number of tanks-in-series (unitless); t_p = peak residence time (d). It can be seen that the second expression of hydraulic efficiency (Eq. 9) is likely more appropriate than the first (Eq. 8) as it simultaneously takes account of the mixing characteristics of water movement, reflecting 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 Eq. 10 (after Persson et al. 1999), reflecting both the fractions of water involved in the flow-through and the dispersion characteristics of water movement.

$$e\lambda = e_v.e_{RTD} \tag{10}$$

where e_{RTD} = residence time distribution efficiency, which can also be written as $(1-\sigma_\theta^2)$; σ_θ^2 = system dimensionless variance, $\frac{\sigma^2}{t_m^2}$ (unitless); σ^2 = tracer flow variance.

Results and Discussion

Treatment Performance Metrics for Lagoons and Wetlands

The lagoons and wetlands receiving ferruginous coal mine water of varying geometry, flow rates and influent iron characteristics were investigated and compared for their efficiencies in hydraulic performance and iron removal (see Tables 1, 2, 3, and 4 for data). Performance data of the investigated wetland systems and lagoons indicate influent waters which are relatively high in iron concentrations; mean of 18.64 and 7.16 mg/L for lagoons and wetlands, respectively (Table 1). These values are comparable to other mine water treatment lagoons and wetlands receiving net-alkaline mine water and are a common feature of coal mine-impacted waters across the UK. Also noted from the table is the markedly higher influent iron loading within the lagoon systems compared to wetlands. Iron concentrations were reduced to a mean of 9.37 mg/L in lagoons and 1.13 mg/L in wetlands, which therefore accounts for mean iron retention in the lagoons and wetlands of 47.07 % and 80.87 %, respectively.

Calculation of area-adjusted removal rate for the systems reveals large deviations of actual removal rate constant for wetlands from the design criteria i.e. mean of 5.98 $g/m^2/d$ compared to the designed 10 $g/m^2/d$. This has been suspected by practitioners since the rate of iron removal is dependent on the influent concentration of iron (Tarutis et al. 1999; Hedin 2008), therefore reliance on constant zero-order removal rate (independent of pollutant concentration) has the potential to result in under-performing systems. While the lagoons demonstrate a closer mean area-adjusted removal constant value to this design metric, 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 h retention. It is also noticeable that there is a very wide range of area-adjusted removal rates in the lagoons (minimum of 1.39 to a maximum of 39.15 $g/m^2/d$). On the other hand, the first-order removal rates for lagoons and wetlands are much closer to one another, although they differ markedly from the 0.18 m/d constant value by Tarutis et al. (1999). However, given the different inflow characteristics from which Tarutis et al. (1999) and Shih et al. (2013) among others developed their constant first-order removal rate, it is inappropriate to simply compare this value of rate removal to those of the systems investigated here. Thus, an alternative approach was adopted to verify the applicability of first-order removal rate, as discussed below.

Test of First-order Removal Model for Wetlands and Settlement Lagoons

The first-order removal model was tested against field data collected during the tracer tests to assess the applicability of the model for prediction of iron retention in the investigated lagoons and wetlands. In addition, such an approach will determine whether residence time has a significant effect on the removal of iron within the systems. Thus, for each of the lagoons

Table 1 Summary treatment performance data for UK coal mine water treatment systems

	Lagoons		Wetlands	
	Mean (S.D)	Min/Max	Mean (S.D)	Min/Max
Influent Fe (mg/L)	18.64 (11.27)	4.36/34.1	7.16 (4.49)	3.01/20.80
Effluent Fe (mg/L)	9.37(7.58)	1.30/24.88	1.13 (0.28)	0.83/1.70
Flow rate (L/s)	29.96 (29.72)	5.85/78.69	46.28 (23.63)	4.25/84.83
[a]Inf Fe loading (kg/d)	39.04 (40.07)	3.77/128.95	26.48 (13.48)	1.11/44.93
[b]Fe retention (%)	47.07 (26.65)	13.83/85.19	80.87 (9.93)	57.67/91.82
[c]Area-adjusted removal ($g/m^2/d$)	14.63 (13.14)	1.39/39.15	5.98 (5.36)	0.69/17.2
[d]First-order removal (m/d)	1.23 (0.91)	0.22/2.60	1.65 (0.76)	0.38/2.29

Data present mean data and standard deviation of mean (S.D) in parentheses, and minimum (min) and maximum (max) values of performance data for lagoons and wetlands, n=11

[a] Calculated as Q×Inf Fe; where Q = flow rate (L/s), regarded as removal efficiency

[b] Calculated as Q(Inf Fe−Eff Fe)/Q*Inf Fe×100

[c] Calculated as Q(Inf Fe−Eff Fe)/A; where A = system area (m^2)

[d] Calculated as Q(ln[Inf Fe−Eff Fe])/A

Table 2 Useful information of the investigated mine water treatment schemes operated by the UK Coal Authority

Site name	Location	Scheme type	No. of settlement lagoon	Total treatment area (m^2)	No. of wetland (cell)	Total treatment area (m^2)	Influent pH	Influent Fe (mg/L)
Lambley	Northumberland, England	Pumped/Passive	–	–	4	4,388	6.65	6.58
Acomb	Northumberland, England	Pumped/Active/Passive	2	750	2	600	7.09	33.69
Whittle	County Durham, England	Pumped/Passive	2	900	3	7,124	7.06	32.59
Allerdean Mill	Northumberland, England	Pumped/Passive	3	1,970	3	3,171	6.60	9.72
Bates	Northumberland England	Pumped/Passive	4	11,400	3	8,000	6.73	18.96
Strafford	South Yorkshire, England	Pumped/Passive	1	850	1	1,690	6.88	6.60
Mousewater	Lanarkshire, Scotland	Gravity/Passive	1	3,036	2	8,400	5.81	14.58
Cuthill	West Lothian, Scotland	Pumped/Passive	1	726	3	2,744	7.18	17.41

and wetlands dataset, iron retention (%) was plotted against corresponding hydraulic residence time. Subsequently, non-linear regression ($y=a[1-\exp^{-bx}]$) was performed using Sigma Plot 11 statistical software to test whether the data fit with the first-order removal model as given in Eq. 3 (Goulet et al. 2001).

As demonstrated in Fig. 2, the first-order removal model failed to fit the data for both lagoons and wetlands systems. In other words, according to this removal model, the hydraulic residence time has no significant effect on the removal of iron within the investigated systems. This, however, is not surprising given the fact that the first-order removal model tested here was basically derived from a plug-flow principle, which is often not evident in actual systems. Kadlec and Knight (1996) have listed nine assumptions that should be met if the first-order removal model is to be satisfactorily applied, including the plug-flow assumption. Additionally, it is also crucial to determine the situations that the first-order model would have good performance and to closely relate RTD and hydraulic residence time (e.g. Shih et al. 2013). Lee et al. (2013) also found that iron removal in a full-scale mine water treatment system did not seem to depend on hydraulic residence time in the system. They however concluded that hydraulic residence time of 1–2 days would be appropriate and economical for such system, and that iron removal was also influenced by other factors such as flow rate, pH and alkalinity production.

Goulet et al. (2001) found that failure of the first-order removal model to predict metal retention in wetland system receiving urban and agriculture runoff was possibly due to lower metal loading to the wetland, and also the effect of vegetation density, which has resulted in non-ideal flow patterns on a seasonal basis. In contrast to this finding, residence time was seen to have corresponded well with iron removal efficiency on a year-to-year basis at a coal mine water treatment wetland in Lambley, Northumberland, UK (Kusin et al. 2010). Such a pattern was mainly ascribable to changes in wetland reed growth from early colonisation after commissioning, to a maturely developed wetland 4 years later, thus suggesting the role of vegetation is significant in controlling the residence time in such systems. Therefore, a model that incorporates non-ideal flow behaviour needs to be adopted for further analysis of tracer residence time. Recently, Bodin et al. (2013) have shown that a tank-in-series model for pollutant removal may be more appropriate such that the model does incorporate the effect of non-ideal flow on wetland hydraulics.

Hydraulic Characteristics of Mine Water Treatment Systems

Taking into account the non-ideal flow behaviour, a TIS flow model was adopted for further analysis of tracer flow in the systems, since such a model has shown reasonable application

Table 3 Measured data for coal mine water treatment wetlands*

Site name	Age of system (years)	Water surface area (m^2)	Water depth (m)	System volume (m^3)	Length-to-width ratio (unitless)	Water flow rate (L/s)
Lambley	1	4,388	0.3	2,163	3.4	81.86
Whittle	5	2,400	0.3	721	5.5	25.00
Allerdean Mill	1.5	1,066	0.21	224	2.1	7.91
Strafford	0.8	1,690	0.25	423	5.7	14.04
Mousewater	5.8	8,400	0.26	2,142	3.5	77.98
Cuthill	7.0	2,744	0.21	571	3.5/5.3[a]	67.98

[a] L-shaped wetland, L:W ratio of first cell/L:W ratio for second and third cell

*Measured data during tracer test

Table 4 Measured data for coal mine water treatment lagoons*

Site name	Age of system (years)	Water surface area (m^2)	Water depth (m)	System volume (m^3)	Length-to-width ratio (unitless)	Water flow rate (L/s)
Acomb	5	375	2.8	1,050	1.5	6.25
Whittle	5	900	1.65	1,305	3.0	25.00
Allerdean Mill	1.5	883	1.6	1,325	4.7	9.67
Bates	5.8	2,850	2.2	6,242	2.0	78.69
Strafford	0.8	850	2.4	2,040	4.5	14.04
Mousewater	5.8	3,036	2.2	6,527	1.2	36.72
Cuthill	7.1	726	2.0	1,089	3.2	10.72

*Measured data during tracer tests

in the investigated treatment systems previously (e.g. Kusin et al. 2012). Based on the TIS model, distribution of system residence time (tracer RTD) was assessed for different mean residence time and the number of completely-mixed tanks in series, n to account for the non-ideal flow pattern across the systems. This may therefore relate the residence time and hydraulic performance of the systems, in particular effective volume and mixing characteristics of flow movement. This is often associated with the extent of flow deviation from ideal plug-flow, ultimately leading to the degree of treatment received for iron removal. It is worth noting that misadoption of inappropriate method of hydraulic analysis may lead to inaccurate estimation of wetlands effective volume and dispersion characteristics (Bodin et al. 2013). Thus, the TIS method used for RTD assessment presented here is considered appropriate for quantifications of wetland hydraulics and removal rate.

Table 5 lists the resulting hydraulic characteristics of the lagoons and wetlands from the TIS flow model and the corresponding hydraulic efficiency measures. As noted in the table, mean nominal residence time for lagoons is relatively high compared to wetland systems, largely because of the considerably higher volume of lagoons relative to wetlands, although the lower flow rate to the lagoons may also contribute to this difference. Accordingly, greater mean residence time is seen for lagoons, although this does not necessarily imply good hydraulic performance. System volumetric efficiency, e_v is a measure of relative importance of mean to nominal residence time, thus indicating the effectiveness of system volume during the treatment processes. It can be seen that the mean wetlands volumetric efficiency is comparatively greater than the lagoons, showing that a greater proportion of the total volume of the systems is involved in the treatment process. Consequently, the overall system hydraulic efficiency, $e\lambda$ for wetlands is greater than lagoons (mean of 0.69 in wetlands compared to 0.24 in lagoons), suggesting that volumetric efficiency is an important measure of overall system hydraulic efficiency. The system RTD exhibits greater efficiency for wetlands compared to lagoons, which indicates a better flow distribution/uniformity i.e. approaching plug-flow across the systems. This can be represented by the greater amount of n for the wetlands which corresponds to lower dispersion number, D/uL, and vice versa for lagoons. $D/uL<0.01$ is the dispersion limit for a system considered as an ideal plug-flow (Levenspiel 1999) which corresponds to about 20 TIS (Kadlec and Wallace 2009). It is therefore, immediately clear that lower hydraulic efficiency of lagoons resulted mostly from the presence of greater fractions of ineffective volume which is apparently due to accumulation of

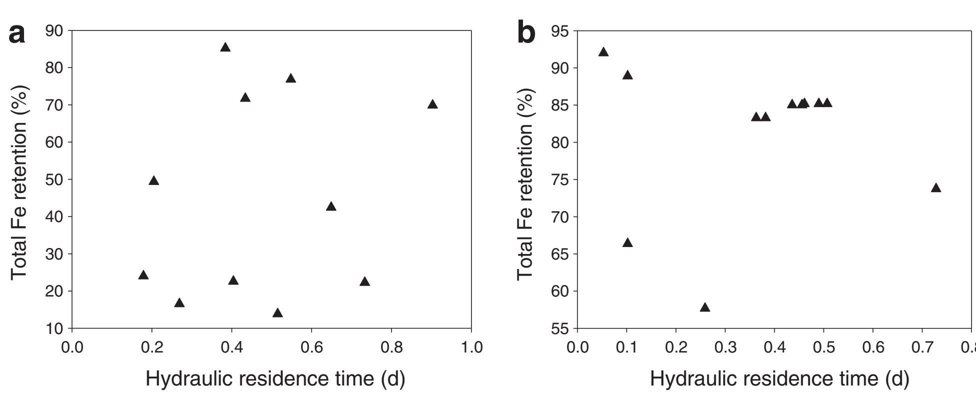

Fig. 2 Effect of hydraulic residence time on iron retention to indicate first-order removal model for **a** lagoons **b** wetlands

Table 5 Hydraulic characteristics of coal mine water treatment lagoons and wetlands

	Lagoons		Wetlands	
	Mean (S.D)	Min/Max	Mean (S.D)	Min/Max
[a]Nominal residence time (d)	1.474 (0.547)	0.611/2.141	0.425 (0.087)	0.280/0.610
Mean residence time (d)	0.550 (0.337)	0.179/1.378	0.362 (0.199)	0.053/0.728
Dispersion number, D/uL	0.337 (0.136)	0.156/0.562	0.213 (0.158)	0.109/0.577
Number of TIS, n	2.1 (0.9)	0.7/3.8	3.9 (1.3)	1.7/5.2
RTD efficiency, e_{RTD}	0.52 (0.27)	0.06/1.12	0.70 (0.15)	0.39/0.81
Volumetric efficiency, e_v	0.37 (0.20)	0.18/0.80	0.89 (0.49)	0.16/1.74
Hydraulic efficiency, $e\lambda$	0.24 (0.24)	0.01/0.89	0.69 (0.41)	0.06/1.40

All parameters are unitless unless otherwise stated

Data present mean data and standard deviation of mean (S.D) in parentheses, and minimum (min) and maximum (max) values of hydraulic performance data for lagoons and wetlands, n=11

[a] Calculated as system volume divided by flow (V/Q)

settled iron hydroxides in the systems. Thus, this results in flow channelling (non-ideal effect) for which n is lower and D/uL is greater than the wetland systems.

Hydraulic Performance and Iron Removal in Wetlands and Lagoons

Within wetlands and lagoons varying in design configuration and influent iron characteristics, treatment performance in terms of iron removal i.e. removal efficiency, area-adjusted removal and first-order removal, in relation to hydraulic performance metrics are discussed here. Generally, for wetlands, 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 trends between iron removal and hydraulic performance metrics within both wetlands and lagoons, the area-adjusted removal indicates contradictory results compared to other iron removal metrics. This probably reflects the concentration-dependence for iron removal as discussed earlier.

A greater volumetric efficiency (which largely reflects the hydraulic efficiency) in the wetland systems (compared to lagoons) (Table 5) may have an important influence on iron attenuation processes. As discussed earlier, the volumetric efficiency is a measure of relative mean residence time for comparing systems with different hydraulic characteristics. Therefore greater volumetric efficiency in the wetlands is indicative of a longer hydraulic residence time, and hence can be expected to result in greater removal of iron. This occurs despite comparatively low influent iron concentrations (Table 1) which, according to a first-order kinetics model, is expected to result in a lower rate of iron removal. Notwithstanding this, volumetric efficiency is also attributable to other influences such as free-water surface, piping network and bearing-layer in a close-to-plug-flow reactor (Qi et al. 2013).

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. It has also been reported that retention of iron in wetlands may be influenced by reeds colonisation i.e. whether vegetation have maturely colonised e.g. Fennessy et al. (2004) and the effect of growing season on wetland hydrology e.g. Skaggs (2012). Other influences include seasonal effects e.g. Goulet and Pick (2001) and the inlet concentration e.g. Wieder (1989); Tarutis et al. (1999); Macias et al. (2012). For initially high iron concentration, induced oxidation process may help in complete removal of the pollutant in a case of highly polluted acid mine drainage (e.g. Macias et al. 2012). Despite efficient iron removal efficiency encountered in the wetlands, caution is needed about the use of subsurface flow constructed wetlands for the treatment of metal-contaminated water as metals are shifted to another environmental compartment, and stable redox conditions are required to ensure long-term efficiency (Haarstad et al. 2012). Harvesting of above-ground macrophytes may help increase retention capacity and nutrient removal in natural wetland (Zhu et al. 2012), and hence improving the flow distribution across the system.

On the other hand, the lagoon systems appear to be less efficient in terms of their treatment efficiency with respect to iron compared to wetlands. 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/uL and hence lower e_{RTD} in Table 5) 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. Consequently, lagoons have lower effective volume for retention and treatment of iron, and hence 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 initially high influent iron concentration. Thus, evidence from the lagoon systems suggests that flow pattern has a great influence on the iron removal processes, due principally to the largely ineffective volume in the lagoons. This has significantly reduced the retention of iron and the degree of treatment received therefore lower removal efficiency. It is again worth noting that appropriate model should be used to avoid overestimation of system performance (Bodin et al. 2013).

Conclusions

The rates of iron removal in the mine water treatment systems have been shown to deviate from the area-adjusted (zero-order) removal model, which was the basis for the design of the systems. This suggests that the removal rate is dependent on initial iron concentration. However, the application of a first-order removal model did not sufficiently describe the attenuation of iron in the treatment systems. This is apparently due to significantly non-ideal flow behaviour in the systems, which influences the length of time for pollutant retention and the degree of treatment received.

It is clear from the work discussed that residence time is an important influence on hydraulic efficiency, and also on iron removal given that the attenuation of iron is a time-dependent process. However, there is no relationship found between residence time and iron removal when using a first-order removal model (Fig. 2). The absence of such a relationship is likely because the first-order removal model assumes plug flow conditions, whereas in these systems, we have shown that flow patterns are non-ideal. A TIS model is better suited to characterising hydraulic performance of these systems. It has been shown here that the mean number of TIS, *n*, for the wetlands and lagoons, is 3.9 and 2.1 respectively, and that the higher value of *n* for wetlands is reflected in the treatment efficiency of the systems for iron; 81 % removal in wetlands compared to 47 % removal in lagoons. Generally, it was found that system hydraulic efficiency (derived from the principle of TIS model) corresponds with iron retention within the treatment systems (i.e. greater hydraulic efficiency in wetlands corresponds with greater iron removal in the systems), suggesting that the TIS model would be more appropriate for evaluation of treatment system performance. It is tentatively concluded that improvement of treatment system performance may be achieved by maximising hydraulic efficiency i.e. greater residence time and a more uniform flow movement.

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