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Hydraulic residence time and iron removal in a wetland receiving ferruginous mine water over a 4 year period from commissioning

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ABSTRACT

Analysis of residence time distribution (RTD) has been conducted for the UK Coal Authority's mine water treatment wetland at Lambley, Northumberland, to determine the hydraulic performance of the wetland over a period of approximately 4 years since site commissioning. The wetland RTD was evaluated in accordance with moment analysis and modelled based on a tanks-in-series (TIS) model to yield the hydraulic characteristics of system performance. Greater hydraulic performance was seen during the second site monitoring after 21 months of site operation i.e. longer hydraulic residence time to reflect overall system hydraulic efficiency, compared to wetland performance during its early operation. Further monitoring of residence time during the third year of wetland operation indicated a slight reduction in hydraulic residence time, thus a lower system hydraulic efficiency. In contrast, performance during the fourth year of wetland operation exhibited an improved overall system hydraulic efficiency, suggesting the influence of reed growth over the lifetime of such systems on hydraulic performance. Interestingly, the same pattern was found for iron (which is the primary pollutant of concern in ferruginous mine waters) removal efficiency of the wetland system from the second to fourth year of wetland operation. This may therefore, reflect the maturity of reeds for maintaining efficient flow distribution across the wetland to retain a longer residence time and significant fractions of water involved to enhance the extent of treatment received for iron attenuation. Further monitoring will be conducted to establish whether such performance is maintained, or whether efficiency decreases over time due to accumulation of dead plant material within the wetland cells.

Key words | hydraulic residence time, iron removal, mine water, wetland

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INTRODUCTION

In the absence of acidity (as is the case at the study site discussed here) the most important contaminant in mine waters is 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 wetland, as follows:

$$Fe^{2+} + 1/4O_2 + H^+ \leftrightarrow Fe^{3+} + 1/2H_2O \quad (1)$$

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 \downarrow + 3H^+ \quad (2)$$

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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 e.g. suspended solids, nutrients and biochemical oxygen demand by the wetland (Persson et al. 1999; Goulet et al. 2001). This can be seen from the expression that relates pollutant removal efficiency and first-order removal as an exponential relationship (Tarutis et al. 1999):

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

where C_i = inlet pollutant concentration (g/m^3); C_o = outlet pollutant concentration (g/m^3); k_v = volumetric removal rate constant (d^{-1}); t = residence time (d). Because removal of iron is dependent on time, (i.e. concentration-time distribution) therefore, a more hydraulically efficient system will achieve better removal of iron. Thus, effective hydraulic performance (i.e. longer hydraulic residence time) should be reflected in effective treatment performance. However, assessment of actual residence time within the UK coal mine water treatment systems has not been widely investigated (Kruse et al. 2007). It is therefore the aim of this study to assess the effect of system hydraulic efficiency (i.e. the extents of hydraulic residence time distribution) on the removal of iron within the system.

Accordingly, residence time distribution (RTD) is a measure of the relative time a tracer spends and the distribution of flow across the system (Kadlec 1994; Martinez & Wise 2003). The time a fraction of water spends within a treatment system in general reflects the extent of the treatment of polluted waters. The hydraulic efficiency of a treatment system is often limited by non-ideal flow effects i.e. flow short-circuiting and the presence of stagnant dead zones, resulting in some fractions of water moving quickly or slowly towards the outlet of a system (Thackston et al. 1987; Martinez & Wise 2003). Evaluation of tracer RTD would therefore, indicate how the non-ideal flow behaviour may affect the hydraulic performance and hence treatment efficiency (primarily for iron in this study). The RTD is used as a tool 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 and impacts on iron removal efficiency as a consequence.

Study site

The study was undertaken at a UK Coal Authority's mine water treatment system, Lambley, Northumberland, over a period of approximately 4 years since site commissioning. The wetland consists of four wetland cells in series with a total treatment area of 4,388 m^2 and receives net-alkaline (i.e. alkalinity > acidity), ferruginous mine water with flow rates ranging between 54–84 L/s. The treatment system was designed using an area-adjusted removal rate of 10 g/m^2/d of iron to achieve the desired wetland area (Hedin et al. 1994; PIRAMID 2003). The design flow-rate was 88 L/s and design influent and effluent iron concentrations were 6 mg/L and 1 mg/L, respectively. Mine water treatment wetlands are typically planted with 200 mm pot-grown reeds, which flourish rapidly over the first few years of operation. Thus, this study in part aimed to evaluate the influence on hydraulic performance of the growth of reeds across the wetland system.

METHODS

Determination of hydraulic residence time by tracer test

Measurement of actual residence time at the treatment wetland was undertaken by conducting tracer tests. This was simply performed by injecting a known mass of inert tracer into the inlet of the wetland system for a specified duration of time. The first tracer test was conducted in February 2007, only 4 months after site commissioning, using sodium bromide (Kruse et al. 2007). The following tracer test was conducted after 21 months of wetland operation (July 2008), using a multi-tracer approach to compare different tracer performances; simultaneous injection of sodium bromide and Na-fluorescein and, one week later, injection of sodium chloride (Kusin et al. 2009). The third tracer test was conducted 36 months after site construction (November 2009) whilst the most recent test was undertaken during the fifth month of the fourth year of site operation (April 2010), both using Na-fluorescein and sodium bromide. 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 wetland system using an Aquamatic Auto Cell P2 Autosampler (for sodium bromide) and logging the fluorescence concentrations (for Na-fluorescein) using a Seapoint fluorimeter. Sodium chloride was monitored as conductivity measured by an Eijelkamp CTD Diver. Overall, the mean tracer recovery was 89%, indicating the desired conservative tracer behaviour during the tests. The flowrates during the tracer tests were continuously monitored at the wetland inlet and outlet using an Eijelkamp CTD Diver set behind a sharp-crested V-notch weir at the outlet from the wetland, and a BaroDiver for atmospheric pressure correction.

Simultaneously during 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. Samples for Fe speciation were also collected (acidified with 1% by volume concentrated hydrochloric acid) for analysis of dissolved Fe(II) and Fe (III). 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. The Fe speciation analysis was performed according to the modified ferrozine method (Vollier *et al.* 2000) to determine the change of dissolved iron species i.e. ferrous iron to ferric iron which corresponds to the rate of iron oxidation.

Analysis of residence time distribution (RTD)

The tracer test results were analysed for the RTD to yield the characteristics of the wetland hydraulics. 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 (Levenspiel 1972; Kadlec 1994), thus illustrating the change of flow movement from the ideal flow patterns. The influent mine water into the Lambley wetland is semi-continuously pumped from a pumping station giving unsteady inflows through the system, therefore showing a reasonable application of RTD for such a system. RTD is typically represented by an E curve as a function of time (Kadlec 1994; Martinez & Wise 2003; Kadlec & Wallace 2009) and is the probability density function for residence time in the wetland (Levenspiel 1972):

$$\text{RTD, } E(t) = \frac{Q(t)C(t)}{M_o} \tag{4}$$

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). Characteristics of tracer movement in a system can be represented by three moment calculations of RTD i) zeroth moment (M_o) yields the amount of tracer recovered, ii) first moment (M_1) yields the centroid of the RTD which corresponds to the mean of RTD and iii) second moment (M_2) yields the variance, characterising the spread of tracer movement from the mean RTD, each of which is given in Equations (5–7), respectively.

$$M_o = \int_0^\infty Q(t)C(t)\mathrm{d}t \cong \sum_{i=1}^{n} Q_i(t)C_i(t)\Delta t \tag{5}$$

$$M_1 = \tau_\mathrm{m} = \int_0^\infty tE(t)\mathrm{d}t \cong \sum_{i=1}^{n} tE_i(t)\Delta t \tag{6}$$

$$M_2 = \sigma^2 = \int_0^\infty (t-\tau_\mathrm{m})^2E(t)\mathrm{d}t \cong \sum_{i=1}^{n} (t-\tau_\mathrm{m})^2E_i(t)\Delta \mathrm{t} \tag{7}$$

where n = number of samples; τ_m = tracer mean residence time (d); $E(t)$ = residence time distribution (RTD) (d^{-1}); $\sigma^2 =$ the variance of the residence time distribution (d^2). The calculated moment values were then used as an early estimation of anticipated shape and scaling parameterisation for adoption in the tanks-in-series (TIS) model.

TIS model for residence time distribution

The tracer RTD curves were modelled in accordance with the tanks-in-series (TIS) model. This is considered to represent a good approximation of most wetland conditions and is a simple and commonly applied model in treatment wetlands and ponds (Kadlec & Wallace 2009). Adoption of the TIS model was basically made upon the presumption that the flow across the wetland approximates a non-ideal pattern (i.e. deviation from ideal plug-flow or completely mixed system) due to the presence of short-circuiting effects and dead zones. A wetland is therefore, often assumed as a series of equally sized, perfectly mixed tanks-in-series and the RTD across the system is represented by the gamma probability density function (Levenspiel 1972; Kadlec & Wallace 2009) characterised by the number of tank-in-series, n, and a residence time in each tank, τ_i given as:

$$g(t) = E(t) = \frac{1}{t_i^n \Gamma(n)} t^{n-1} \exp\left(-\frac{t}{\tau_i}\right) \tag{8}$$

where $g(t)$ = gamma distribution function, equals the RTD for a number of perfectly mixed tanks-in-series (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}). Therefore, the mean residence time, τ_m of a non-ideal system approximates a number of ideal perfectly-mixed system is, $\tau_m = n\tau_i$. In order to apply the gamma distribution function, which is available as a computer spreadsheet tool e.g. GAMMADIST and GAMMALN in Microsoft Excel (Kadlec & Wallace 2009), the values of n (shape parameter) and τ_i (scaling parameter) are to be selected for the model to fit with the actual tracer test data. In the first instance, the values calculated from moment calculations were used to produce the TIS fit. Note that the n and τ_i were obtained following the relation given by Levenspiel (1972) for the TIS model as follows:

$$\sigma_\theta^2 = \frac{\sigma^2}{\tau_m^2} = \frac{1}{n} \tag{9}$$

where σ_θ^2 = dmensionless variance (d^2). τ_i is thus simply τ_m divided by n. However, the use of moment parameter values does not always provide satisfied TIS fit to actual data except that it gives early prediction values. Accordingly, SOLVER application was used to minimise the summation of squared errors between the TIS model and the observed data where n and τ_i values were simultaneously solved for a gamma distribution function to produce the best TIS fit for tracer RTD. Modification on a gamma distribution function was performed upon cases with delay in tracer detection as in the case of this study to produce even better fit to actual tracer data and also solved for the least squares error (Kadlec & Wallace 2009).

$$g(t) = E(t) = \frac{1}{\tau_i(n-1)!} \left(\frac{t-t_D}{\tau_i}\right)^{n-1} \exp\left(-\frac{t-t_D}{\tau_i}\right) \tag{10}$$

where t_D = delay time (d).

Accordingly, assessment of system hydraulic efficiency was performed using the resultant hydraulic parameters from the TIS model, based on the expression introduced by Kadlec & Wallace (2009) as the following (after Persson et al. 1999). The hydraulic efficiency ($e\lambda$) is the product of system volumetric efficiency (e_v) and the efficiency of residence time distribution (e_{RTD}), thus 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, given as:

$$e\lambda = e_v \cdot e_{RTD} \tag{11}$$

where $e_v = t_m/t_n = V_{eff}/V$; 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), while $e_{RTD} = 1 - \sigma_\theta^2$; σ_θ^2 = system dimensionless variance, σ^2/t_m^2 (unitless); σ^2 = tracer flow variance.

RESULTS AND DISCUSSION

Seasonal variation in Lambley wetland

As shown in Table 1, water chemistry varied from year to year (also on a seasonal basis) and differed between inlet and outlet. However, there was no significant variations of water chemistry for Lambley wetland over the four seasons (or years) except temperature and Eh ($P < 0.05$). Significant temperature difference was seen between winter and summer seasons (the lowest 8.4°C at the outlet during winter 2007 and the highest 17.5°C at the inlet during summer 2008). Eh was significantly different for winter 2007 and fall 2009. Overall, inlet and outlet water chemistries were not significantly different ($P > 0.05$). Regardless of seasonal variations, mean pH, conductivity, Eh, temperature and alkalinity for inlet of the wetland was 6.71, 450.8 μS/cm, −8 mV, 12.6°C and 162 mg/L $CaCO_3$, respectively. For wetland outlet, mean pH, conductivity, Eh, temperature and alkalinity was 6.67, 436.7 μS/cm, 10 mV, 11.6°C and 157 mg/L $CaCO_3$, respectively.

The wetland received influent Fe loading in the range of 28.15–35.91 kg/d, the highest during summer 2008, with the highest influent Fe concentration of all seasons. Flow

Table 1 | Seasonal variation in water chemistry and hydraulics of Lambley wetland from 2007–2010

Variable	Inlet/outlet	Feb 2007 (winter)	July 2008 (summer)	Nov 2009 (fall)	Apr 2010 (spring)
pH	In	7.73	6.65	6.09	6.35
	Out	6.96	6.40	6.65	6.65
Temperature (°C)	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
Fe loading (kg/d)	In	28.15	35.91	30.63	28.49
	Out	11.92	5.35	5.12	4.27
Flow rate (L/s)	–	84.83	61.03	53.92	54.32
Hydraulic loading rate (m/d)	–	1.67	1.20	1.06	1.07

rates ranged between 53.92–84.83 L/s, the highest during winter 2007. For the treatment area of 4,388 m^2, hydraulic loading rate ranged from 1.06 m/d during fall 2009 up to 1.67 m/d during winter 2007.

Residence time distribution of Lambley wetland

The results of the tracer RTDs are illustrated in the form of normalised (unitless) RTD curves to compare the different experimental conditions, i.e. tracer concentrations and flow rates. Significantly different RTD shapes are clearly seen in Figure 1, demonstrating the changes in flow movement within the wetland system over the 4 years of site monitoring. As shown in the figure, multiple narrow sharp peaks are observed in February 2007 (Figure 1(a)) 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. Residence time monitoring within the second year of wetland operation (July 2008) indicated much improved results, whereby considerably wider RTD curves were observed compared to 2007 (Figure 1(b)). 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 (November 2009) demonstrated an intermediate shape of RTD between the tracer flow patterns observed in 2007 and 2008 (Figure 1(c)). The relatively narrower 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, showing the consistency of wetland performance throughout the tracer test and the reliability of the results. The most recent tracer monitoring in April 2010 indicated RTD shapes which are reasonably wider than the year before (Figure 1(d)), showing an improvement of flow distribution across the wetland at this stage.

It can be seen in Figure 1 that the shape of tracer RTDs for 2007 and 2009 exhibit multiple early peaks and long tails, the curves are relatively narrower than those seen in 2008 and 2010. The pattern indicates that there are some fractions of water moving faster through the system, but also

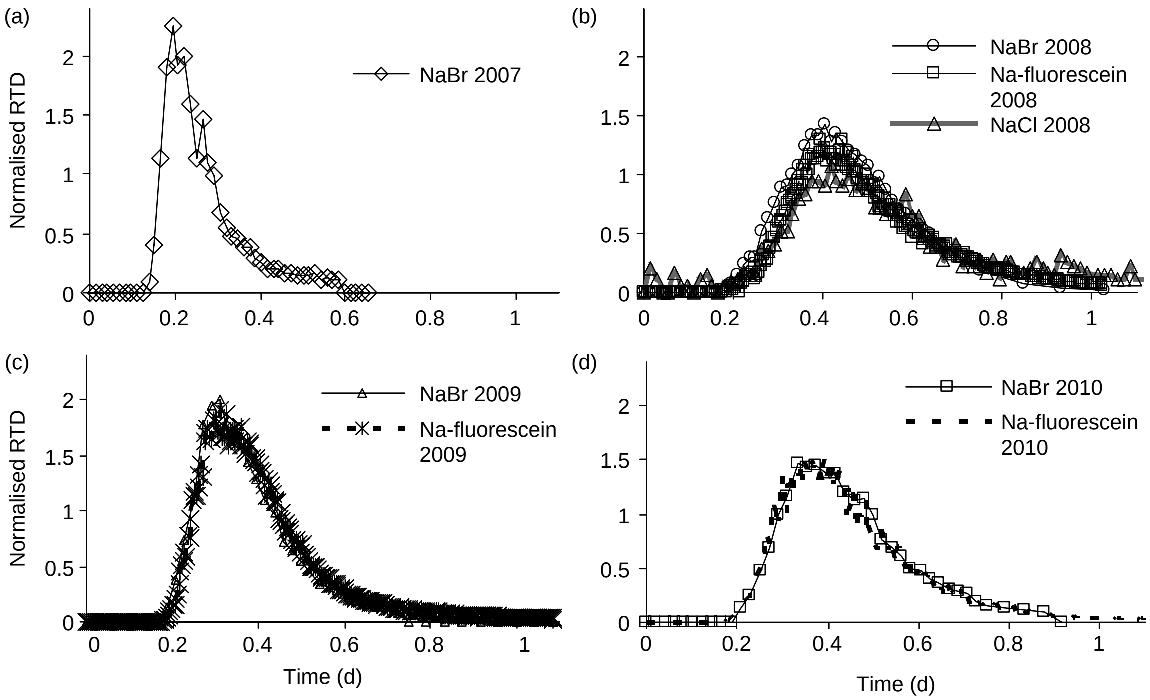

Figure 1 | Normalised RTD curves for Lambley wetland, showing actual tracer responses during (a) 2007 (b) 2008 (c) 2009 and (d) 2010 tracer test, respectively. RTDs are results from different tracers employed i.e. sodium bromide (NaBr), sodium chloride (NaCl) and sodium-fluorescein (Na-fluorescein) for the different years, e.g. NaBr 2007 denotes tracer test using sodium bromide in 2007.

a fraction that moves more slowly. In 2007, the sparsely-populated reeds could be the cause of some fractions of water being transmitted rapidly through the poorly vegetated system, but with a longer time for the latter water fractions to exit the system during a period of operation when the wetland had a comparatively large open water body. For 2009, the streaming effect could well 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. The long RTD tail could be due to retention of some fractions of slow moving (lower layer) water being trapped within the stagnant zones at the bottom of the wetland, created by the accumulation of dead plant material and/or the build-up of precipitated iron hydroxide within the mature reeds. Reasonably well distributed flows were seen in 2008 and 2010, indicating the role of wetland vegetation to retain a longer residence time so as to sustain efficient hydraulic performance over its operation.

TIS model for Lambley wetland RTDs

As described earlier, the TIS model was adopted to model the tracer RTDs. The TIS fit for each RTD was calibrated against several n and τ_i values from different approaches until the best fit to actual data was obtained; (i) n and τ_i calculated from moment analysis (ii) n and τ_i simultaneously solved to produce the least squares error between the TIS model and the observed data (iii) n and τ_i from least squares error for the modified gamma distribution function to account for delay in tracer detection (Kadlec & Wallace 2009). In most cases, the TIS from moment exhibited 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 has significantly resulted in greater magnitude of errors as indicated by the root mean squares error between TIS and RTD data. TIS fit from least squares method showed a lesser magnitude of errors between the model and actual tracer RTDs. Nevertheless, whenever there is delay in tracer detection, adoption of this method has simultaneously minimised the extents of

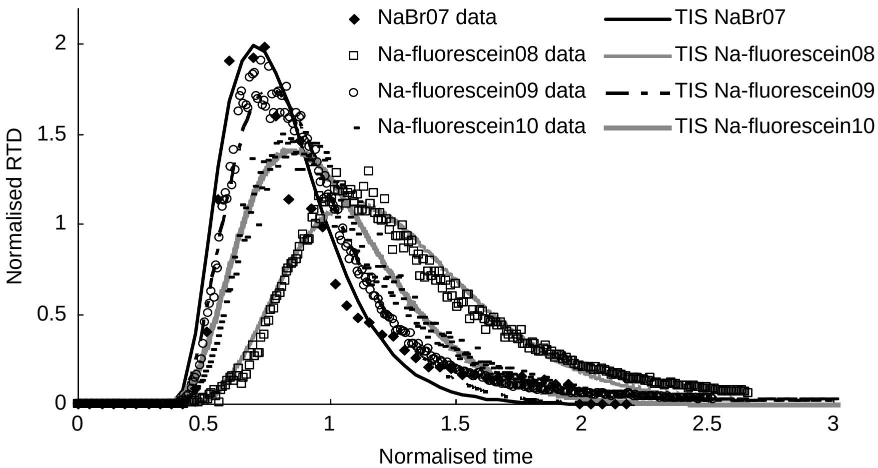

Figure 2 | TIS fit of actual tracer RTDs for Lambley wetland to illustrate the changes in distribution of system residence time from 2007–2010, e.g. NaBr07 data denotes RTD data from sodium bromide tracer test in 2007, TIS NaBr07 denotes TIS fit for 2007 RTD data. Only the best TIS fit with the least root mean squares error of the different tracers employed each year are presented in the figure.

system dispersion, characterised by the significantly low dimensionless variance (and thus dispersion number). This in turn, has led to n being substantially large, which seemed unrealistic. The delayed TIS from the least squares method, on the other hand, yielded the best fit to actual RTDs in all cases as it takes into account the delay in tracer detection and gave realistic values of n and degree of dispersion.

Figure 2 illustrates the result of the TIS model fitted to actual tracer RTDs from 2007–2010. Note that the TIS fit obtained from delayed TIS from least squares method to produce the best TIS fit to actual tracer data (after Kadlec & Wallace 2009). In 2007, the mean residence time of 0.26 days (92% of the nominal residence time) was found to correspond to about four TIS ($n = 3.9$), illustrated by a slightly high and narrow curve with a long tail (Figure 2 and Table 2). This corresponds to system dispersion number, D/uL of 0.149. Monitoring of the wetland system in 2008 indicated considerable changes in RTDs (from 3 different tracers with essentially identical shapes), which correspond to about five TIS (n ranged between 5.0–5.2). This has resulted in

Table 2 | Hydraulic characteristics of Lambley wetland over the 4 year period after site commissioning

Tracer test	Nominal residence time Day	Mean residence time Day	Dimensionless variance σ_θ^2	Dispersion number D/uL	No of TIS n	RTD efficiency e_{RTD}	Volumetric efficiency e_v	Hydraulic efficiency $e\lambda$
2007*	0.28†	0.26	0.254	0.149	3.9	0.75	0.92	0.69
2008‡	0.40†	0.46	0.196	0.112	5.0	0.80	1.16	0.93
	0.39§	0.51	0.210	0.119	4.8	0.79	1.29	1.02
	0.39‖	0.49	0.198	0.111	5.1	0.80	1.27	1.02
2009¶	0.43‖	0.38	0.236	0.137	4.2	0.76	0.89	0.68
	0.43†	0.36	0.244	0.142	4.1	0.76	0.85	0.64
2010**	0.44‖	0.44	0.222	0.127	4.5	0.78	1.00	0.78
	0.44†	0.46	0.232	0.134	4.3	0.77	1.04	0.80

*Tracer recovery of 84%.
†Tracer test using sodium bromide (NaBr).
‡Mean tracer recovery of 94%.
§Tracer test using sodium chloride (NaCl).
‖Tracer test using sodium-fluorescein (Na-fluorescein).
¶Mean tracer recovery of 85%.
**Mean tracer recovery of 95%.

relatively longer mean residence time of between 0.46–0.50 days (16–29% greater than the nominal residence time). These apparent changes of TIS shapes were characterised by the relatively smaller extents of flow dispersion than the year before, for D/uL was between 0.111–0.119. The TIS curve demonstrated considerably wider curve with relatively shorter tail, approximating an ideal tracer flow curve compared to previous system monitoring in 2007. Further monitoring of the wetland in 2009 demonstrated rapid change of n from about five to four TIS (n between 4.1 and 4.2), which corresponds to tracer mean residence time of between 0.36–0.38 days (85–89% of the nominal residence time). The TIS curve was illustrated by a reasonably narrower and higher peak curve than that observed in 2008. Greater extent of dispersion was seen during this year, D/uL of between 0.137–0.142 to result in the lower n TIS. In 2010, the n had increased to between 4.3–4.5, with a longer mean residence time between 0.44–0.46 days, as the D/uL had decreased to 0.127–0.134. This was shown by the slightly wider and lower peak TIS curve than observed in the year before. Overall, the wetland was found to be significantly dispersed from ideal plug–flow, indicated by the large extents of system dispersion, D/uL ranged between 0.111–0.149 and n ranged between 4–5 TIS (Table 2). $D/uL < 0.01$ is the dispersion limit for a system considered as an ideal plug-flow (Levenspiel 1972) which corresponds to about 20 TIS (Kadlec & Wallace 2009).

Tabulated mean residence time and corresponding hydraulic characteristics (i.e. RTD, volumetric and overall hydraulic efficiency) for the wetland are as shown in Table 2. Overall, it can clearly be seen that the wetland mean residence time has significantly increased during the second year of wetland operation compared to its early operation. This could well mean that the maturity of the wetland system has greatly improved the residence time i.e. the densely-populated reeds ensure 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 seems 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 effects can be represented by the changes in wetland volumetric efficiency, e_v reflecting the fractions of water involved in the flow-through (Table 2). Also noted from the table, is the wetland RTD efficiency, e_{RTD} which characterises the mixing behaviour of water movement, reflecting the extent of flow deviation from ideal plug-flow. Greater e_{RTD} corresponds to larger n TIS for the wetland. This indication of the effect of flow deviation from an ideal system could be due to flow streaming effects, mainly associated with reed growth. It is therefore, immediately clear that the changes in mean residence time have resulted in great changes in system number of TIS, n reflecting the overall hydraulic efficiency of the treatment system. As noted, the wetland hydraulic efficiency, $e\lambda$ has improved from 0.69 to 0.93–1.02 between 2007–2008, which then decreased to 0.62–0.68 in 2009. Thus, the system has 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, improvements of e_{RTD} and e_v were seen to result in $e\lambda$ to increase compared to 2009, which reflects the maturity of reeds during this stage and suggests that the wetland vegetation controls overall hydraulic system performance from the beginning of wetland operation.

Relationship between hydraulic characteristics and iron removal

It has been noted that, 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 higher removal of iron would be anticipated for system with a more hydraulically efficient performance. Iron is removed from the wetland system by means of oxidation of ferrous to ferric iron and hydrolysis of ferric iron to ferric oxyhydroxide which will then settle in the system (Younger et al. 2002; Hedin 2008). Iron removal efficiency of the wetland was found to be in the range of 57.67–85.11% from 2007–2010 (Table 3).

As shown in Table 3, iron removal efficiency within the wetland was relatively low during early wetland operation in 2007, whereby a year later significant iron removal was observed, and slightly decreased and increased over the next

Table 3 | Iron removal in Lambley wetland over the 4 years operation since site commissioning

	Fe total in (mg/L)*	Fe total out (mg/L)*	Flow rate (L/s)	Fe dissolved in (mg/L)†	Fe dissolved out (mg/L)†	Fe removal efficiency (%)	Area adjusted removal ($g/m^2/d$)	Fe oxidised ($g/m^2/d$)‡	Fe settled ($g/m^2/d$)§
Feb/2007	3.84	1.63	84.83	3.65	1.25	57.67	3.70	4.00	3.70
July/2008	6.81	1.01	61.03	5.85	0.82	85.11	6.97	6.05	6.97
Nov/2009	6.58	1.10	53.92	6.31	0.38	83.28	5.81	6.29	5.81
Apr/2010	6.07	0.91	54.32	5.90	0.49	85.01	5.52	5.79	5.52

*Unfiltered iron concentration at system's influent and effluent, respectively.
†Filtered iron concentration at system's influent and effluent, respectively, in which predominantly of ferrous Fe at circum-neutral pH.
‡Calculated as the difference of dissolved ferrous iron at system's influent and effluent ($Fe_{dissolved}$ in − $Fe_{dissolved}$ out). Calculated after Hedin (2008).
§Calculated as the difference of total iron at system's influent and effluent (Fe_{total} in − Fe_{total} out). Calculated after Hedin (2008).

two years. This pattern clearly corresponds to the overall hydraulic efficiency, most notably the changes in system volumetric efficiency except during the first year of wetland operation (Table 2). As discussed earlier, changes in RTD and volumetric efficiency are significant factors that affect the overall hydraulic efficiency of the wetland. Despite comparatively low iron removal in 2007, RTD and volumetric efficiency were rather high. The considerably high volumetric efficiency in 2007 was in fact due to the long mean relative to nominal residence time during the year, which was notably the result of the long RTD tail carrying slower fractions of water across the sparsely-vegetated wetland. However, the relatively fast flow rate had limited the retention of iron within the wetland, hence only a small degree of treatment was received. This was coupled with the immaturity of the wetland system during early colonisation, limiting the efficiency of iron attenuation processes in the wetland e.g. adsorption onto plant material, physical filtering of precipitated iron (Kruse *et al.* 2009), and generation of strongly oxidising conditions via the rhizosphere. Notwithstanding this, from 2008–2010, iron removal was found to consistently correspond with the overall hydraulic efficiency, as reeds have developed well, thus providing a relatively larger surface area for precipitation and adsorption of iron onto plant material. This also suggests the role of wetland vegetation in maintaining efficient hydraulic performance i.e. flow distribution across the system to retain longer hydraulic residence time and significant fractions of water to enhance the degree of treatment received for iron attenuation.

In addition to iron removal efficiency, 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. Using this metric it can be seen that the area-adjusted removal rate is greatly increased between 2007 and 2008, whilst a slight reduction in the removal rate are seen in 2009 and 2010 (Table 3). During the second year, the wetland was in fact receiving comparatively higher influent iron. The same effects were seen in 2009 and 2010 where the system received slightly lower influent iron than in 2008, thus a slightly lower area-adjusted iron removal rate given the minor changes in flow rates. The markedly different removal rates between 2007–2010 may therefore reflect the first-order kinetics for iron attenuation that have been 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. As shown in Table 3, a greater oxidation rate was seen with higher dissolved influent iron load (concentration multiplied by flow), whilst greater settlement rate was found to correspond with higher total influent iron load. Thus, in general, the results from this study satisfied the first-order kinetics for iron attenuation, that greater iron removal was seen for higher influent iron concentration and longer hydraulic residence time; where the latter suggests that this may be controlled by the reeds growth that reflects a more hydraulically efficient wetland performance. Therefore, it should be noted that, hydraulic residence time and influent iron concentration are important variables that must be taken into account when designing such a system.

CONCLUSIONS

Monitoring of the UK Coal Authority's Lambley wetland treatment system has indicated significant changes in the hydraulic performance of the wetland since its commissioning. The residence time distribution analysis showed that the hydraulic residence time had a significant influence on the overall efficiency of the wetland performance, albeit influent iron concentration also appears to be important. The significant improvement of the performance of the wetland seen during the second year of the wetland operation (i.e. longer residence time, greater hydraulic efficiency and higher removal of iron) 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 will be confirmed by further monitoring in future years. Nevertheless, the data presented here suggest that (a) hydraulic residence time is an important metric to include in both assessment of mine water treatment system design and performance monitoring and (b) the growth of reeds over the lifetime of such systems may have an influence on hydraulic performance, with implications for the implementation of concerted maintenance programmes to ensure good performance over the medium- to long-term.

As noted above, further monitoring will be conducted to observe whether good performance is maintained, or whether efficiency decreases over time due to accumulation of dead plant materials within the wetland cells. As part of a wider programme of investigation of the design and performance of mine water treatment wetland systems, multiple systems in the UK will be monitored to establish whether new design criteria for such systems should incorporate hydraulic residence time metrics, as the data presented here seem to suggest.

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REFERENCES

Goulet, R. R., Pick, F. R. & Droste, R. L. 2001 Test of first-order removal model for metal retention in a young constructed wetland. *Ecol. Eng.* **17**, 357–371.

Hedin, R. S. 2008 Iron removal by a passive system treating alkaline coal mine drainage. *Mine Water Environ*. **27**(4), 200–209.

Hedin, R. S., Nairn, R. W. & Kleinmann, R. L. P. 1994 *Passive Treatment of Coal Mine Drainage*. Bureau of Mines Information Circular 9389. United States Department of the Interior, Washington, DC. p. 35.

Kadlec, R. H. 1994 Detention and mixing in free water wetlands. *Ecol. Eng.* **3**, 345–380.

Kadlec, R. H. & Wallace, S. D. 2009 *Treatment Wetlands*, 2nd edition. CRC Press, Boca Raton, FL, p. 106.

Kruse, N., Gozzard, E. & Jarvis, A. 2007 *Determination of Hydraulic Residence Time at Coal Authority Mine Water Treatment System and Their Relationship to Iron Removal*. Report to the Coal Authority. University of Newcastle upon Tyne, UK. p. 21.

Kruse, N., Gozzard, E. & Jarvis, A. 2009 Determination of hydraulic residence time in several UK mine water treatment systems and their relationship to iron removal. *Mine Water Environ*. **28**(2), 115–123.

Kusin, F. M., Kruse, N., Mayes, W. M. & Jarvis, A. P. 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 ICARD*, 22–26 June, 2009, Skellefteå, Sweden.

Levenspiel, O. 1972 *Chemical Reaction Engineering*, 1st edition. John Wiley & Sons, New York.

Martinez, C. J. & Wise, W. R. 2003 Hydraulic analysis of Orlando Easterly wetland. *Environ. Eng.* **129**, 553–559.

Persson, J., Somes, N. L. G. & Wong, Y. H. F. 1999 Hydraulics efficiency of constructed wetlands and ponds. *Water Sci. Technol.* **40**(3), 291–300.

PIRAMID Consortium 2003 *Engineering Guidelines for the Passive Remediation of Acidic and/or Metalliferous Mine Drainage and Similar Wastewaters*. European Commission 5th Framework Programme "Passive In-situ Remediation of Acid Mine/Industrial Drainage" (PIRAMID). University of Newcastle upon Tyne, UK. p. 166.

Tarutis, W. J., Stark, L. R. & Williams, F. M. 1999 Sizing and performance estimation of coal mine drainage wetlands. *Ecol. Eng.* **12**, 353–372.

Thackston, E. L., Shields, F. D., Jr. & Schroeder, P. R. 1987 Residence time distributions of shallow basins. *J. Environ. Eng. (ASCE)* **113**(6), 1319–1332.

Viollier, E., Inglett, P. W., Hunter, K., Roychoudhury, A. N. & Van Cappellen, P. 2000 The ferrozine method revisited: Fe(II)/Fe(III) determination in natural waters. *Appl. Geochem.* **15**(6), 785–790.

Younger, P. L., Banwart, S. A. & Hedin, R. S. 2002 *Mine Water: Hydrology, Pollution, Remediation*. Kluwer Academic Publishers, Dordrecht, Netherlands, p. 442.