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Assessing subsurface flow hydraulics of a coal mine water bioremediation system using a multi-tracer approach☆

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ABSTRACT

Understanding the hydraulic behaviour of subsurface flow bioremediation systems is a pre-requisite for characterising their biogeochemical functioning, yet it is often overlooked. Using multiple tracers in parallel, considerable hydraulic insight can be gained. A quantitative multi-tracer test was conducted at a passive coal mine water bioremediation system in the UK (Bowden Close Colliery, County Durham) to assess its hydraulic behaviour. Four tracers were used: bromide (Br^-), uranine (Na-fluorescein), lithium (Li^+) and NaCl. The system comprises two parallel treatment streams: one receiving 30–50 L min^{-1} of moderately acidic adit drainage and the other one 90–110 L min^{-1} of strongly acidic spoil leachate. Each of these treatment streams has a separate 'RAPS unit' (Reducing and Alkalinity Producing System) and their effluents are eventually mixed in a single aerobic wetland. The RAPS units are downward-flow porous media with mixed substrates of limestone gravels and compost; RAPS I has a surface area of 1511 m^2 and RAPS II 1124 m^2. The aerobic wetland (990 m^2) is a basin of mineral soil planted with *Typha latifolia* and a shallow (15–50 cm) water level. For the two RAPS units, residence times of 4–5 d and effective velocities of 0.7–0.9 m h^{-1} were deduced. In terms of tracer performance, in contrast to earlier findings, bromide and Na-fluorescein tracers were applied successfully, while NaCl and lithium were found to be least useful, particularly during dilution events caused by intense rainfall.

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1. Introduction

Post mining management at sites where no former owner can be held responsible for remediation requires durable low cost solutions. A number of such solutions have been proposed in the past (Brown et al., 2002; Hedin et al., 1994; Younger et al., 2002) and successfully implemented at abandoned mine sites throughout the world. Besides the most commonly applied constructed aerobic and anaerobic wetlands, the technology of RAPS (Reducing and Alkalinity Producing System) is getting more and more attention since its first introduction in the 1990s by Kepler and McCleary (1994). These three types of systems have in common that they are porous media based and their treatment efficiency largely depends on the mean residence time of the mine water in the substrate.

Typically, the design of these porous media treatment systems for polluted waters is based on 'nominal residence times' ('first-order-residence times'), calculated simply from porosities and flow rates (e.g. Langergraber, 2008; PIRAMID Consortium, 2003; Watzlaf et al., 2000). Yet, the problem with this approach is that it assumes piston flow (i.e. plug flow), completely neglecting short cuts within the system or flow retardation and mixing of waters with different residence times resulting in advection-dispersion flow. Kadlec (2000) pointed out the shortcomings of this simple approach and provided solutions to that issue using an example treatment wetland. Younger and Henderson (2014) indicated that the overall removal rate depends also on the hydraulic processes of a passive treatment system, and Persson et al. (1999) investigated the relationship between the pond shape and the system's hydraulic behaviour. They formulated the "hydraulic efficiency" λ (Eq. 5), a coefficient which indicates how efficiently the water flows through a constructed wetland, with $\lambda = 1$ designated to the most efficient flow.

Tracer tests offer one of the best options for obtaining more realistic information about the hydraulics (e.g. advection, dispersion, mixing, hydraulic efficiency) and residence times, with the ultimate goal of improving design criteria. General details about conducting and interpreting tracer tests are given by many scholarly books and papers and shall not be repeated here (e.g. Goldscheider and Drew, 2007; Käß, 1998; Leibundgut et al., 2009; Wolkersdorfer, 2008). Flury and Wai (2003) reviewed a large number of potential dye tracers for the

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☆ Earlier results of this investigation have been published in the 2005 proceedings of the "Berg- und Hüttenmännischer Tag" Freiberg/Sachsen, Germany (Wolkersdorfer et al., 2005).

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vadose zone, of which uranine was chosen for the test described here. In most cases, the cheapest tracer is the common salt NaCl (e.g. Diaz Goebes and Younger, 2004), although simply dosing large quantities of salt into a treatment system has a tendency to create pockets of brine. These density effects of injected tracers have been studied during several tracer tests and indicate that those higher density solutions can behave rather differently to the ambient waters (LeBlanc and Celia, 1991; Schmid et al., 2004). At the Tan y Garn RAPS in Wales, Watson et al. (2009) conducted a series of tracer tests with 0.5 kg of LiBr and 10–20 kg of NaCl with positive results for NaCl. Bromide is a tracer substance that is easy to detect at low concentrations and displays conservative (i.e. non-reactive) behaviour in most tracer test studies (Käß, 1998). It is a common constituent in natural and coal mining impacted water, but commonly has low background concentrations in those environments. Hem (1985) reports background concentrations of 5–150 μg/L in rainwater and LaPierre (1999) reported Br^- concentrations in the range of 50–220 μg/L in shallow and up to 6250 μg/L in deep coal mine waters. Successful applications of bromide as a tracer in wastewater treatment wetlands has already been reported by several authors with recovery rates between 16 and 96% (e.g. Keefe et al., 2004; Kruse et al., 2009; Kusin et al., 2012; Lin et al., 2003; Machate et al., 1998a; Małoszewski et al., 2006; Whitmer et al., 2000). Observed bromide losses might have been caused by plant uptake (Whitmer et al., 2000). Another tracer successfully used in subsurface flow constructed wetlands is lithium (King et al., 1997) and Cheong et al. (2011) used a green food dye for a RAPS tracer test. Although uranine (Na-fluorescein) is often assumed to be an unsuitable tracer for wetlands and similar systems because of its potential decomposition at low pH-conditions, microbial activity or photodecomposition (Behrens and Teichmann, 1982; Gutowski et al., 2015; Käß, 1998; Machate et al., 1998a, b; Sayer, 1991), some investigators reported comparatively good recoveries of 14–50% in constructed wetlands (Machate et al., 1998a; Netter and Behrens, 1992). Rigorous testing in an experimental subsurface flow passive system at Gernrode (Germany) also showed positive results for that tracer (Hasche and Wolkersdorfer, 2004).

The hypothesis for the investigations described here was that the above mentioned tracers can be used for passive subsurface mine water treatment systems and that the observed differences in the remedial effectiveness of the two systems might be explained by differences in the mean residence time in the RAPS units. Therefore, the main aim of the quantitative tracer test was to directly quantify the mean hydraulic residence times in the systems. Based on the results it should be possible for future systems to thoroughly quantify bioremediation processes in this type of passive mine water treatment systems. At the time of the multi-tracer test, no hydraulic investigations of the Bowden Close RAPS system had been conducted. Preliminary results of this multi-tracer test were reported earlier and will be updated and (as regards to flow calibration) partly revised in this paper (Wolkersdorfer et al., 2005).

2. Description of the location and the passive treatment system

Coal mining was one of the most important industrial activities in County Durham/England/UK until the end of the 20th century (Kruse and Younger, 2007) and the remnants of some 72 collieries can be found within a 5 km radius of the Bowden Close study site. The Bowden Close Colliery, located in the West Durham Coalfield, opened in the early 1840s (Fig. 1, coordinates: UTM ETRS 30 582820 6063940, UK national grid NZ 185 357) and is situated at an elevation of 130—140 m above sea level. Both, the Colliery and the associated coke works closed in the 1930s (Durham Mining Museum, 2016; Roy, 2002). Mining took place predominantly in the Carboniferous (Westphalian) Harvey to Main Coal seams of the Lower and Middle Coal Measures with sulphur contents between 0.8 and 3.6% and a mean of 1.9% (Durham Mining Museum, 2016; Fielding, 1982; Turner and Richardson, 2004). These coals where deposited in a fluvio-lacustrine dominated environment in the northern Pennine Basin which encountered frequent marine transgressions (Waters and Davies, 2006). One of the most prominent legacies of mining these coals are surface water bodies impacted by ochreous or acidic mine discharges which usually stain the rivers and brooks with unaesthetic red, yellow and brown precipitates (Kruse and Younger, 2007). These problems commonly prompt the authorities and communities to search for cheap and reliable remediation solutions (Younger, 1995), and a still increasingly favoured option for such abandoned mine discharges is passive mine water treatment (Parker, 2003; Ranson et al., 2000).

In the mid-1970s, Durham County Council reclaimed the mine site by demolishing derelict buildings, reshaping spoil heaps, emplacing top soil and re-vegetating the area (Roy, 2002; Younger, 2000). At that time no investigations of the mine spoil and underground workings were conducted and no measures were taken to minimise infiltration and through-flow of water through the spoil heaps. Hence, acidic metalliferous mine water began emanating from a number of points,

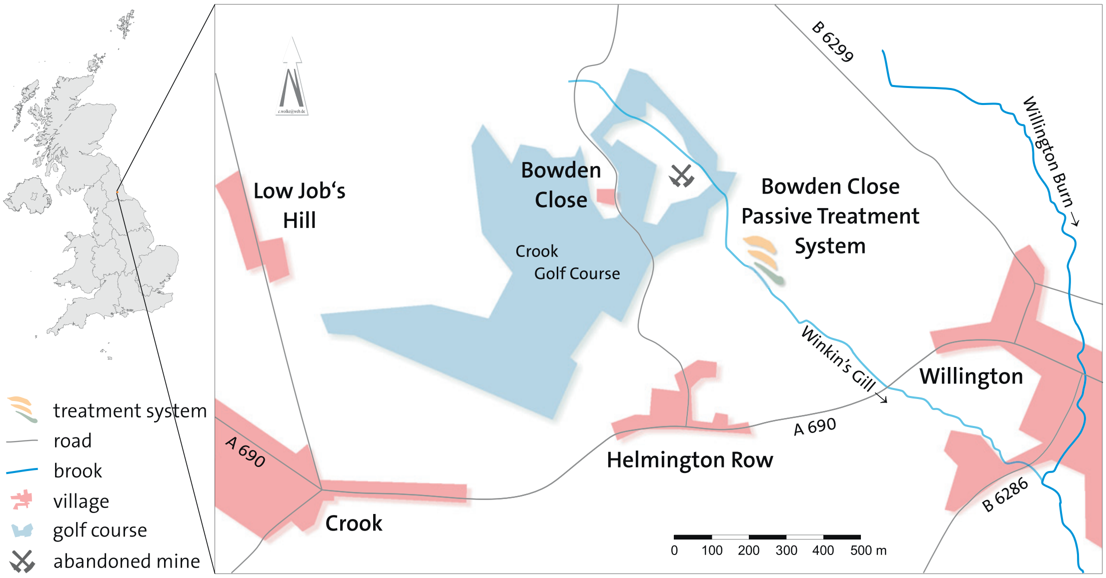

Fig. 1. Location of the Bowden Close mine water treatment system (UTM ETRS 30 582820 6063940, National Grid coordinates NZ 185 357).

causing degradation in the quality of the nearby brook, Winkin's Gill — it should be noted that in all preceding publications about the Bowden Close treatment system, Winkin's Gill (Ordnance Survey, 1861) is erroneously referred to as “Willington Burn”, which, however, is a brook north east of Winkin's Gill. Investigations in the early 1990s identified several highly polluted discharges of mine water from the mine site: acidic leachate from the land drains on the site causing pollution of Winkin's Gill with iron, aluminium and manganese which originates from an old abandoned mine adit near the Crook Golf Course (inflows Nos. 1 and 2) and a subsurface flow (No. 3) containing mobile tar compounds seeping to the surface near the southern boundary of the site (Younger, 2000, 2002). It originates from a mine spoil heap on the western side of the brook which contains two buried tanks from the abandoned coke works of the Bowden Close site (Younger et al., 2003; Younger et al., 2004). This tar seepage was addressed in a separate remediation programme which is not reported here. Subsequently, with funding from the County Durham Environmental Trust (Younger, 2000) a pilot scale RAPS-system (Reducing and Alkalinity Producing System) was constructed with the initial purpose to investigate the feasibility of treating the mine water at this site by using passive treatment technology (Brown et al., 2002).

Mine water treatment systems based on the RAPS technology (also called “vertical” flow through reactor or SAPS – successive alkalinity producing system) mostly consist of an upper layer of manure and a lower layer of limestone with a drainage pipeline therein. The water is theoretically forced to flow vertically through the RAPS, thus first becoming reduced in the organic layer due to oxygen consumption as a result of the decomposition of the organic layer and then, while flowing through the limestone, the alkalinity of the water is increased (Kepler and McCleary, 1994). Previous papers have shown that such systems also work with a mixture of both substrates (Watzlaf et al., 2000) and that the substrates do not necessarily have to be separated from each other. Therefore, the Bowden Close RAPS was constructed as suggested by the latter authors and both substrates were mixed with each other.

Most of the results showed that the pilot-scale system functioned well for the short time it was operational and yielded acceptable treatment results as well as residence times (Diaz Goebes and Younger, 2004; Younger, 2000). Consequently, two RAPS-units, followed by aeration cascades and an aerobic wetland were installed (Younger, 2002) and using preliminary hydrogeochemical investigations (Younger et al., 2003), the volumes of the full-scale RAPS and the wetland were estimated to be 1209 m^3, 899 m^3 and 792 m^3, respectively (Fig. 2). Both RAPS units consist of a mixture of horse manure and limestone with a thickness of 0.8 m with an additional liner at the bottom of RAPS I. In total, the RAPS units and polishing wetland have surface areas of 1511 m^2, 1124 m^2 and 990 m^2, respectively. While RAPS I receives highly polluted mine water from discharges No. 1 and 2, RAPS II receives the discharge No. 3 water and flow measurements proved that no measurable water volumes leave the systems through their base.

At the time of the tracer test, drainage water No. 1 was characterised by a mean flow of 15 L min^{-1}, a pH of around 5.5 and mean Fe concentrations of 30 mg L^{-1}. Discharge No. 2 had a similar mean flow of 12 L min^{-1}, a pH of 6.7 and Fe concentrations of 8 mg L^{-1}. Finally, discharge No. 3 had a large flow of 198 L min^{-1}, a low pH of 4.0, Fe concentrations of up to 80 mg L^{-1} and it is characterised by elevated concentrations of polycyclic aromatic hydrocarbons (PAH) (Taylor and Jones, 2001; Younger et al., 2003; Younger et al., 2004). In regards to the vegetation, there is a substantial difference between RAPS I and RAPS II. While RAPS I is densely vegetated with typical wetland flora such as grass, *Typha latifolia*, *Phragmites australis* and *Juncus effusus*, RAPS II is only loosely vegetated with grass and *Juncus effuses* on the edges and small patches within the RAPS (Fig. 3). This can be attributed to the differences in the mine water chemistry, which supports or suppresses vegetation in RAPS I and II, respectively.

Several detailed studies about the geochemical processes occurring in the Bowden RAPS system have been conducted and were presented after the tracer test was terminated (e.g. Matthies, 2010; Matthies et al., 2010; Matthies et al., 2009; Mudashiru, 2008). Because these authors mainly focus on the geochemical behaviour of the system, they will not be discussed in further detail here.

3. Methods

Four different tracers were used: uranine (CAS 518–47-8, Na-fluorescein), NaBr (CAS 7647–15-6), LiBr (7550-35-8) and NaCl (CAS 7647-14-5). Using Eq. 1, the necessary tracer masses *M* were calculated on the basis of the flow *Q* of the fully constructed RAPS systems during the seven months preceding the tracer test (mean flow in both RAPS units: $Q = 66 \pm 38$ L min^{-1}) multiplied with the expected mean

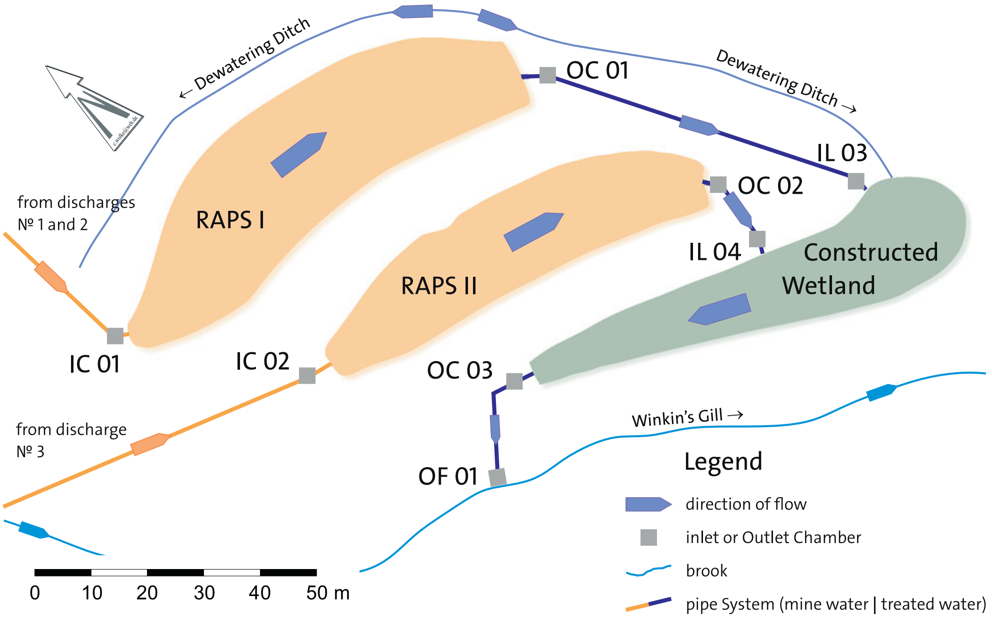

Fig. 2. Map of the Bowden Close mine water treatment scheme with the two RAPSes in the upper part and the wetland in the lower part. Modified after Younger et al. (2004).

Fig. 3. RAPS I (left) and RAPS II (right) exemplifying the different vegetation intensity (March 2006). RAPS I: looking to the east; RAPS II: looking to the south east.

residence time *t*, the water volume *V* in the RAPS and wetland systems and mean expected tracer concentrations $\bar{c}$ of 0.1 mg L^{-1} uranine, 5 mg L^{-1} bromide and an electrical conductivity of 100 µS cm^{-1} for the NaCl.

$$M = (Q \cdot t + V) \cdot \bar{c}. \tag{1}$$

All results were rounded to the nearest 10 g or 100 g. This conservative, empirical type of calculation proved successful in previous tracer tests conducted by the first author and, as all calculations for potential tracer masses in the literature, takes into account potential sorption as well as dilution (Wolkersdorfer, 2008). Accordingly, the following tracer amounts were used: RAPS I: 69.96 g uranine, 1710 g LiBr, 2860 g NaBr; RAPS II: 50.41 g uranine, 1270 g LiBr, 2130 g NaBr; wetland: 25.8 kg NaCl. Uranine was diluted with deionised water in 1-L-bottles, LiBr and NaBr with deionised water in 10-L-canisters and NaCl on-site in a 200-L-container with the wetland water.

Before the tracers were injected, a one-day set of blind samples to account for background concentrations was collected. Thereafter, the NaCl-tracer was slug injected into the wetland system at the outflow of IL03, and uranine, NaBr and LiBr were slug injected into RAPS I at the outflow of IC01 and RAPS II at the outflow of IC02 (Table 1).

While NaCl was detected by electrical conductivity changes, uranine was detected with two in-line Seapoint SFF fluorometers connected to a Dataron Data Bank logger in the field (OC01, OC02) and with a Cary Eclipse Fluorescence spectrophotometer in the laboratory (Excitation Wavelength 475 nm, Emission Wavelength 530 nm). Furthermore, three auto samplers were installed at the outlet chambers OC01, OC02 and OC03 of the two RAPS and the polishing wetland (Fig. 2). During the 4 ½ weeks of the tracer test, those auto samplers collected a water sample every 11 min and 9 sample aliquots where collected into each 1-L-bottle. Every 2–3 days, the samples were removed from the auto samplers for further analysis in the laboratory. In addition, three Van Essen CTD Diver DI 218 loggers were installed in every outlet chamber for continuous measuring of the pressure (hence hydraulic head), temperature and electrical conductivity at 5-min intervals.

Table 1
Parameters for the RAPS, wetlands and tracer test. Physico-chemical parameters are arithmetic means for December 2003 to September 2004 for in | out; k_A: acid capacity ("alkalinity"); calculation of λ based on Persson et al. (1999).

System	RAPS I	RAPS II	Wetland
No. samples	266	264	216
Length, m	81	74	48…74
Width, m	20	17	14
Area, m^2	1511	1124	990
Volume, m^3	1209	899	792
Hydraulic efficiency λ, –	–	–	0.66
NaBr, g	2860	2130	–
LiBr, g	1710	1270	–
Na-fluorescein, g	69.96	50.41	–
NaCl, g	–	–	25,800
pH	5.1 | 7.5	5.1 | 7.1	– | 7.2
electrical conductivity, mS cm^{-1}	0.9 | 1.1	1.4 | 1.6	– | 1.3
k_A, mmol L^{-1}	0.1 | 2.3	0.1 | 2.2	– | 1.4
Fe_{tot}, mg L^{-1}	17 | 2	48 | 4	– | 6
SO_4^{2-}, mg L^{-1}	450 | 240	920 | 670	– | 540
Flow before tracer test, L min^{-1}	27.1 ± 13.5	115.8 ± 101.5	153.9 ± 118.8
Flow during tracer test, L min^{-1}	44.7 ± 32.9	84.1 ± 40.2	150.9 ± 81.7

All samples were analysed for Br with an ion-selective probe (IOS) ELIT 8271 Br 57,461 connected to a pH-metre Jenway 3310 and a reference electrode ELIT 002n KNO_3 57810. Li was analysed with a flame photometer, as the ICP-MS was in maintenance during the time of the tracer test. At every laboratory measuring day, three calibrations for the bromide IOS were conducted to account for sensor drift. Detection limits for uranine were 0.1 µg L^{-1} for the field and the laboratory fluorometers. For Br, the detection limit was 0.2 mg L^{-1} and Li had a detection limit of 0.1 mg L^{-1}. The relatively high detection limits are a result of the complex matrix of the mine water and available lab technology. Lithium was analysed as an additional tracer, though the bromide anion was the main tracer substance applied. No pH adjustment for uranine detection was conducted to obtain comparable results for the on-site and the laboratory analysis. This was possible, because the pH of the mine water at the outfall chambers was 7.18 ± 0.37 (1 σ) during the tracer test (pre-test data in Tab. 1), which relates to a fluorescent intensity of 87–99% (Behrens, 1988).

At the wetland inlets IL03, IL04 and the Outfall OF01, the flow was measured every 2–3 days by using multiple measurements with bucket and stopwatch (Fig. 2). Besides the drainage pipes at the base, each RAPS unit is equipped with overflow pipes to exclude overbank erosion during high rainfall events. To drive the entire tracer and the water through both of the RAPS, these overflow pipes were closed for the duration of the tracer test. Yet, due to the unexpectedly high rainfall during the tracer test and the closure of these overflow pipes, the RAPS started to overflow across its banks. To account for this overflow, the overflowing water was measured as accurately as possible with buckets and the flow corrected with Eqs. 2 to 4, using the total outflow Q_{OF01} of the wetland for adjusting the individual flows, as most of the overflow discharged into the wetland. Q_{diff}, the difference between the outflow from the wetland and the sum of the flows in the two RAPS units, ranged between −13 and 71 L min^{-1} (−11–32% of total flow at Q_{OF01}).

$$Q_{diff} = Q_{OF01} - (Q_{IL03} + Q_{IL04}) \tag{2}$$

$$Q_{IL03,corr} = Q_{IL03} + \frac{Q_{IL03}}{Q_{IL03} + Q_{IL04}} \cdot Q_{diff} \tag{3}$$

$$Q_{IL04,corr} = Q_{IL04} + \frac{Q_{IL04}}{Q_{IL03} + Q_{IL04}} \cdot Q_{diff} = Q_{OF01} - Q_{IL03,corr}. \tag{4}$$

After installation of the data loggers and auto samplers, the on-site parameters pH, redox potential, electrical conductivity and temperature were measured at the inlets, outlets and the outfall with a Myron P6 (Myron L Company, Karlsbad, USA; all the treated mine water leaves the system at the outfall and is discharged into Winkin's Gill). At each site visit the on-site parameters were again recorded.

Rainfall data for Bowden Close were calculated with the inverse distance method (Davis, 2002), using rainfall data from the surrounding meteorological stations: Tunstall Reservoir (NZ 064 407, 12.9 km distance), Esh Village (NZ 198 440, 8.4 km distance), Dryderdale Farm

(NZ 089 340, 9.9 km distance) and Redworth (NZ 249 237, 13.6 km distance).

Mass recovery was calculated by integrating the tracer loading (tracer concentration × flow rate) assuming mean flow measurement errors of 2.1% for RAPS I, 2.8% for RAPS II and 6.6% for the wetland system. Those errors are based on the standard deviation of the multiple measurements at each location. The wetland tracer should have been detected by changes in electrical conductivity but the flow was more than 5 times higher than expected, causing a substantially higher dilution of the NaCl; therefore it was not possible to detect the NaCl over the natural electrical conductivity fluctuation (Fig. 6). However, the results are reported here to show the relationship between the electrical conductivities in the three systems and the low *Q*.

Tracer test data can be analysed with different analytical and numerical methods. For ideal breakthrough curves, analytical methods are the method of choice (Leibundgut et al., 2009). Yet, in most tracer tests, ideal breakthrough curves are not obtained, and “peaks” are merely identified as the maximum of the tracer concentration (for example in Fig. 9 between 500 and 525 h). Therefore, the Bowden Close tracer test was modelled quantitatively with QTRACER2 (Field, 2002), which is based on the method of moments (Yu et al., 1999). In this paper, the mean residence time and the dominant residence time will be used for evaluation. While the mean residence time represents the time at which 50% of a tracer passes through the system, the dominant time represents the time at which the tracer concentration reaches its maximum concentration in the breakthrough curve (Käß, 1998). Details about their calculation can be found in Field (2002). For evaluating the efficiency of the wetland, the hydraulic efficiency λ was calculated using the expression introduced by Persson et al. (1999):

$$\lambda = \frac{t_p}{t_n}. \qquad (5)$$

This dimensionless quotient of the time t_p for a conservative tracer to reach a peak at the outlet and the nominal hydraulic residence time t_n (Jenkins, 2003) denotes how efficiently water flows through a constructed wetland (Table 1).

4. Results and 1-D transport modelling

Rainfall in October 2004 was higher than usual (1881–2004 mean: 65.6 mm) with daily rainfall of up to 17 mm and a total rainfall of 129.1 mm recorded for the duration of the tracer test. As a result, RAPS I and RAPS II started to overflow across the dividing banks. While RAPS I began to overflow at a total inflow of about 30–40 L min^{-1}, RAPS II started to overflow at 100–110 L min^{-1}.

Inflow measurements before the tracer test showed flows of 27.1 ± 13.5 L min^{-1} for RAPS I, 115.8 ± 101.5 L min^{-1} for RAPS II and a total outflow of 153.9 ± 118.8 L min^{-1} for the outfall into Winkin's Gill (n = 12–17, 1 σ) with a flow maximum in the months January–March (268 ± 100 L min^{-1}) and a minimum in the months April–September (85 ± 64 L min^{-1}). However, the weeks of the tracer test were some of the wettest in the second half of 2004 (Fig. 4) and the maximum flow during the tracer test reached as much as 247 L min^{-1} (Fig. 5) with mean flows of 44.7 ± 32.9 L min^{-1}, 84.1 ± 40.2 L min^{-1} and 150.9 ± 81.7 L min^{-1} in RAPS I, RAPS II and the wetland system, respectively (n = 15, error 1 σ).

This intense rainfall also caused the flooding of the outlet chambers in the last week of the tracer test and subsequently the auto samplers in RAPS II and the wetland (4 and 3 weeks of data available, respectively). Only a few samples, due to wet batteries, are missing from RAPS I (Table 2). All three van Essen CTD Diver electrical conductivity probes in outlets 1 to 3 worked without failure and the data are complete for the whole 4 ½ weeks period of the test.

Temperature fluctuations in the RAPS systems were in the range of 1–2 K at a mean temperature of 9.8 °C, while the temperature in the wetland system decreased from around 11 °C to 7 °C. Its daily temperature fluctuations reached up to 5 K on November 12th and decreased from 9 to 10 °C to 5–7 °C at the end of the test. These temperature data can be used to indicate subsurface or surface flow conditions.

At the beginning of the tracer test, the electrical conductivities in RAPS I, RAPS II and the wetland were 920, 1650 and 1520 µS cm^{-1}, respectively. They decreased to 750, 1000 and 740 µS cm^{-1} by the end of the test with a relatively high fluctuation of the values (Fig. 6).

Uranine showed comparably high background levels of 1–3 µg L^{-1} and arrived 45 h after its injection in RAPS I with a peak after 140 h. In

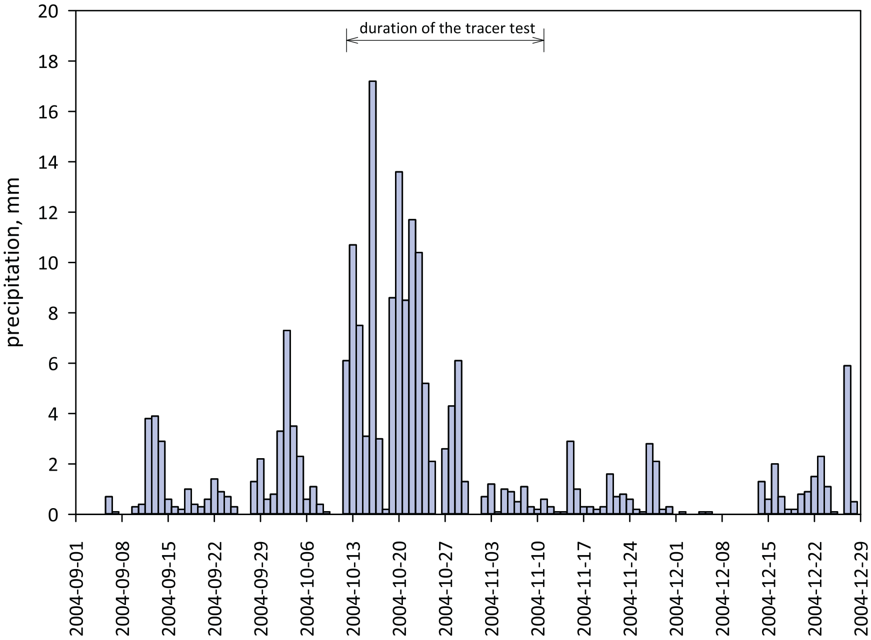

Fig. 4. Precipitation at the Bowden Close Mine Water Treatment scheme between September and December 2004. The tracer test was conducted between October 12 and November 11 (data calculated from Esh Village, Dryderdale Farm and Redworth rain gauging with the inverse distance method).

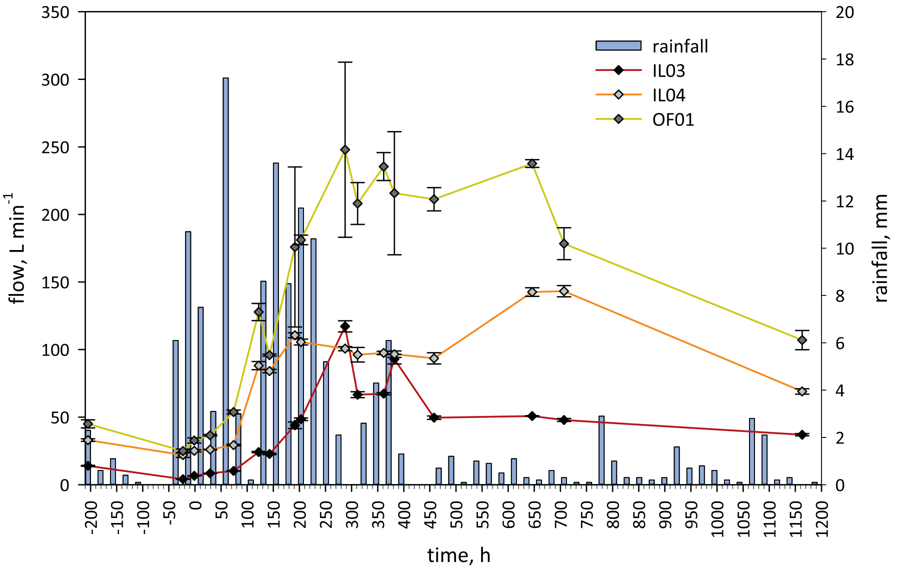

Fig. 5. Flow through the two RAPS systems and the wetland and the daily precipitation for Bowden Close during the duration of the tracer test. Error bars show the mean errors for each measuring point based on 3–5 flow measurements at each measuring occasion. RAPS I: 1.5%; RAPS II 3%, wetland: 4%. 0 on abscissa denotes start of the tracer test.

RAPS II, the uranine needed approximately 160 h for its first appearance with a peak after 510 h. Background values were not met in either of the two systems before the end of the tracer test (Fig. 7 and Fig. 8).

Bromide background concentrations ranged between 4 and 10 mg/L. The first Br-tracer from RAPS I arrived several hours after its injection, peaked 90 h later and declined to background levels after 350–370 h, showing a second peak at around 445 h. In RAPS II, the bromide arrived 8 h after injection, peaked at 106 h and declined to background levels after 310 h. The Br concentrations showed a tailing slightly above background levels until the end of the tracer test (Fig. 7 and Fig. 8).

Lithium background levels ranged between 0.1 and 0.7 mg/L and the concentrations after injecting the tracer between 0.1 and 0.8 mg/L. No first arrivals or peaks could be detected and, consequently, no breakthrough curve could be constructed. Yet, the Lithium concentrations show a very good correlation with the electrical conductivity of the mine water (r^2 between 0.85 and 0.96 at a significance level α of 0.01 for the different sampling locations).

As can be seen from Fig. 7 to Fig. 9, only bromide is suitable for a 1-D transport model because lithium is usually below the detection limit and the uranine tracer breakthrough curves are incomplete except for the constructed wetland. To evaluate the results, the 1-D porous aquifer model of QTRACER2 (Field, 2002) was used to model the two RAPS (convection dispersion model) and the 1-D fissured aquifer model for the wetland system. This is possible, because the water layer on the wetland substrate has characteristics equal to a horizontal fracture. Both analytical solutions assume a Dirac-injection ("slug injection") of the tracer. The results of the 1-D transport model with QTRACER2 (Table 2) will be discussed in the next section.

Table 2
Details of the injected tracers, recoveries and injection times as well as the results of the 1-D transport modelling with QTRACER2. Differences are due to rounding errors. The errors of the recovery are based on the mean errors of the flow measurements which were 2.1% for RAPS I, 2.8% for RAPS II and 6.6% for the wetland system. d_l: longitudinal dispersivity, – denotes that a parameter cannot be calculated or is not applicable. Two numbers for the wetland: actually flown into the wetland (sum of recovery RAPS I and RAPS II) | theoretically flown into the wetland (sum of injected RAPS I and RAPS II).

Tracer	RAPS I	RAPS II	Wetland
Bromide			
Injected, mol	47.5	35.3	54.9 | 82.8
Recovery, mol	19.9 ± 0.3	35.0 ± 2	19.6 ± 1.3
Recovery, %	42 ± 1	99 ± 2	36 ± 3 | 24 ± 2
Injection time	Oct 13, 2004, 13:05	Oct 13, 2004, 13:10	–
d_l, m	14.65	5.89	3.78
Na-fluorescein			
Injected, mol	0.19	0.13	0.15 | 0.32
Recovery, mol	0.12 ± 0.1	0.03 ± 0.005	0.05 ± 0.01
Recovery, %	64 ± 1	20 ± 1	31 ± 2 | 14 ± 1
Injection time	Oct 13, 2004, 12:49	Oct 13, 2004, 12:57	–
Last dataset	Nov 11, 2004, 8:00	Nov 9, 2004, 5:20	–
d_l, m	–	–	–

5. Interpretation and discussion

5.1. Rainfall, flow and temperature

According to the UK Met Office historical data, October 2004 was the wettest October since 1976, with twice as much rainfall as the long term mean (1880 to 2004, Durham data). Because the overflow pipes were closed during the tracer test in order to force all the water through the RAPS systems, the excess water completely filled the freeboard and occasionally, both RAPS overflowed. This provided useful information on maximum water treatment capacities of the RAPS systems. While RAPS I can treat a discharge of up to 30–40 L min$^{-1,}$ RAPS II is capable of treating 100–110 L min^{-1}, which results from the different volumes and particular hydraulic conductivities of the RAPSs. As both systems are constructed similarly, the difference cannot be explained from construction variances *per se*. Yet, no consolidation investigations were conducted during or after construction, which would have given valuable information about the elastic modulus, i.e. compaction, of the RAPS. It can be concluded that the variability of the limestone plus manure mixture and truck driving over this mixture during construction caused differences in compaction and consequently the hydraulic conductivity.

The temperature fluctuations and the mean temperature decrease in the wetland system are a result of the weather change and the unexpectedly intense rainfall during the tracer test. Those fluctuations are substantially smaller in the RAPS systems, as the water is subsurface flow dominated, while it is surface dominated in the wetland.

5.2. Electrical conductivity

Electrical conductivities show an inverse power correlation with the total flow through the system ($r^2 = 0.789$) and can therefore be explained by dilution due to the rainfall. In addition, this rainfall caused high fluctuations of the electrical conductivity in the wetland and

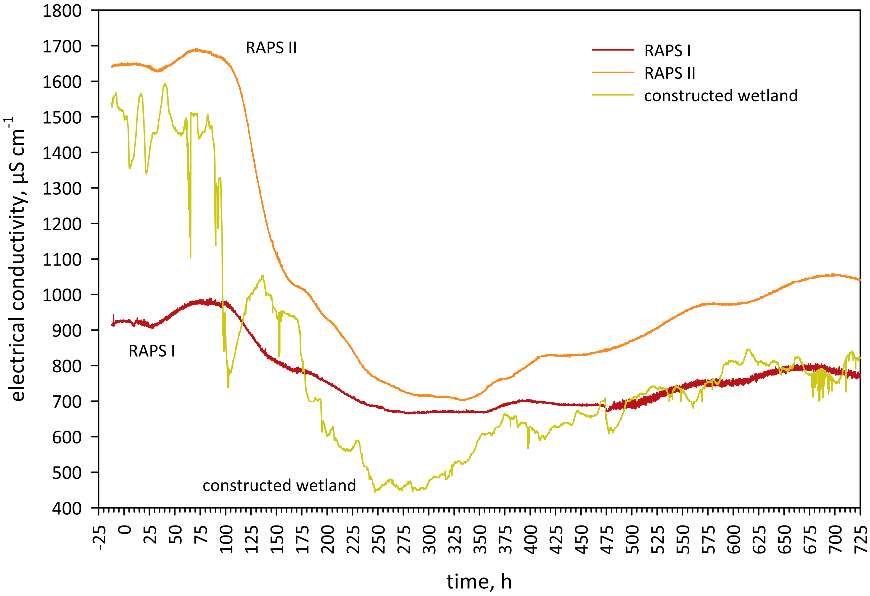

Fig. 6. Continuous electrical conductivity measurements in the RAPS 1 (upper line), constructed wetland (middle line), and RAPS 2 (lower line) outlets. No correction for loadings. The drop in the wetland curve at the end of the measuring period is due to the flooding of the outfall chamber 3 with non-treated rain water. 0 on abscissa denotes start of the tracer test.

consequently, the NaCl tracer, which theoretically should have increased the electrical conductivity by about 100 µS cm^{-1}, cannot be used to evaluate the wetland's hydraulic properties. Even after normalisation with the flow data, no electrical conductivity peak could be observed.

5.3. Lithium tracer

The lithium concentrations, as expected, are too low. Because the analysis of the lithium concentration and the electrical conductivity shows a positive correlation, this is an indication of the lithium being related to the inflowing mine water, indicating its ubiquitous occurrence in the rocks and not the LiBr tracer injected. Presumably, the injected lithium was affected by ion exchange, as has been observed by earlier authors (Haas, 1959; Leibundgut et al., 2009), and therefore could not be detected.

5.4. Uranine background concentrations

Although it is well known that water might be contaminated with uranine from washing detergents or bathing foams (Käß, 1998), such a potential source causing the elevated uranine background concentration at Bowden Close could not be identified. Yet, US patents 20,050,096,420 ("Luminescent plastics", 2005–05-05) and 20,040,259,665 ("Golf ball comprising UV-cured non-surface layer", 2004–12-23) describe the use of uranine in yellow and orange golf balls for lost ball detection with UV-lamps. In addition, fertilisers and insecticides used for golf courses are commonly marked with uranine (Zhu et al., 2005). Therefore, uranine from the adjacent Crook Golf

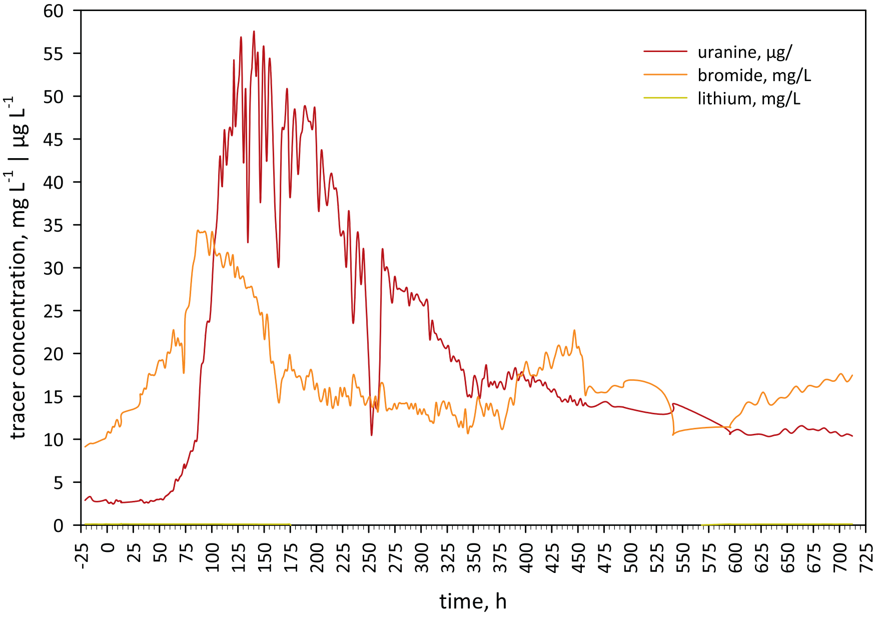

Fig. 7. Breakthrough curves for RAPS I. No correction for loadings. Units for Li and Br in mg L^{-1}, for uranine in µg L^{-1}. 0 on abscissa denotes start of the tracer test.

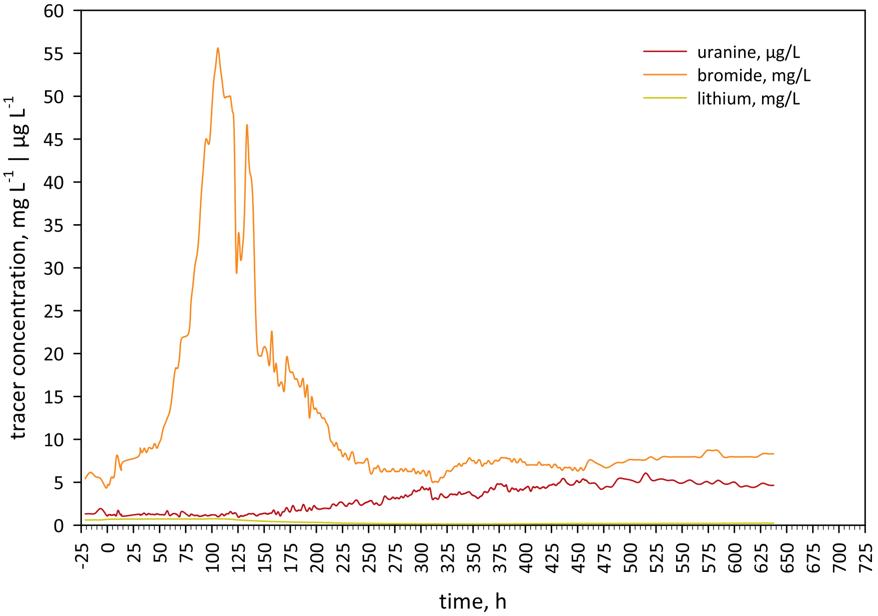

Fig. 8. Breakthrough curves for RAPS II. No correction for loadings. Units for Li and Br in mg L^{-1}, for uranine in μg L^{-1}. 0 on abscissa denotes start of the tracer test.

Course is very likely the source of the observed background concentrations of uranine.

5.5. Uranine and bromide tracers

Uranine and bromide tracers show flattening breakthrough curves which do not decline to background values. This is an indication for advection-dispersion flow as well as diffusion based matrix flow (Benischke et al., 2007) and can therefore be used to interpret the hydraulic behaviour of the system. This means that the tracer penetrates through the RAPS at different locations which is supported by the fact that the tracer could be seen on the RAPS's surface for nearly two days.

Uranine, as could be observed visually, spread over the area of RAPS I, and it can be concluded that the breakthrough curve is a result of exponential flow over and through the RAPS substrate. The long tailing of the breakthrough curve is related to the uranine in the shallow layer of water on top of the RAPS, which could still be observed visually three days after tracer injection and infiltrated into RAPS I.

The fast arrival of bromide (Fig. 8) in RAPS II is also due to its relatively fast flow through the 0.8 m thick substrate and partial surface stormflow on the RAPS's surface. Similar to RAPS I, the tailing towards the end of the tracer test indicates that slow flow through the deeper parts of the substrate matrix or diffusion from pockets of bromide established within the system.

The explanation for the unequal behaviour of the Br- and uranine tracers, that were applied in succession, is that the highly concentrated Li/NaBr brine, due to its higher density of around 1.25 kg L^{-1}, penetrated through the mixture of the organic and inorganic substrate to the

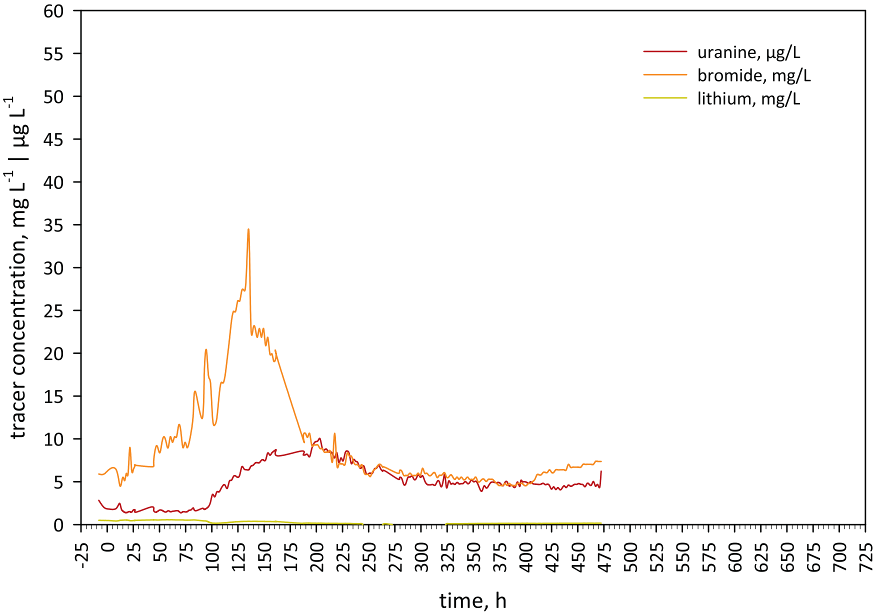

Fig. 9. Breakthrough curves for the constructed wetland. Due to a data logger failure, data ends at November 1st. No correction for loadings. Units for Li and Br in mg L^{-1}, for uranine in μg L^{-1}. 0 on abscissa denotes start of the tracer test.

drainage pipelines while the uranine solution with a lower density first flowed on or close to the RAPS' surface and slowly penetrated through the system at different locations. As such, the Br gives the fast reaction time for the system with preferential flow through the coarser part of the substrate matrix and the uranine gives the mean reaction time.

An unanticipated result was obtained for the wetland system, as the Br and the uranine injected in the RAPS systems could also be found in detectable concentrations in the constructed wetland (Fig. 9, Table 2). Those data, instead of the electrical conductivity data, were used to evaluate the hydraulic parameters for the wetland.

5.6. Recovery rates

Recovery rates for the two treatment systems and the tracers differ from each other. The Bromide recovery rate was 42% in RAPS I and 99% in RAPS II while uranine recovery rates were 64% in RAPS I and 20% in RAPS II (Table 2). Those recovery rates are within the range described in the introduction. Three possible explanations for the broad range of recovery rates are possible: the complex chemistry of the mine water, potential uptake by plants and the hydraulic performance of the systems. Because of the matrix flow in the RAPS, the breakthrough curves show long tails indicating long mean residence times of the tracer in the compost-limestone-matrix. As the tracer test was terminated before those tails declined to background values, not all the tracer could be collected, adding to the lower recovery rates. Because RAPS I, compared to RAPS II, is vegetated (Fig. 3), it can be assumed that part of the bromide tracer is taken up by the wetland plants, as also observed by Whitmer et al. (2000). RAPS II, with almost no vegetation, is therefore showing a higher recovery rate for bromide.

Several hypotheses can explain both the low recovery rates of uranine and the differences in the recovery rates between RAPS I and RAPS II: a) water loss through the base of the RAPS systems, b) degradation of the tracer, c) sorption, d) pH-effects on the tracer fluorescence, and e) tracer loss as a result of the system's overflow. Water loss can be rejected as RAPS I is lined and RAPS II constructed in impermeable glacial till (Younger et al., 2004). Uranine has been reported to be decomposed by photolysis, microbial activity, or organic reactants (Bottrell et al., 2010; Gutowski et al., 2015; Käß, 1998; Machate et al., 1998a, b; Sayer, 1991; Smart and Laidlaw, 1977), such as the PAHs emerging from discharge No. 3. Photochemical decay coefficients reported in the literature are summarised in Smart and Laidlaw (1977) and vary from $1.3 \cdot 10^{-2}$– $3.9 \cdot 10^{-1}$ d^{-1} for sunny and $5.1 \cdot 10^{-2}$ – $1.5 \cdot 10^{-2}$ d^{-1} for cloudy conditions, such as during the tracer test. As part of the uranine was visible in the supernatant water on top of the RAPSes for 3–4 days, photochemical decay could be responsible for up to 20% of the initial uranine concentration. Sorption of uranine is generally minimal due to its low adsorption capacity on organic matter, clay and silts (Käß, 1998; Vereecken et al., 1999) and is therefore eliminated from this discussion. Because of the relatively high pH-values of the treated mine water, pH-effects can only explain 4% of the difference between RAPS I and RAPS II and 1% of the total loss. As described above, overflowing water has been accounted for by measuring the overflow and calibrating the differences using Eq. 2. Part of the uranine loss might therefore be attributed to degradation, but mainly to the too short duration of the tracer test. No recovery rates could be calculated for lithium and NaCl due to the reasons described above.

The fast arrival of the Br-tracer in RAPS I (Fig. 7) indicates that part of the tracer flows relatively fast through the 0.8 m thick substrate reaching the drainage pipes at the base of the RAPS. This behaviour might result from the macropores in the inhomogeneous and coarse substrate. In addition, it is an indication of partial surface stormflow on the surface of the RAPS. The second peak at around 450 h seems to be connected to deeper subsurface flow within the matrix of RAPS I.

5.7. Residence times

Using all of the above data, the mean residence time in RAPS I is about 12–16 d and in RAPS II about 6–20 d and the dominant residence times 4–5 d and 4–20 d, respectively. An approximate estimation of the uranine's mean residence time in RAPS II results in 20–24 d. Because the breakthrough curves in the wetland are incomplete, and the overlap of the two input functions arising from RAPS I and II simultaneously, the mean residence times in the wetland can't be calculated with the same precision as for RAPS I and II, but ranges between 2 and 3 days.

In RAPS I, the distance between the injection and the outflow is about 81 m, in RAPS II 74 m and in the wetland 48–74 m. The mean effective velocities in the systems are 0.7–0.9 m h^{-1} in both RAPSes and 0.7 m h^{-1} in the constructed wetland. Those data are seven- to nine fold faster than the results obtained by Diaz Goebes and Younger (2004) for the Bowden Close pilot scale RAPS, which were 0.1 m h^{-1}. One of the reasons might be that Diaz Goebes and Younger (2004) used the thickness of the substrate as the characteristic length instead of the length of the RAPS system. If the thickness of the RAPS is included in the characteristic length as well, the effective velocities become approximately 0.01 m h^{-1}, which fits exactly into the results of the Pelenna III RAPS, evaluated by Diaz Goebes and Younger (2004). These data by itself cannot sufficiently explain the efficiency of the RAPS systems, as both systems treat the mine water to a quality that has been predetermined in the pilot scale system and laboratory tests. Fabian et al. (2005) observed that the treatment efficiency of RAPS II usually surpasses that of RAPS I. This observation can now be explained from the different mean residence times with RAPS II having a longer one than RAPS I.

Taking the thickness of a RAPS as the characteristic length is a misconception about the flow in a RAPS. According to Diaz Goebes and Younger (2004) “the essence of a RAPS unit is that the polluted water is forced to flow vertically downwards through two consecutive layers of reactive media” which is in accordance with the first description of a RAPS system by Kepler and McCleary (1994) or later by Watson et al. (2009). This concept mistakenly resulted in the name “vertical flow through reactor”. Hydrogeologically, vertical flow predominates in unsaturated media and horizontal flow in saturated media (Hiscock and Bense, 2014). Because a RAPS can be considered a saturated aquifer, vertical flow through the system is not dominant, which could be seen during the injection of the uranine tracer spreading in the supernatant water of nearly the whole RAPSes surfaces. If vertical flow would predominate, the tracer would have been disappeared immediately into the RAPSes. In addition, a vertical flow through a comparably thin substrate layer would not be matrix dominated, as indicated by the results of the numerical modelling with QTRACER2. Finally, the Bowden Close RAPS consists of only one layer of mixed limestone-manure which also excludes simple vertical flow into the system's drainage pipes. Consequently, the characteristic length of a RAPS must be considered to be the total length of the potential flow through the system, usually being the distance between the inflow and the outflow.

6. Conclusions

Two types of conclusions can be drawn from the Bowden Close tracer test: general ones and site specific ones. Generally, it could be shown that the mean first-order residence time approach for designing subsurface RAPS systems is adequate to design those systems. Of the tracers used, Br and uranine are suitable for these systems. Both of them reacted non-conservatively under the very specific conditions of a RAPS. Therefore, similar to mine water tracer tests (Wolkersdorfer, 2008), tracer investigations in mine water treatment systems should be designed as multi-tracer experiments to account for potential tracer losses as a result of uptake or decomposition. Furthermore, it can be concluded that the effective velocity through the substrate matrix of a 0.7—0.8 m thick RAPS with manure and limestone is in the range of about

0.01 m h^{-1} and a total mean effective velocity of 0.7–0.9 m h^{-1} for the whole system. To verify if this effective velocity is typical for RAPS system, more tracer investigations in RAPS systems will be necessary. Yet, because of the lack of comparable data from other RAPS tracer tests — the only one published being the one in Tan y Garn (Watson et al., 2009) — no further general recommendations can be given.

Site specific conclusions are that the design parameters of the treatment systems which targeted on a mean first-order residence time of 4—6 days could be outperformed. Due to the unexpected intense rainfall during the tracer test, causing dilution, NaCl could not be used as a tracer in the aerobic wetland system, yet bromide and uranine flowing in from the two RAPS units could be used as a tracer. The differences in the mean residence times of the two RAPS systems, and consequently their functioning, mirror the different hydraulic conductivities of the system. This might be explained by different compactions of the substrate during construction.

It has also been shown that elevated tracer background concentrations might be expected in the vicinity of golf courses when conducting tracer test with uranine. It is therefore essential, to measure enough background samples preceding the tracer test to identify background concentrations. To be able to verify the results of a RAPS tracer test, it is fundamental to investigate the compaction of the RAPS. Different RAPS may show different results due to different hydraulic conductivities as a result of compaction during or after construction. Especially driving on the RAPS substrate during construction might compact the substrate and consequently alter the hydraulic conductivity. In order to get reliable results, this tracer test should have been longer. It is therefore essential to measure the tracer concentrations promptly so that the criteria for stopping the tracer test can be developed. It is also essential to weigh auto samplers down to ensure that they are not floating in case of higher than expected flows when used in a confined space.

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