Science of the Total Environment 621 (2018) 265–272

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Evaluation of the hydrological flow paths in a gravel bed filter modeling a horizontal subsurface flow wetland by using a multi-tracer experiment

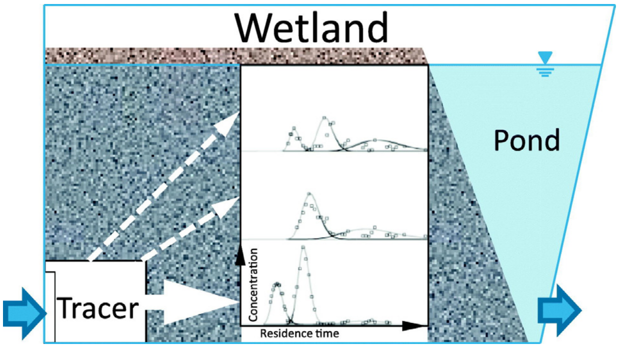
Jan Birkigt [a], Christine Stumpp [b], Piotr Małoszewski [b,c,1], Ivonne Nijenhuis [a,*]

[a] Helmholtz Centre for Environmental Research - UFZ, Department of Isotope Biogeochemistry, Permoserstraße 15, D-04318 Leipzig, Germany
[b] Helmholtz Zentrum München, German Research Center for Environmental Health – Institute of Groundwater Ecology, Ingolstädter Landstraße 1, D-85764 Neuherberg, Germany
[c] AGH University of Science and Technology Kraków, Department of Hydrogeology and Engineering Geology, Al. Mickiewicza 30, 30-059 Kraków, Poland

HIGHLIGHTS

- The three-dimensional hydrological flow path was studied in an active constructed wetland remediation system.
- A multiple flow system was inferred from a combination of tracer test and mathematical modeling.
- Main water flow was at the bottom of the wetland.
- An advanced interpretation of remediation efficiencies of such systems was proposed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 September 2017
Received in revised form 14 November 2017
Accepted 19 November 2017
Available online xxxx

Editor: D. Barcelo

Keywords:
Constructed wetland
Multi tracer test
Mathematical modeling
Chlorobenzene

ABSTRACT

In recent years, constructed wetland systems have become into focus as means of cost-efficient organic contaminant management. Wetland systems provide a highly reactive environment in which several removal pathways of organic chemicals may be present at the same time; however, specific elimination processes and hydraulic conditions are usually separately investigated and thus not fully understood. The flow system in a three dimensional pilot-scale horizontal subsurface constructed wetland was investigated applying a multi-tracer test combined with a mathematical model to evaluate the flow and transport processes. The results indicate the existence of a multiple flow system with two distinct flow paths through the gravel bed and a preferential flow at the bottom transporting 68% of tracer mass resulting from the inflow design of the model wetland system. There the removal of main contaminant chlorobenzene was up to 52% based on different calculation approaches. Determined retention times in the range of 22 d to 32.5 d the wetland has a heterogeneous flow pattern. Differences between simulated and measured tracer concentrations in the upper sediment indicate diffusion dominated processes due to stagnant water zones. The tracer study combining experimental evaluation with mathematical modeling demonstrated the complexity of flow and transport processes in the constructed wetlands which need to be taken into account during interpretation of the determining attenuation processes.

1. Introduction

Constructed wetlands have become of increasing interest in recent years as an economical solution for treating wastewater. Subsurface

---

[*] Corresponding author.
E-mail address: ivonne.nijenhuis@ufz.de (I. Nijenhuis).
[1] Deceased 21 March 2017.

https://doi.org/10.1016/j.scitotenv.2017.11.217
0048-9697/

flow constructed wetlands provide a heterogeneous filter and buffer system where abiotic and biotic processes, e.g. sorption, hydrolysis, photolysis, evaporation and biodegradation, may take place simultaneously, resulting in contaminant removal (Imfeld et al., 2009). Wetlands have been shown efficient in the removal of organic contaminants such as the chlorinated solvents, pharmaceuticals, personal health care products, pesticides as well as the immobilization of metals (Gambrell, 1994; Imfeld et al., 2009; Kidmose et al., 2010; Li et al., 2014; Onesios et al., 2009; Schmidt et al., 2014; Verlicchi and Zambello, 2014). However, the processes contributing to the removal are not fully understood and of high interest for future wetland applications. The currently developed applications for industrial and urban scale water treatment, however, require a detailed understanding of the intertwined processes occurring in the highly heterogeneous environment of wetland systems (Imfeld et al., 2009). In particular, a thorough understanding of the water flow characteristics determining the retention time and flow paths will be a requisite to run such systems efficiently (Zahraeifard and Deng, 2011) and before up-scaling of these approaches can be successful. Then the implementation can be considered as feasible alternative or supplement for conventional wastewater treatment or contaminated site management (Gearheart et al., 1989).

To date, several studies were published addressing constructed wetland processes in more detail. For example, the contributing processes to chloroethene (Imfeld et al., 2010), monochlorobenzene (Braeckevelt et al., 2007; Schmidt et al., 2014) as well as MTBE (Jechalke et al., 2010; Rakoczy et al., 2011), pharmaceuticals (Matamoros and Bayona, 2006) or metals (Weis and Weis, 2004) removal and immobilization and related microbial biomass (Tietz et al., 2007; Truu et al., 2009) was described (Imfeld et al., 2009). However, these processes also need an insight into the hydrology and the flow characteristics of such wetland systems (King et al., 1997; Machate et al., 1997; Małoszewski et al., 2006a; Małoszewski et al., 2006b; Ranieri et al., 2011). Indeed, the understanding of the flow characteristics in a wetland is of utmost importance for determining the overall residence time of the water in the system and thus the contact time between the reactive surfaces and contaminant of interest (Małoszewski et al., 2006b). Overall, the residence time of a contaminant in a treatment system needs to be longer to the time required for its degradation to reach a complete removal. Often, only the average residence time is determined as only samples at a single point without depth distinction within the gravel bed or at the outlet are considered in constructed wetlands (Guo et al., 2017; Małoszewski et al., 2006b; Ranieri et al., 2011). The theoretical retention time can be approximated as the ratio between pore water volume within the bed and the applied volumetric flow rate assuming homogeneous and plug flow conditions and that all water in the wetland is mobile. In reality, no such homogeneous systems exist and not only average residence times are of importance but the residence time distributions (RTD) covering the entire range of potential reaction times. Particularly heterogeneities like preferential flow or stagnant water zones are of importance as they decrease or increase the residence time, respectively. In surface water dominated wetlands (Holland et al., 2004; Lange et al., 2011) as well as in subsurface flow systems (Kidmose et al., 2010; Langergraber, 2008; Małoszewski et al., 2006b), the combined use of tracers and mathematical modeling have been adequate tools to identify and quantify heterogeneous flow paths and residence times which can be different from theoretical calculations. Most of these tracer applications measure the tracer breakthrough curves (BTCs) only at the outlet. The contribution of different process towards removal, e.g. aerobic, anaerobic or abiotic, are not clear as such systems are from high complexity in their flow path due to changes in flow, evapotranspiration, rain gains, heterogeneous distribution of plants, of load and so on which make each system almost unique (Imfeld et al., 2009). Therefore, the objective of this study was to identify complex horizontal and vertical transport processes in a constructed wetland. Specifically, we aimed to use a combined multiple tracer and mathematical modeling approach to quantify different flow paths, transport processes and residence times within the constructed wetland. The outcome of this study will contribute to a general understanding of heterogeneous hydrological conditions in similar systems which are crucial to understand observed removal of contaminants. As a model system, a constructed wetland fed with monochlorobenzene (MCB) contaminated groundwater was used, consisting of a planted and unplanted segment (Schmidt et al., 2014). For this study, only the unplanted segment was investigated. In the unplanted gravel bed filter of this horizontal subsurface-flow constructed wetland system, about 40% of the MCB was removed in the gravel bed while over the transition zone into the pond another 50% was eliminated leading to an overall reduction of MCB of 90% compared to the inflow. The removal was apparently linked to iron reduction, however, due to the uncertainties in flow paths and actual residence time, the rate of removal and active regions could not be assessed.

2. Material and methods

2.1. Model constructed wetland system

The horizontal subsurface flow wetland system within the SAFIRA project located directly at the contaminated field site in Bitterfeld, Germany consisted of a stainless steel basin with the dimension of 6 m (length) × 1 m (width) × 0.7 m (depth) (Fig. 1) with a gravel bed (5 m × 1 m × 0.6 m) and a free water pond (1 m × 1 m × 0.5 m) at the outflow side (Figs. S1–S3) (Kaschl et al., 2005; Schmidt et al., 2014). The grain size grading of the filter material was assessed following standard test DIN 18123 resulting in Gaussian distribution of the granular size between 0.63 mm and 6.3 mm. Total measured porosity was 41% ($\varepsilon = 0.41$). The water flow was generated through external pumps at the inflow and outflow. Inflow was continuous using a rotary piston pump from Ismatec (Wertheim, Germany) with a flow rate (q) held at 1 L h^{-1} representative for the conditions in the aquifer corresponding to a hydraulic loading rate (HLR) of the subsurface flow gravel bed and free water pond of 4.8 mm d^{-1} and 24 mm d^{-1}, respectively (Kadlec and Wallace, 2008). The water level at the outflow was held constant at 50 cm (10 cm under gravel bed surface) using a tubing pump from Ismatec (Wertheim, Germany) controlled by a float sensor from Kobold Messring (Hofheim, Germany). Water flow mass balances during the tracer test were calculated from the pump rates.

2.2. Tracer test

A multi tracer test was performed from April to May 2011 (16.3 °C mean air temperature). The gravel bed was covered with polyethylene foil to minimize processes like evaporation, dilution through rain or photodegradation of the tracer chemicals. A mixture of bromide (as KBr; 550 mg L^{-1}), uranine (120 μg L^{-1}) and deuterium oxide (0.14 at%; $\delta D = 8050‰$) in contaminated groundwater from the regional aquifer was injected. Three tracers were chosen which had different diffusion coefficients, thus allowing identifying stagnant water zones and diffusion dominated transport processes (Knorr et al., 2016). The tracers were added as a pulse injection over 20 h at the flux of 1 L h^{-1} from a separate tank which was connected to the inflow of the wetland. Afterwards, the inflow was reconnected directly to the groundwater feed keeping the same flow conditions. Samples were taken at 4 m and, as indicated, at 4.5 m from the inflow central in the gravel bed at three different depths (−27.5 cm; −37.5 cm; −47.5 cm from water surface level) simultaneously with a peristaltic pump from Ismatec (Wertheim, Germany) at a relatively low flow rate of 4 mL min^{-1} to minimize artificial influences to the flow. Polyethylene scintillation vials from VWR (Darmstadt, Germany) were filled with 20 mL pore water for each sampling point and time and were stored in 8 °C temperature in the dark prior to analysis. The sampling regime is listed in detail in SI.

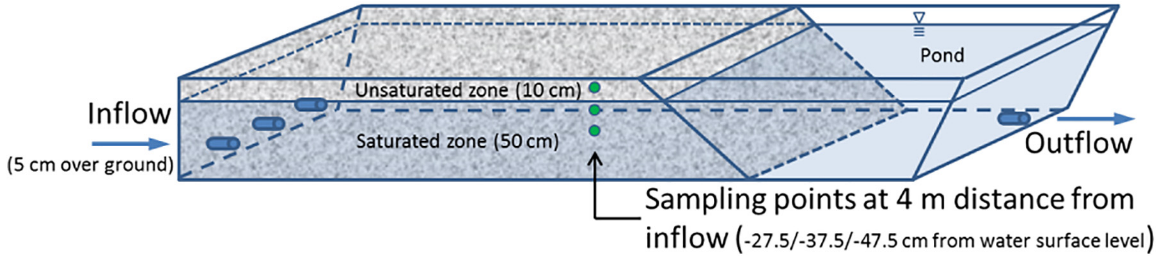


Fig. 1. Schematic model of the constructed wetland system in Bitterfeld with the dimension of 6 m (length) × 1 m (width) × 0.6 m (depth) consisted of a gravel bed (5 m × 1 m × 0.6 m) and a free water pond (1 m × 1 m × 0.5 m) at the outflow side. Green dots represent the sampling points in 4 m after the inflow in direction of flow in three different depths (−27.5 cm; −37.5 cm; −47.5 cm from water surface level). Injection of tracer solution was done at decoupled inflow pump via a 40 L stainless steel tank. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.3. Analysis of the tracer chemicals

Bromide concentrations were determined using an ion chromatography from Dionex-Thermo Scientific (Bremen, Germany) set up with Ion Pac pre-column and analytical column Ion Pac AS 11-HC (4 × 50 mm; 4 × 250 mm) from Dionex-Thermo Scientific (Bremen, Germany) with an analytical uncertainty of 0.05 mg L^{-1}. Uranine concentrations were measured using a fluorescence photometer from Taurus Instruments (Weimar, Germany) in a daylight-darkened laboratory using a non-UV lamp, to avoid errors caused by photodegradation processes during analysis. Deuterium analyses were done using a high temperature pyrolysis from HEKAtech (Wegeberg, Germany) coupled to an isotope ratio mass spectrometry from Thermo Scientific (Bremen, Germany) (HTP-IRMS) with an analytical uncertainty of 0.44‰ (Gehre and Strauch, 2003).

Concentration corrections of the applied tracers were done based on background analyses of the groundwater. Bromide was below detection limit ($c_{Br} < 0.5$ mg L^{-1}), deuterium present at natural abundance $\delta D = -69 \pm 1$‰ and uranine was corrected considering natural fluorescence of the groundwater (equal to $c_{Uranine} = 0.176 \pm 0.002$ μg L^{-1}).

2.4. Mathematical model

In the present pilot system, the tracer migration can be considered as dispersive-convective transport within several flow-paths, which meet in the observation port, when considering that (1) injection takes place in several inflow pipes equally distributed horizontally, resulting in the transversal line injection close to the bottom of the wetland; (2) transversal vertical dispersion is small and can be neglected; and (3) the flow conditions are in steady state. Depending on the results of the tracer breakthrough curves, an appropriate model approach has to be chosen. Due to similarities in BTCs compared to the previous study by Małoszewski et al. (2006b), investigating the flow paths in artificial wetlands, the Multi-Flow Dispersion Model (MFDM) was chosen. The MFDM model assumes that the tracer transport between the inlet to the wetland (injection site) and the observation site (flow distance x) can be estimated by a combination of singular 1-D dispersion-convection equations. Each flow-path is characterized by a specific volumetric flow rate (q_i), mean transit time of water ($t_{oi} = v_i / x$) or velocity (v_i), and longitudinal dispersivity (α_{Li}) or dispersion parameter ($P_{Di} = \alpha_{Li} / x$). It is assumed that there is no interaction between the flow paths and that the whole injected mass of tracer is divided into several flow-paths proportionally to the respective volumetric flow rates (q_i). The transport of an ideal tracer along i^{th} flow-path is described by the following equation:

$$\alpha_{Li} v_i \frac{\partial^2 C_i}{\partial x^2} + v_i \frac{\partial C_i}{\partial x} = \frac{\partial C_i}{\partial t} \tag{1}$$

where $C_i(t)$ is the concentration of tracer in the effluent from the i^{th} flow-path. The solution to Eq. (1) for a pulse injection was given e.g. in Hendry et al. (1999) and Stumpp et al. (2009) and has the following form:

$$\begin{aligned} C_i(t) &= C_0 \int_0^t g_i(\tau) d\tau \ \text{ for } \ t \leq t_{pulse} \\ C_i(t) &= C_0 \int_{t-t_{pulse}}^t g_i(\tau) d\tau \ \text{ for } \ t > t_{pulse} \end{aligned} \tag{2}$$

where C_0 is the concentration of tracer in the pulse injection, t_{pulse} is duration of the pulse and the function $g_i(\tau)$ is equal to:

$$g_i(\tau) = \frac{1}{t_{oi}\sqrt{4\pi (P_D)_i (\tau/t_{oi})^3}} \cdot \ \exp\left[-\frac{(1-\tau/t_{oi})^2}{4(P_D)_i(\tau/t_{oi})}\right] \tag{3}$$

Mean transit time for the flow-system between injection site and detection port (being in different depths "j") is the flux weighted mean described by the following equation:

$$(t_o)_{j\,mean} = \sum_{i-1}^{N} p_i \cdot (t_o)_i = \frac{V_j}{q_j} \tag{4}$$

where V_j is the active volume of water between injection and detection port and q_j is the water flux through the volume V_j observed in different depths ("j"), and N is the number of flow-paths, which has to be found in modeling procedure applied for each depth "j", and

$$p_i = \frac{\int_0^\infty C_i(t)_{port} dt}{\int_0^\infty C(t)_{port} dt} \tag{5}$$

where $C(t)_{port}$ is the whole concentration curve measured in the water at the observation port and $C_i(t)_{port}$ is the partial measured concentration curve, resulting at the port from the tracer transport within the i-the flow-path, which must be found by modeling procedure.

When the flow rate at the observation port (q_j) is known or can be estimated, the volume of water in the wetland layer between injection site and observation port (V_j) can be calculated as:

$$V_j = \sum_{i-1}^{N} V_i \tag{6}$$

where

$$V_i = p_i \cdot t_{oi} \cdot q_j \tag{7}$$

and j corresponds to upper, middle and lower port. The fluxes q_j was finally found from the surfaces under the whole tracer curve modelled for each depth by adopting Eq. (5).

3. Results

3.1. Tracer experiment

All three tracers, bromide, deuterium oxide and uranine, were detected at all three sampling depths at the sampling point at 4 m (Fig. 2). The highest concentrations of all tracers were observed at the lowest level (Fig. 2c). Here, two main partial breakthrough curves were detected for all tracers, after approximately 300 and 510 h, respectively. Interestingly, the observed second peak with up to 18.4% of the initial concentration was relatively higher compared to the first peak with up

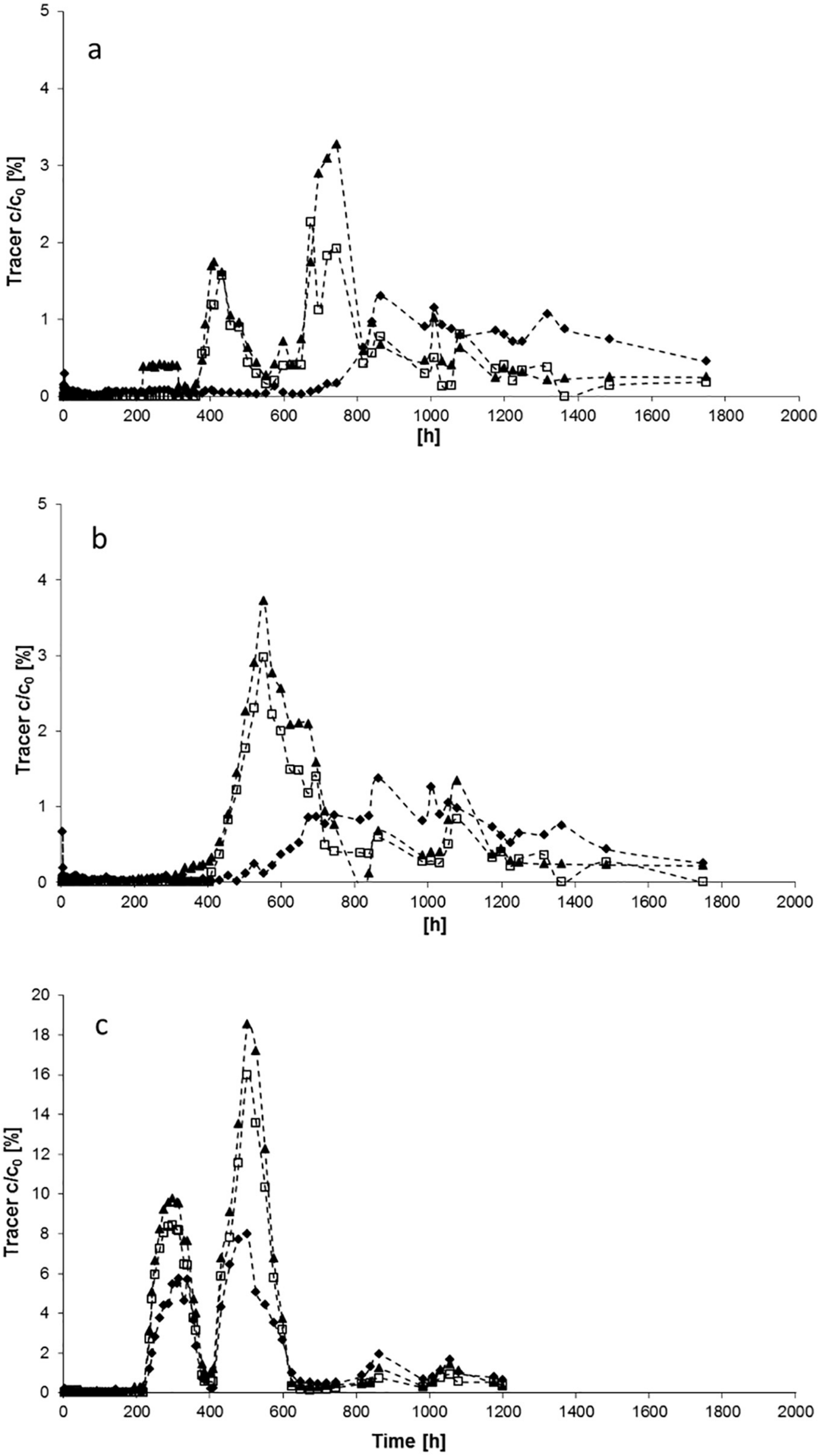


Fig. 2. Results of breakthrough curves of the tracers deuterium (▲), bromide (□) and uranine (◆) at 4 m from inflow in the sampled depths. Response of tracer concentrations normalized to the initial concentrations (c/c$_0$) over time after pulse injection in the upper level (a), middle level (b) and lower level (c), respectively.

to 9.7%. A third, minor, breakthrough curve was observed after approx. 800 h.

At the upper levels, bromine and deuterium behaved similarly, different from uranine. Bromine and deuterium had one main breakthrough peak at approximately 550 h at the middle level (Fig. 2b) and two peaks at approximately 400 and 720 h at the upper level (Fig. 2a). Surprisingly, uranine did not have a clear breakthrough curve at the middle and upper level. Following an increase after approximately 600 and 750 h at the middle and upper level, respectively, uranine remained at a low but relatively constant concentration over the time frame of the experiment.

While the maximum concentration was up to 18.4% in the lower level, maximum concentrations in the middle and upper level were only 3.7% and 3.2%, respectively, of the initial concentration (Fig. 2). Even though the two tracer breakthrough curves in the upper level arrived around 100 and 200 h later than in the lower level, respectively, they followed the same trend transporting more tracer mass in the second curve as compared to the first curve. However, contrastingly, the only main BTC in the middle level arrived 250 h later than in the lower level.

Comparing the tracers, D_2O generally had the highest relative concentrations in the breakthrough curves, followed by bromine. Uranine generally behaved similar, although with lower relatively concentrations, in the lower level, however behaved quite differently from D_2O and bromine in the middle and upper level, likely due to higher interactions with the sediment (Davis et al., 1980).

3.2. Mathematical modeling

The mathematical multi-flow dispersion model was used to model the breakthrough curves of the different levels. Exemplary bromide was chosen to discuss the results of the modeling (Fig. 3). The fitted model curves using the MFDM for the other two tracers are shown in SI (Figs. S4, S5). Resulting modeling parameters are summarized in Table 1. The measured data were well reproduced by the chosen MFDM indicating the presence of complex, multiple flow paths in the system. The modeling confirmed the preferred flow along the bottom (lower) layer with 65–70% of mass flowing along the bottom and 14–18% and 16–17% of mass at the middle and upper level, respectively (Table 2). Highest flow fractions were found for the second partial BTC in the lower and upper levels, respectively, and for the first partial BTC in the middle layer. Fitting parameters were similar for deuterium and bromide for all BTCs in all levels (Table 1). BTCs of uranine resulted in similar transport parameters in the main flow paths (lower layer), but transport in the middle and upper level were different indicating a retardation and non-conservative transport behavior of uranine in these layers; therefore, no results are presented in Table 2 for uranine. Due to a larger mass fraction of uranine in the third partial BTC at the

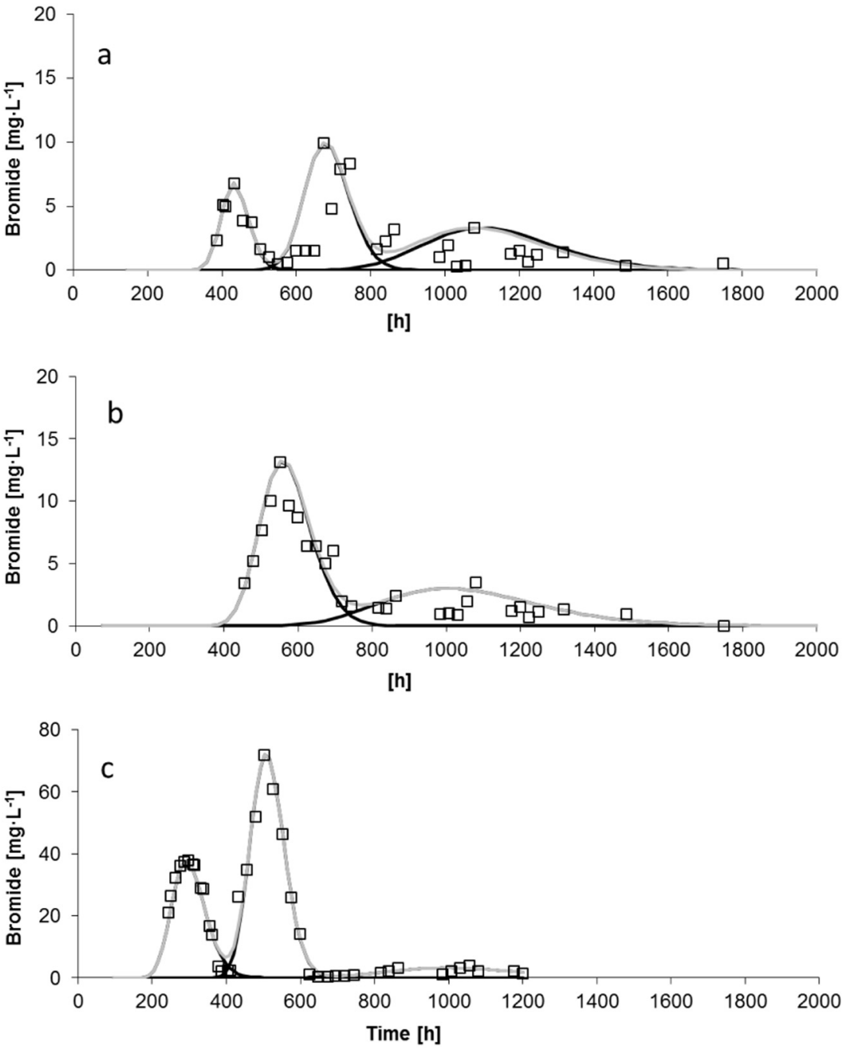


Fig. 3. Calibration the MFDM to bromide concentration over time after pulse injection in the different levels at z = −27.5 cm (a), z = −37.5 cm (b) and z = −47.5 cm (c), respectively at x = 4 m. Observed sampled bromide concentrations (☐) and fitted RTD curves obtained with the MFDM of each breakthrough curve (black lines) and complete tracer regime (grey line).

Table 1
Overview of parameters derived from the MFDM of all tracers and different sampled levels at 4 m horizontal distance from inflow where T represents the transit time, v the velocity, α_L the longitudinal dispersivity and p the portion of tracer mass.

		Lower level Depth z = −47.5 cm			Middle level Depth z = −37.5 cm			Upper level Depth z = −27.5 cm		
		Deuterium	Bromide	Uranine	Deuterium	Bromide	Uranine	Deuterium	Bromide	Uranine
Curve 1	T [d]	12.7	12.6	12.6	24.1	23.8	32.0	18.0	18.2	40.8
	v [m d^{-1}]	0.32	0.32	0.32	0.17	0.17	0.13	0.22	0.22	0.10
	α_L [cm]	4.6	4.6	3.8	3.6	2.9	7.0	1.5	1.4	4.0
	p [−]	0.30	0.29	0.31	0.78	0.59	0.49	0.22	0.18	0.47
Curve 2	T [d]	21.4	21.4	20.1	46.0	44.5	46.0	30.4	28.6	59.7
	v [m d^{-1}]	0.19	0.19	0.20	0.09	0.09	0.09	0.13	0.14	0.07
	α_L [cm]	1.6	1.6	2.2	0.5	8.3	3.5	1.0	1.5	3.0
	p [−]	0.57	0.54	0.49	0.22	0.41	0.28	0.48	0.42	0.53
Curve 3	T [d]	41.2	43.5	40.0	–	–	61.5	41.7	46.5	–
	v [m d^{-1}]	0.10	0.09	0.10	–	–	0.07	0.10	0.09	–
	α_L [cm]	4.0	6.4	4.3	–	–	2.0	2.8	5.0	–
	p [−]	0.13	0.17	0.20	–	–	0.23	0.30	0.40	–
Weighted mean transit time	T [d]	21.4	22.6	21.8	28.9	32.3	42.7	31.1	33.9	50.8

upper level, also retardation of uranine was found here despite similarities of individual transit times. Weighted mean transit times were shortest in the lower level ranging between 21.4 and 22.6 d (see Table 1). Transit times were longer for the middle and upper level resulting in weighted mean transit times of 28.9 and 31.1 d, and 32.3 and 33.9 d for deuterium and bromide, respectively. Dispersivities varied within one order of magnitude (0.5–8.3 cm). Dispersivities for bromide and deuterium were similar except for the last BTC in all levels; here, bromide resulted in larger dispersivities compared to deuterium (see Table 1). Mean transit times found as an average for deuterium and bromide varied between 22.0 and 32.5 d for lower and upper layer, respectively (see Table 2). Table 2 also shows resulting mean calculated water flux q_j assuming that the tracer distribution observed in each level is representative for the horizontal plain in that level. It was the largest in the lower level (0.68q) while in middle and upper levels it was similar and equal to 0.16q (see Table 2). Taking into account that $q = 1\ \mathrm{L\ h^{-1}}$ and a total pore water volume of 0.82 m^3 it yields to an active pore water volume of 0.61 m^3 in the lower part of the wetland which corresponds to effective porosity being approximately 40%.

4. Discussion

4.1. Flowpath and residence times

The resulting BTCs and transport parameters showed, in contrast to findings of Headley et al. (2005), that flow and transport in our pilot constructed wetland was complex and heterogeneous, both in vertical and horizontal direction. The highest concentrations of all tracers were observed at the lowest level (Fig. 2c) suggesting a main flow path along the bottom of the wetland. Here, two main and one minor, partial breakthrough curves were detected for all tracers, indicating multiple flow paths at the lower level. All three tracers showed similar BTC distributions without any pronounced differences in the tailing of the concentration curves. Consequently, diffusion in this lower level seems to be negligible. Interestingly, the observations implied the higher mass of tracer transported through the second main flow path. On the one hand, the heterogeneity can results from not fully mixed conditions between injection and sampling ports along the main flow direction. Hence, the first BTC at the lower level likely represented water flowing from the middle injection port to the sampling point and the second peak with higher mass recovery then resulted from water originating from the two outer injection points. The third BTC could have been the consequence of water mixed with less mobile water between injection ports (Kadlec and Wallace, 2008). On the other hand, the different flow paths in the lower level can result from multiple porous sediment developed from settled organic material resulting in multiple BTCs like found for heterogeneous aquifers (Vanderborght and Vereecken, 2002).

A non-uniform flow through the wetland is obvious when looking at the vertical distribution of BTCs. First, the mass of the tracer is not equally distributed within the wetland (Table 2). Second, transit times and distributions of BTCs at the middle and upper level were similar but rather different from the lower level. The sampling procedure itself - due to pumping - is expected to not substantially influence the tracer migration because the pump rate (0.24 L h^{-1}) was only one fourth of the total flux (1 L h^{-1}) through the wetland. From total flux and assuming uniform flow, a mean flow velocity and transit time of 0.16 m d^{-1} and 25 d could be estimated, respectively.

4.2. Differences between tracers

Comparing the used tracers, deuterium can be considered as an ideal tracer of water sources and movements (Kendall and McDonnell, 1999). Minor difference in relative concentrations (Fig. 2) between deuterium and bromide can be explained either by analytical uncertainties, which are relatively higher for bromide compared to deuterium, or by anion properties of bromide. Bromide has been reported to be affected by sorption or anion exclusion under specific conditions (Gilley et al.,

Table 2
Calculated relative portions of tracer mass of two ideal tracers (deuterium, bromide) and mean values of flux portion, transit time and volume of active water in the different levels derived from the MFDM.

	Portion of whole tracer mass p_j [−]		Mean portion of tracer mass	Mean transit time	Mean volume of active water
Level	Deuterium	Bromide	$p_{j\ \mathrm{mean}}$ [−]	$T_{j\ \mathrm{mean}}$ [d]	$V_{j\ \mathrm{mean}}$ [m^3]
Lower (−47.5 cm)	0.70	0.65	0.68	22.0	0.36
Middle (−37.5 cm)	0.14	0.18	0.16	30.6	0.12
Upper (−27.5 cm)	0.16	0.17	0.16	32.5	0.13

1990; Korom, 2000; Levy and Chambers, 1987) and on plant uptake especially in wetlands (Whitmer et al., 2000). The latter is irrelevant because the wetland was unplanted.

Substantial differences were found for uranine compared to the other two tracers. Most notable was the different transport behavior of uranine with the initial absence and delayed occurrence of uranine in the upper levels compared to bromide and deuterium. There the modeling results clearly indicated retardation of uranine (Table 1). Even though uranine is generally considered to be a non-sorbing conservative tracer (Käss et al., 1998), as it does not sorb to negatively charged media such as silica and sandstone, it was found to sorb to positively charged media such as alumina and carbonate (Kasnavia et al., 1999; Sabatini, 2000). Since the gravel material consisted primarily of silica sand, sorption onto the aquifer material was not expected. Additionally, uranine is not an ideal tracer in presence of high organic content (Kasnavia et al., 1999; Smart and Laidlaw, 1977) or salt concentrations (Magal et al., 2008) which were identified to enhance sorption. Particularly the first may apply to the investigation site due to presence of brown coal particles in the contaminated groundwater which were transported and deposited over the years in the gravel bed (Weiss et al., 1998). This effect was strongest in the middle and upper level of the pilot system where flow velocities were lowest. In the lower level with high flow velocities, uranine appeared slightly later and tailing was observed of the BTCs compared to deuterium. This tailing is likely a consequence of sorption effects, which has also been previously observed in other wetland systems (Holcová et al., 2013).

4.3. Evaluation of the wetland performance

The actual residence time in the system is a key factor for evaluating the performance of a constructed wetland for contaminant removal. Our study shows that tracer studies were necessary to revise results from water balance approaches based on in- and outflow. Unlike initially assumed, the overall residence time of the groundwater and conservative tracers in the wetland system (22.0–32.5 d, see Table 2) was lower compared to the theoretical one (34.2 d) resulting in a lower contact and reaction time than previously assumed (Schmidt et al., 2014). In addition, a preferential flow along the bottom of the wetland system can be concluded, which is likely due to the constructional design of the inflow resulting in lower water and contaminant infiltration in the middle and upper levels. Considering mass fluxes in the wetland, different reactive compartments have to be considered. From a hydrological point of view the middle and upper layer had 8.6 d and 10.5 d, respectively, longer residence times compared to the lower level and therefore more potential for reaction and thus, the removal of contaminants should be higher here. However, lower contaminant mass will be transported through these regions.

To assess the MCB removal efficiency of the model wetland system, MCB concentration changes during passage in the gravel bed were investigated for the different depths (Fig. S6). There, MCB removal was estimated (see SI) to be 34% in the upper level and 20% in the middle and lower level, respectively, based on analyzed concentrations only (Table S1). Highest removal rate and most active zones therefore would supposedly be located in the upper parts of the wetland. By including the observations from the tracer study our approximation resulted in similar relative MCB mass removal than estimated above for the upper and middle layers with 31% and 17%, respectively, while the lower part contributed to a higher extent with 52% (see Table S1).

Based on average oxygen concentrations and redox potentials of the gravel bed (0.09 ± 0.03 mg L^{-1}, 147 ± 45 mV) and especially in the lower level of 0.08 ± 0.01 mg L^{-1} (Fig. S7) and 108 ± 22 mV, respectively, the overall wetland can be considered as anoxic in contrast to the apparent system analogy and the measured values from Schmidt et al. (2014). Combining the results, major biological processes driving the MCB removal were likely anaerobic. The underestimation of MCB degradation in the anoxic zone at the bottom of the wetland could be only revealed by applying a tracer test combined with the modeling approach.

4.4. Implications for the investigation and implementation of constructed wetlands

Our study stresses the importance of hydrological investigations of constructed wetland as it can provide valuable insights into water flow, transport and residence times of contaminants in these systems. The combination of a multi-tracer test with sampling at multiple depths in the wetland filter, and a mathematical modeling allowed identifying main water flow paths, variable flow conditions and precise definition of residence times. In our case, the overall water flow and thus contaminant transport was much faster than expected. Furthermore, the tracer approach connected with a depth resolved sampling allowed to locate the preferential flow paths and transport processes. This will help to design and optimize nature-like model wetland systems for future treatment purposes. The horizontal subsurface flow wetland system was designed to simulate aquifer-like conditions and to provide as system for investigation of microbial processes at geochemical gradients. However, in reality the system turned out to consist of rather heterogeneous flow paths with strongly different transit times between levels. Consequently, contaminant removal rates were overestimated when only based on concentration values. Especially, previous assumption of evenly distributed fluxes and over-estimation of residence times resulted in underestimation of degradation in the lower level. The contaminant removal efficiency may be improved by altering the wetland design providing either a more homogeneous flow of groundwater through all parts of the system with higher reaction times or in an even more heterogeneous flow pattern through different geochemical zones in the system enhancing gradient based degradation processes. Therefore, for implementation of constructed wetlands as treatment systems, the effect of design parameters, causing the hydraulic behavior and thus their effect on physical-chemical parameters, can strongly influence the removal efficiencies of contaminants of the interest (Kidmose et al., 2010; Onesios et al., 2009). By combining results of multiple conservative tracers additional information on characteristics such as sorption and flow paths could be obtained. Overall, even a simple appearing model subsurface flow constructed wetland was shown to be a complex and heterogeneous system.

The HLR in our system was only 4.8 mm d^{-1}, which is in the lower range for horizontal subsurface flow constructed wetlands treating polluted water (2–30 mm d^{-1}) (Kadlec and Wallace, 2008; Wood, 1995). For feasible, commercial, treatment, however, HLR should be higher, with 50–80 mm d^{-1} (Morel, 2006). Implemented by increasing the inflow rate, an improved vertical mixing of the treated water and a decrease of the zones of stagnant water may be accomplished (Headley et al., 2005). Further tests, however, are needed to determine the limits of the system and maximum loading rates, in concurrence with tracer and mathematical modeling experiments, to provide a full understanding of the three dimensional flow and reactive zones within constructed wetland systems.

5. Conclusions

This work presents the investigation of hydrological flow paths for understanding of the interactions of biodegradation and transport processes important for remediation approaches and wetland process based technologies. The design of the constructed wetland basin determined the flow path, resulting in different zones of stagnant and moving water and retention times. As a result, contaminants will have different contact times to undergo biotic or abiotic processes in these zones. In zones of stagnant water the transport of nutrients as well as electron acceptor and donor, respectively, essential for biotic processes is limited due to restricted diffusion into these zones. Therefore, degradation reactions might be slower compared to high mobility zones such as at the bottom of the wetland. Especially the transitions zones between stagnant and mobile water, with related biogeochemical gradients, are of high interest for an understanding and controlling wetland processes. Overall, this tracer study combining experimental evaluation with mathematical modeling demonstrated the complexity of flow and transport processes in the constructed wetlands. This complexity needs to be taken into account during interpretation of the determining attenuation processes during treatment of contaminated waters in these engineered systems.

Acknowledgement

We dedicate this article to the memory of our dear colleague and friend Piotr Maloszewski, who passed away during the final stages of manuscript preparation. We would like to thank the Department of Groundwater Remediation, laboratory Bitterfeld, especially Jörg Ahlheim, Oliver Thiel and Heidrun Paschke for bromide analysis. From the Department of Isotope Biogeochemistry many thanks to Sameer Devkota, Diana Wolfram, Sascha Lege, Safdar Bashir, Sara Herrero-Martín and Barbara Klein for volunteering during sampling period and Falk Bratfisch for D_2O analysis and Hans-Hermann Richnow for overall support. This study was funded by the EU FP7 project Genesis (contract number: 226536) and SAFIRA II Project "Compartment Transfer" (CoTra) of the Helmholtz Centre for Environmental Research – UFZ.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2017.11.217.

References

Braeckevelt, M., Rokadia, H., Mirschel, G., Weber, S., Imfeld, G., Stelzer, N., et al., 2007. Biodegradation of chlorobenzene in a constructed wetland treating contaminated groundwater. Water Sci. Technol. 56, 57–62.

Davis, S.N., Thompson, G.M., Bentley, H.W., Stiles, G., 1980. Groundwater tracers - short review. Ground Water 18, 14–23.

Gambrell, R.P., 1994. Trace and toxic metals in wetlands - a review. J. Environ. Qual. 23, 883–891.

Gearheart, R., Klopp, F., Allen, G., 1989. Constructed free surface wetlands to treat and receive wastewater: pilot project to full scale. Constructed Wetlands for Wastewater Treatment. Lewis Publishers, Chelsea, MI, pp. 121–138.

Gehre, M., Strauch, G., 2003. High-temperature elemental analysis and pyrolysis techniques for stable isotope analysis. Rapid Commun. Mass Spectrom. 17, 1497–1503.

Gilley, J.E., Finkner, S., Doran, J.W., Kottwitz, E., 1990. Adsorption of bromide tracers onto sediment. Appl. Eng. Agric. 6, 35–38.

Guo, C.Q., Cui, Y.L., Dong, B., Liu, F.P., 2017. Tracer study of the hydraulic performance of constructed wetlands planted with three different aquatic plant species. Ecol. Eng. 102, 433–442.

Headley, T.R., Herity, E., Davison, L., 2005. Treatment at different depths and vertical mixing within a 1-m deep horizontal subsurface-flow wetland. Ecol. Eng. 25, 567–582.

Hendry, M.J., Lawrence, J.R., Maloszewski, P., 1999. Effects of velocity on the transport of two bacteria through saturated sand. Ground Water 37, 103–112.

Holcová, V., Šíma, J., Dušek, J., 2013. A comparison of fluorescein and deuterated water as tracers for determination of constructed wetland retention time. Cent. Eur. J. Chem. 11, 200–204.

Holland, J.F., Martin, J.F., Granata, T., Bouchard, V., Quigley, M., Brown, L., 2004. Effects of wetland depth and flow rate on residence time distribution characteristics. Ecol. Eng. 23, 189–203.

Imfeld, G., Braeckevelt, M., Kuschk, P., Richnow, H.H., 2009. Monitoring and assessing processes of organic chemicals removal in constructed wetlands. Chemosphere 74, 349–362.

Imfeld, G., Aragones, C.E., Fetzer, I., Meszaros, E., Zeiger, S., Nijenhuis, I., et al., 2010. Characterization of microbial communities in the aqueous phase of a constructed model wetland treating 1,2-dichloroethene-contaminated groundwater. FEMS Microbiol. Ecol. 72, 74–88.

Jechalke, S., Vogt, C., Reiche, N., Franchini, A.G., Borsdorf, H., Neu, T.R., et al., 2010. Aerated treatment pond technology with biofilm promoting mats for the bioremediation of benzene, MTBE and ammonium contaminated groundwater. Water Res. 44, 1785–1796.

Kadlec, R.H., Wallace, S., 2008. Treatment Wetlands. Second edition. CRC Press.

Kaschl, A., Vogt, C., Uhlig, S., Nijenhuis, I., Weiss, H., Kastner, M., et al., 2005. Isotopic fractionation indicates anaerobic monochlorobenzene biodegradation. Environ. Toxicol. Chem. 24, 1315–1324.

Kasnavia, T., Vu, D., Sabatini, D.A., 1999. Fluorescent dye and media properties affecting sorption and tracer selection. Ground Water 37, 376–381.

Käss, W., Behrens, H., Himmelsbach, T., Hötzl, H., 1998. Tracing Technique in Geohydrology. Balkema, Rotterdam.

Kendall, C., McDonnell, J.J., 1999. Isotope Tracers in Catchment Hydrology. Elsevier.

Kidmose, J., Dahl, M., Engesgaard, P., Nilsson, B., Christensen, B.S.B., Andersen, S., et al., 2010. Experimental and numerical study of the relation between flow paths and fate of a pesticide in a riparian wetland. J. Hydrol. 386, 67–79.

King, A.C., Mitchell, C.A., Howes, T., 1997. Hydraulic tracer studies in a pilot scale subsurface flow constructed wetland. Water Sci. Technol. 35, 189–196.

Knorr, B., Maloszewski, P., Kramer, F., Stumpp, C., 2016. Diffusive mass exchange of non-reactive substances in dual-porosity porous systems - column experiments under saturated conditions. Hydrol. Process. 30, 914–926.

Korom, S.F., 2000. An adsorption isotherm for bromide. Water Resour. Res. 36, 1969–1974.

Lange, J., Schuetz, T., Gregoire, C., Elsasser, D., Schulz, R., Passeport, E., et al., 2011. Multi-tracer experiments to characterise contaminant mitigation capacities for different types of artificial wetlands. Int. J. Environ. Anal. Chem. 91, 768–785.

Langergraber, G., 2008. Modeling of processes in subsurface flow constructed wetlands: a review. Vadose Zone J. 7, 830–842.

Levy, B.S., Chambers, R.M., 1987. Bromide as a conservative tracer for soil-water studies. Hydrol. Process. 1, 385–389.

Li, Y.F., Zhu, G.B., Ng, W.J., Tan, S.K., 2014. A review on removing pharmaceutical contaminants from wastewater by constructed wetlands: design, performance and mechanism. Sci. Total Environ. 468, 908–932.

Machate, T., Noll, H., Behrens, H., Kettrup, A., 1997. Degradation of phenanthrene and hydraulic characteristics in a constructed wetland. Water Res. 31, 554–560.

Magal, E., Weisbrod, N., Yakirevich, A., Yechieli, Y., 2008. The use of fluorescent dyes as tracers in highly saline groundwater. J. Hydrol. 358, 124–133.

Małoszewski, P., Wachniew, P., Czupryński, P., 2006a. Hydraulic characteristics of a wastewater treatment pond evaluated through tracer test and multi-flow mathematical approach. Pol. J. Environ. Stud. 15.

Małoszewski, P., Wachniew, P., Czupryński, P., 2006b. Study of hydraulic parameters in heterogeneous gravel beds: constructed wetland in Nowa Słupia (Poland). J. Hydrol. 331, 630–642.

Matamoros, V., Bayona, J.M., 2006. Elimination of pharmaceuticals and personal care products in subsurface flow constructed wetlands. Environ. Sci. Technol. 40, 5811–5816.

Morel, A., 2006. Greywater Management in Low and Middle-income Countries. Swiss Federal Institute of Aquatic Science and Technology, Dubenforf, CH.

Onesios, K.M., JT, Yu, Bouwer, E.J., 2009. Biodegradation and removal of pharmaceuticals and personal care products in treatment systems: a review. Biodegradation 20, 441–466.

Rakoczy, J., Remy, B., Vogt, C., Richnow, H.H.A., 2011. Bench-scale constructed wetland as a model to characterize benzene biodegradation processes in freshwater wetlands. Environ. Sci. Technol. 45, 10036–10044.

Ranieri, E., Verlicchi, P., Young, T.M., 2011. Paracetamol removal in subsurface flow constructed wetlands. J. Hydrol. 404, 130–135.

Sabatini, D.A., 2000. Sorption and intraparticle diffusion of fluorescent dyes with consolidated aquifer media. Groundwater 38, 651–656.

Schmidt, M., Wolfram, D., Birkigt, J., Ahlheim, J., Paschke, H., Richnow, H.-H., et al., 2014. Iron oxides stimulate microbial monochlorobenzene in situ transformation in constructed wetlands and laboratory systems. Sci. Total Environ. 472, 185–193.

Smart, P., Laidlaw, I., 1977. An evaluation of some fluorescent dyes for water tracing. Water Resour. Res. 13, 15–33.

Stumpp, C., Nutzmann, G., Maciejewski, S., Maloszewski, P., 2009. A comparative modeling study of a dual tracer experiment in a large lysimeter under atmospheric conditions. J. Hydrol. 375, 566–577.

Tietz, A., Kirschner, A., Langergraber, G., Sleytr, K., Haberl, R., 2007. Characterisation of microbial biocoenosis in vertical subsurface flow constructed wetlands. Sci. Total Environ. 380, 163–172.

Truu, M., Juhanson, J., Truu, J., 2009. Microbial biomass, activity and community composition in constructed wetlands. Sci. Total Environ. 407, 3958–3971.

Vanderborght, J., Vereecken, H., 2002. Estimation of local scale dispersion from local breakthrough curves during a tracer test in a heterogeneous aquifer: the Lagrangian approach. J. Contam. Hydrol. 54, 141–171.

Verlicchi, P., Zambello, E., 2014. How efficient are constructed wetlands in removing pharmaceuticals from untreated and treated urban wastewaters? A review. Sci. Total Environ. 470, 1281–1306.

Weis, J.S., Weis, P., 2004. Metal uptake, transport and release by wetland plants: implications for phytoremediation and restoration. Environ. Int. 30, 685–700.

Weiss, H., Daus, B., Fritz, P., Kopinke, F.-D., Popp, P., Wuensche, L., 1998. In situ groundwater remediation research in the Bitterfeld region in eastern Germany (SAFIRA). IAHS Publ. 443–450.

Whitmer, S., Baker, L., Wass, R., 2000. Loss of bromide in a wetland tracer experiment. J. Environ. Qual. 29, 2043–2045.

Wood, A., 1995. Constructed wetlands in water pollution control: fundamentals to their understanding. Water Sci. Technol. 32, 21–29.

Zahraeifard, V., Deng, Z.Q., 2011. Hydraulic residence time computation for constructed wetland design. Ecol. Eng. 37, 2087–2091.