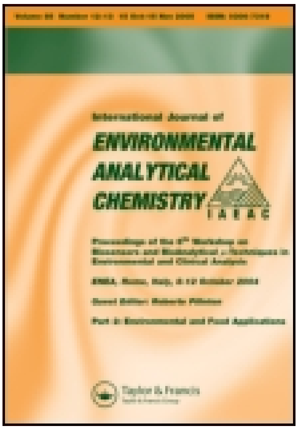

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Jens Lange [a] , Tobias Schuetz [a] , Caroline Gregoire [b] , David Elsässer [c] , Ralf Schulz [c] , Elodie Passeport [d] & Julien Tournebize [d]

[a] University of Freiburg, Institute of Hydrology, Fahnenbergplatz, Freiburg 79098, Germany

[b] University of Strasbourg, Laboratoire d'Hydrologie et de Géochimie, Strasbourg, France

[c] University of Landau, Landau, Germany

[d] CEMAGREF, Antony, France

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Multi-tracer experiments to characterise contaminant mitigation capacities for different types of artificial wetlands

Jens Lange[a]*, Tobias Schuetz[a], Caroline Gregoire[b], David Elsässer[c], Ralf Schulz[c], Elodie Passeport[d] and Julien Tournebize[d]

[a]*University of Freiburg, Institute of Hydrology, Fahnenbergplatz, Freiburg 79098, Germany;* [b]*University of Strasbourg, Laboratoire d'Hydrologie et de Géochimie, Strasbourg, France;* [c]*University of Landau, Landau, Germany;* [d]*CEMAGREF, Antony, France*

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Salt tracers (sodium bromide/sodium chloride) and two different fluorescent tracers, uranine (UR) and sulforhodamine-B (SRB), were injected as a pulse into six different surface flow wetlands (SFWs). Salt tracers documented wetland hydraulics. The fluorescent tracers were used as a reference to mimic photolytic decay (UR) and sorption (SRB) of contaminants as illustrated by a comparison to a real herbicide (Isoproturon), which was used as a model for mobile pesticides. Tracer breakthrough curves were used to document residence time distributions, hydraulic efficiencies, peak attenuation and retention capacities of completely different wetland systems. A 530 m^2 forest buffer zone showed considerable peak attenuation but limited retention capabilities despite its large area. Approximately 80% of SRB was permanently retained in a re-structured 325 m^2 flood detention pond. These two non-steady SFWs indicated long-term tracer washout. The remaining four SFWs displayed constant outflow rates and steady-state flow conditions. Due to photolytic decay in a 330 m^2 row of three wetlands, UR was almost entirely degraded, but the SRB breakthrough suggested relatively low sorption. A 65 m^2 shallow flow-through wetland yielded negligible photolytic decay but showed considerable sorption losses. Finally two types of vegetated ditches were analysed. In one case, vegetation was removed from a 413 m long ditch immediately prior to tracer injection. A 30% loss by sorption to sediment and plant remnants occurred at the very beginning of the tracer breakthrough. Inside a second ditch, 80 m long and densely vegetated by *Phragmites australis*, sorption was even higher and yielded eightfold higher specific SRB retention rates. Although the present findings are only valid for low flow conditions, they indicate that a shallow water depth seems to be a key variable which may increase sorption of tracers and therefore contaminants. Large wetlands with deep water bodies may attenuate concentrations efficiently, but unit load reduction was found to be more significant in shallow systems even at much higher flow velocities.

Keywords: surface flow wetlands; residence time distribution; fluorescent tracers; reference tracer; contaminant mitigation; sorption; pesticides

*Corresponding author. Email: jens.lange@hydrology.uni-freiburg.de

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1. Introduction

Wetlands can be defined as transitional environments between dry land and open water where saturation is the key factor for soil development and determines the composition of flora and fauna living in the soil and on its surface [1]. They are found naturally occurring on every continent except Antarctica and have long been a component in treating contaminated waters [2]. Within the past 20 years, constructed wetlands – engineered systems utilising treatment processes of natural wetlands – have become increasingly popular [3]. Many of the systems are subsurface flow wetlands (SSFWs) where no free water level exists and the underground passage through layers of gravel or sand plays an important role for water purification. For the particular case of nonpoint source pollution, constructed surface flow wetlands (SFWs) may serve as buffer zones to limit the transfer of pesticides at the watershed scale [4]. Drainage ditches may also perform similarly to wetlands and effectively mitigate concentrations of contaminants [5]. By intercepting agricultural runoff or subsurface drainage before reaching protected water bodies, contaminants can be removed by natural processes, and water quality may improve to meet Water Framework Directive criteria of the European Union [6]. For this purpose, hydrological characteristics appear to be key parameters influencing the removal effectiveness of wetlands [7]. However, field scale characterisation of wetland hydrological properties is challenging [8]. Tracer tests provide a convenient method to assess retention times, the degree of mixing or water velocities [2].

Fluorescent tracers have become a standard tool for process research, since they are environmentally harmless and can be detected at very low concentrations [9]. As they can be applied in very small quantities, they usually do not affect water density or flow patterns. Netter and Behrens [10] applied five different tracers, three fluorescent and two non-fluorescent, to constructed SSFWs and compared tracer recoveries and mean residence times.

However, non-fluorescent tracers such as lithium chloride (LiCl) have gained popularity due to their more conservative nature than fluorescent tracers [11]. Kadlec [12] used lithium to study mixing processes in a SFW. He fitted three different conceptual solute transport models to obtain tracer breakthrough curves and found a flow pattern intermediate between plug flow and well-mixed. Maloszewski *et al.* [13] used tritium and bromide together with mathematical lumped parameter models to evaluate hydraulic characteristics of three parallel SSFWs. Resulting differences among the wetlands suggested improper design and maintenance. Lin *et al.* [14] compared bromide with the fluorescent tracer rhodamine WT (RWT) and showed the limits of RWT to characterise hydraulic conditions of large SFW systems. Residence time distributions were blurred by irreversible sorption.

Still, RWT remains an important tracer for wetland studies. Keefe *et al.* [15] performed RWT tests in three constructed SFWs to quantify tracer removal rates by photolysis and sorption. Holland *et al.* [16] used RWT to study the distribution of residence times in a SFW used for stormwater treatment. They found that short-circuiting and mixing scale increased with water depth. Also, Dierberg *et al.* [17] used RWT to illustrate how short circuits may limit phosphorus removal in a SFW. Ascuntar Ríos *et al.* [18] used RWT to investigate the effect of plant development on the hydrodynamic behaviour of an experimental SSFW. When plants reached their maturity, dispersion inside the system reached its maximum. Finally, Giraldi *et al.* [19] fitted a numerical plug-flow dispersion model to RWT-breakthrough curves in a constructed SSFW. They showed that dispersivity was inversely affected by water content.

These studies have been valuable for (a) describing hydraulic conditions of wetland systems; (b) investigating the effect of changing boundary conditions (e.g. water depth); and (c) calibrating solute transport models. When tracers are applied at the same time with a specific contaminant and are found to behave similarly, they may also serve as a surrogate for this contaminant and directly show wetland mitigation capacities.

Isoproturon ($C_{12}H_{18}N_2O$, IPU) has been one of the most commonly used herbicides in the last decade [20]. It is mainly used for the control of weeds in fields of cereals including wheat. De Wilde *et al.* [21] termed it as a herbicide of the non-persistent-mobile category. Adsorption coefficients (K_{OC}) range from 36 to $240\,cm^3\,g^{-1}$ and half-life (DT50) times from 12 to 33 days. IPU is soluble in water ($65\,mg\,L^{-1}$) and can easily be mobilised [22]. This leads to temporally high IPU concentrations in natural waters [23].

We applied two different fluorescent tracers uranine (UR, $C_{20}H_{10}Na_2O_5$, also called fluorescein) and sulforhodamine-B (SRB, $C_{27}H_{29}N_2NaO_7S_2$) to six different SFW types. Those tracers were selected to mimic photolytic decay and sorption of herbicides. Sodium bromide (NaBr) and sodium chloride (NaCl) were also applied and assumed to be conservative. From the inorganic tracer breakthrough curves, hydraulic parameters, e.g. normalised residence time distributions and hydraulic efficiencies, were obtained. The fluorescent tracers were used to assess mitigation capacities to IPU, e.g. peak attenuation and retention capacities, of each SFW type, which were related to SFW volume and area.

2. Experimental

2.1 *Wetland systems*

The investigated SFW systems are located at four sites in France and Germany (Figure 1). They can be classified into two types: intermittent-flow (SFW1, 2) and constant in- and outflow SFWs (SFW3-6). Artificial inflow was created before tracer injection in the intermittent-flow systems. At all systems' outlets flow measurements facilitated accurate

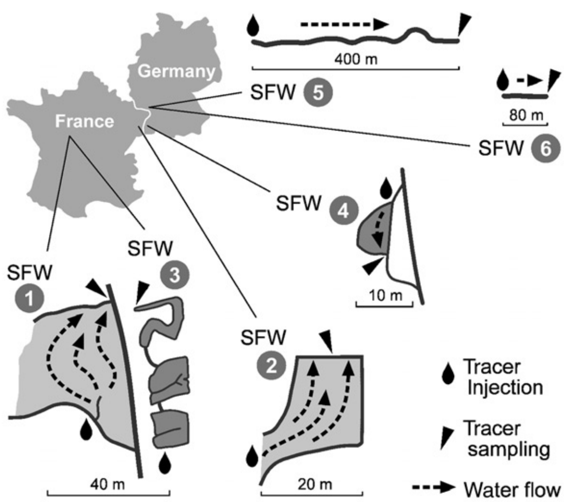

Figure 1. Location and schematic layout of the six investigated wetland systems.

Figure 2. Views of the investigated surface flow wetlands.

calculations of tracer recovery rates. Nevertheless, SFW sizes and layouts were totally different (Figure 2, Table 1).

SFW1 consists of a 1600 m^2 forest stand of oak (*Quercus robur*) located 63 km south east of the city of Tours, France. Terrain is gently sloping (1%) and the soil is

Table 1. Wetland geometry and basic hydraulic characteristics.

	Outflow ($L\,s^{-1}$)	Length of main flow path (m)	Average water depth (m)	Area (m^2)	Water volume (m^3)
SFW1	0.3*	71	0.025**	530	40**
SFW2	0.3*	23	0.15	325	50
SFW3	0.8	200	0.25	1280	330
SFW4	5.7	10	0.1	65	6.5
SFW5	5.0	413	0.2	206	31
SFW6	0.9	80	0.1	40	4.0

*Non-steady system, outflow determined as mean value during the experiment.
**Estimated according to soil properties.

characterised by a high clay content (37% at a depth of 0.45 m) limiting downward percolation to groundwater. The inflow is intermittent and regulated by an elbow tube extracting water from an agricultural drainage ditch. Water passes through an electromagnetic flowmeter (MAG 8000, SIEMENS) and is distributed on the forest soil by a primary inlet ditch and several secondary trenches. Due to the high clay content, the water flows close to the soil surface which is partly covered by a shallow layer of organic material. After approximately 70 m an outlet ditch collects the water which is measured by a second electrometric flowmeter before entering a natural river. During the tracer experiment the inflow rate into the forest plot was increased from 0.2 to 1.6 $L\,s^{-1}$ for 7.5 hours. Only a portion of the forest (530 m^2) was used for the tracer experiment.

SFW2 is a 325 m^2 flood detention pond located in the village Rouffach 15 km south of the city of Colmar, France. The pond is designed to retain up to 1050 m^3 of flood water. The bottom of the pond is covered by a 0.5 m layer of sediments (8.3% sand, 69.7% silt and 22% clay). A constant 0.04 $L\,s^{-1}$ natural inflow maintains saturated soil conditions facilitating a dense cover of *Phragmites australis* inside the pond. At its eastern end, water leaves the pond through several holes in a concrete wall. During the tracer experiment an artificial inflow of 8.3 $L\,s^{-1}$ was created for 75 min yielding a total water volume of 37.5 m^3. Most outflow holes were blocked to facilitate volumetric flow measurements using 10 L buckets at two outflow holes.

SFW3 consists of three wetlands in series with maximum depths of 0.70, 0.77 and 0.14 m, respectively. All three wetlands cover a combined area of 1280 m^2 and a total water volume of 330 m^3. Similar to SFW1 which is located in the immediate vicinity, sediments have a silty clay texture (10.7% sand, 53.1% silt, 36.2% clay). Dams create tortuous flow paths increasing length-to-width ratios to about 5 : 1 in the first two rectangular wetlands (73 and 177 m^3). The third wetland (80 m^3) is elongated and S-shaped with a length to width ratio of 14 : 1. At the time of the tracer experiment, vegetation cover was approximately 10%, and consisted of *Typha latifolia*, *Phragmites vulgaris*, *Juncus conglomeratus*, and *Festuca arundinacea*. During the tracer experiment an electromagnetic flowmeter (MAG 8000, SIEMENS) measured an almost constant inflow rate of 1.4 $L\,s^{-1}$. Approximately one third of this flow exited the wetlands through percolation losses into a network of underground drainage pipes. These were collected in a manhole and measured electromagnetically. A V-notch at the outlet of the third wetland measured the surface outflow of the system. For more details about SFW3 and SFW1 see Passeport *et al*. [24].

SFW4 represents a small 65 m^2 flow-through wetland located near the village of Eichstetten, approximately 15 km west of the city of Freiburg, Germany. The volume is relatively small (6.5 m^3) due to its shallow (0.1 m) water depth. The wetland is 10 m long and reaches a maximum width of 8 m. Inflow is measured continuously by a V-notch weir. Due to the small wetland area and heavy soils (10% sand, 80% silt and 10% clay) water losses by evapotranspiration or percolation are assumed to be negligible. During the experiment the wetland was covered by approximately 15% of *Typha latifolia* and *Phragmites australis*. Inflow was constant at 5.75 $L\,s^{-1}$.

SFW5 and SFW6 represent vegetated ditches located approximately 5 km north- and southwest of the city of Landau, Germany. No hydrometric instrumentation was installed to measure flow rates, thus discharge was determined by the salt dilution method during the experiment. SFW5 is 413 m long and vegetation was removed just before tracer injection. Hence it may be regarded as a small stream that also included several pool-riffle sequences. Water depth is highly variable with a mean value of about 0.2 m. During the tracer experiment flow was constant at 5.0 $L\,s^{-1}$. SFW6 is a straight 80 m ditch densely vegetated by *Phragmites australis*. During the experiment water depth was shallow (0.1 m) owing to a very small discharge (0.9 $L\,s^{-1}$).

2.2 *Tracer application, field measurements and laboratory analysis*

Conductivity, which served as a surrogate for NaCl concentration, was measured continuously by portable conductivity meters (LF-92 sensors, WTW, Weilheim, Germany) at 0.5% accuracy. Chloride is characterised by high natural background values, necessitating the injection of large amounts of NaCl. This changes water densities and may preclude a correct representation of flow paths. Bromide, on the contrary, has a low natural background and negligible sorption. Hence, it is a more ideal tracer for use in wetlands [13]. In the present study analysis was performed by ion chromatography (Dionex-DX 500) at an accuracy of ±8%.

Breakthrough curves of the fluorescent tracers were obtained by two different ways. First, at fixed time intervals water samples were collected in 100 mL brown glass bottles. They were stored in a dark and cool place and analysed in the laboratory 2–5 days after the experiment using a fluorescence spectrometer (LS-50B, Perkin-Elmer). A pulsed xenon discharge lamp was used as light source. For UR the excitation wavelength was set to 488 nm and the emitted light was measured at 512 nm. For SRB the values were 561 and 583 nm, respectively. For each SFW the instrument was calibrated using standard concentration samples. They were obtained by dilution with water collected on site prior to tracer injection. This prevented a background correction due to fluorescence of e.g. dissolved organic matter. Detection limits were low (UR: 0.002 $\mu g\,L^{-1}$, SRB: 0.01 $\mu g\,L^{-1}$) and high concentration samples were diluted to keep the linear concentration range (UR up to 100 $\mu g\,L^{-1}$, SRB up to 250 $\mu g\,L^{-1}$). Second, fluorescent tracer concentrations were determined continuously by a filter fluorometer placed directly into the wetland outlet. The flow-through fluorometer GGUN-FL30 [25] allowed parallel measurements of UR and SRB down to concentrations of 0.02 $\mu g\,L^{-1}$. Fluorometer readings were calibrated by water samples collected at the same location and analysed in the laboratory according to the above-mentioned procedure.

Tracer application was adapted to the hydraulic characteristics of the wetlands (Table 2). All tracers were injected as an instantaneous (1–3 s) pulse into the SFW inlets

Table 2. Summary table of the tracer experiments.

Salt/IPU						
	Type	Injected mass (g)	Injected volume (L)	Sampling interval (min)	Sampling duration (d)	Recovery (%)
SFW1	IPU	50	60	240–600	3	21
SFW2	NaBr	5000	20	5–360	34	81
SFW3	IPU	50	60	60–480	6	31(70*)
SFW4	NaBr	50	2	0.5	0.03	93
SFW5	NaCl	2000	8	0.5–5	0.17	100
SFW6	NaCl	1000	8	1–5	0.08	100

UR/SRB					
	Injected mass* (g)	Injected volume (L)	Sampling interval (min)	Sampling duration (d)	Recovery* (%)
SFW1	2.0/5.0	20	60–240	3	43/31
SFW2	50/100	7.5	5–360	25	42/18
SFW3	1.0/5.0	20	60–240	6	4(19**)/54(87**)
SFW4	0.01/0.02	0.1	0.5	0.03	100/68
SFW5	0.05/0.2	0.5	1–5	0.17	83/68
SFW6	0.02/0.1	0.5	1–5	0.08	100/65

*First value for UR, second for SRB.
**Including drainage.

and tracer breakthroughs were measured at the outlets (Figure 1). Only at SFW1 and SFW3 were the injections longer (108 s), but still short compared to the duration of the tracer response curve at the wetland outlet. At these two SFWs no salt was injected. However, to directly compare the behaviour of herbicide and tracers, IPU was injected simultaneously with the fluorescent tracers UR and SRB. For details about this comparison see also Passeport *et al*. [24]. IPU samples were analysed by ELISA immunoassay tests [26].

2.3 *Computations for determining hydraulic parameters*

At SFW5 and SFW6 sodium chloride (NaCl) was injected instantaneously for measuring discharge Q ($\mathrm{L\,s^{-1}}$) according to the following equation [27]:

$$Q = \frac{M}{\int_0^\infty C(t)\mathrm{d}t} \tag{1}$$

where M (g) is the mass of the injected tracer, $C(t)$ ($\mathrm{g\,L^{-1}}$) is the tracer concentration at a certain time t (s) after injection. At every SFW outlet the first tracer appearance yielded the maximum flow velocity ($v_{\max}$ ($\mathrm{m\,s^{-1}}$)):

$$v_{\max} = x/t_1 \tag{2}$$

where x (m) is the flow distance between injection (i.e. SFW inlet) and tracer sampling (i.e. SFW outlet) and t_1 (s) is the time of first tracer appearance after injection. The tracer response curve can be interpreted as a probability density function $E(t)$ (h^{-1}) for residence times in the wetland; i.e. the hydraulic residence time distribution (RTD) [12]:

$$E(t) = \frac{C(t) * Q(t)}{\int_0^\infty C(t) * Q(t)\mathrm{d}t} \tag{3}$$

where $Q(t)$ ($\mathrm{L\,s^{-1}}$) is the outflow rate. The first moment of the RTD is the mean detention time τ (s):

$$\tau = \int_0^\infty t * E(t)\mathrm{d}t \tag{4}$$

The second central moment of the RTD, its variance σ^2, characterises the spread of the RTD around τ:

$$\sigma^2 = \int_0^\infty (t - \tau)^2 * E(t)\mathrm{d}t \tag{5}$$

RTDs can be normalised by τ to compare the flow performance of different SFWs.

Persson *et al.* [28] proposed to use the 50th percentile of the RTD (t_{50} (s)) instead of τ to assess the mean residence time. At t_{50} 50% of the injected tracer has passed the outlet and the mean flow velocity (v_{mean} ($\mathrm{m\,s^{-1}}$)) can be determined:

$$v_{\mathrm{mean}} = x/t_{50} \tag{6}$$

Wetland geometry and average flow rate yield the nominal residence time (t_{N} (s)):

$$t_{\mathrm{N}} = V/Q_{\mathrm{mean}} \tag{7}$$

where V (L) is the water volume of the SFW and Q_{mean} ($\mathrm{L\,s^{-1}}$) is the mean outflow rate. According to Thackston *et al.* [29] the effective volume ratio ε can be calculated relating t_{50} to t_{N}:

$$\varepsilon = t_{50}/t_{\mathrm{N}} \tag{8}$$

Theoretically, small values of ε suggest dead zones or preferential flow paths. Additionally, Persson *et al.* [28] proposed the hydraulic efficiency λ:

$$\lambda = t_{\mathrm{P}}/t_{\mathrm{N}} \tag{9}$$

where t_{P} (s) is the time of the peak outflow concentration. They categorised three groups: (1) good hydraulic efficiency ($\lambda > 0.75$); (2) satisfactory hydraulic efficiency ($0.5 < \lambda \leq 0.75$); and (3) poor hydraulic efficiency ($\lambda \leq 0.5$).

2.4 *Computations for determining mitigation capacities*

Using the conservative tracers (NaCl and NaBr), Equations (2)–(9) were applied to characterise internal wetland hydraulics. However, to describe mitigation capacities by non-conservative tracers, additional parameters were required which also quantify tracer losses. For many contaminants acute toxicity depends on peak concentration. Hence peak attenuation is an important mitigation capacity of wetlands. To compare systems of different sizes, specific peak attenuation (SPA ($\mathrm{g\,\mu g^{-1}}$) of reference tracers can be calculated as:

$$SPA = M/(C_{max} * V) \tag{10}$$

where C_{max} is the peak concentration at the outlet. Large values of SPA indicate favourable conditions for peak attenuation, caused e.g. by sorption or by mixing in a relatively small water volume. However, to assess the environmental value of SFW systems, permanent detention of contaminants and a reduction of total loads are often more important than attenuation. When the entire tracer response curve is recorded, tracer recovery (R (%)) can be determined:

$$R = \frac{\int_0^\infty C(t) * Q(t)\mathrm{d}t}{M} * 100 \tag{11}$$

For SFWs of similar type (similar layout, hydraulics, vegetation) and the same tracer, R is a function of wetland size. This dependency can be avoided by specific tracer retention (STR ($\%\,\mathrm{m}^{-3}$)):

$$STR = (1 - R)/V \tag{12}$$

Since frequently only a limited area for the installation of SFWs is available, retention capacity can also be related to area:

$$ATR = (1 - R)/A \tag{13}$$

where ATR ($\%\,\mathrm{m}^{-2}$) is the tracer retention by area and A (m^2) is the area of the SFW. Large values of STR and ATR suggest an efficient reduction of tracer loads in a relatively small water volume or wetland area.

3. Results

3.1 *Individual tracer responses*

Quick tracer passages were observed in both intermittent-flow SFWs (SFW1 and SFW2) in response to increased inflow and rainfall events (Figure 3). A 5-hour rainstorm of 25 mm about three days after tracer injection in SFW1 caused runoff to bypass the outlet ditch. Moreover, high turbidity in the samples impeded accurate tracer and IPU analysis. These conditions precluded the calculation of tracer recoveries. Only small rainfall events occurred in SFW2 and tracer recoveries could be evaluated for a period of two months after injection. Recovery rates were higher for UR than for SRB (Table 2). The majority of the fluorescent tracers exited during times of increased outflow, whereas high NaBr concentrations remaining three days after injection in SFW2 suggested high retention. Overall SRB recovery was smallest in SFW2 when compared to all investigated wetlands (Table 2). Apparently, sediments and dense vegetation caused efficient sorption but at the same time limited photolytic decay. This yielded measurable UR concentrations at the pond outlet, four weeks after injection. IPU concentrations deviated from that of SRB in SFW1, but both showed a similar decreasing trend with time.

Located in the immediate vicinity to SFW1, SFW3 also responded to the 25 mm rainstorm occurring on 10 March 2008 (Figure 4). The analysis of tracer breakthroughs was more complicated in SFW3, since about one third of the inflow was lost into the underground drainage during the experiment. While the rainstorm resulted in sharp discharge peaks, water losses through the drainage system ceased. Similar to SFW1, tracer

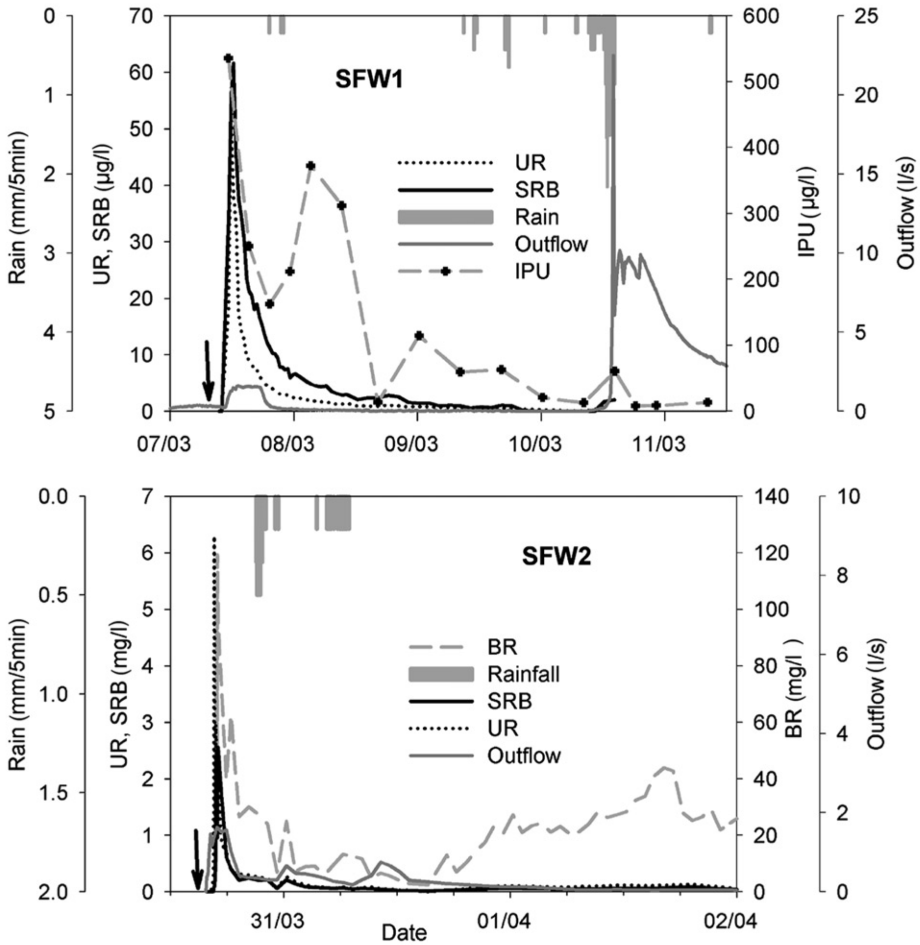

Figure 3. Breakthrough curves measured at the outlet of the intermittent-flow wetland systems SFW1 (upper graph) and SFW2 (lower graph). Arrows denote tracer injection.

recoveries were only calculated for low constant inflow prior to the rainstorm event. Rapid breakthroughs of both fluorescent tracers and IPU at the drainage outflow were observed (Figure 4). At the surface outflow the SRB breakthrough was slow and attenuated, while UR concentrations were barely detectable. Due to light degradation, UR recovery was lowest in SFW3 compared to all other SFWs. Overall, similar responses for IPU and SRB were observed during transit through SFW3.

Discharge rates were relatively large compared to water volumes in the remaining wetland systems (SFW4–6) (Table 1). Therefore, rather short and well defined tracer breakthroughs were observed with high recovery rates (Figure 5, Table 2). In SFW4 tracer breakthrough curves had two peaks indicating two main flow paths, whereas single flowpaths occurred in SFW5 and SFW6. The overall shape of the breakthrough curves suggested water residence time distributions that were closer to one-dimensional plug than continuously stirred tank reactor flow conditions.

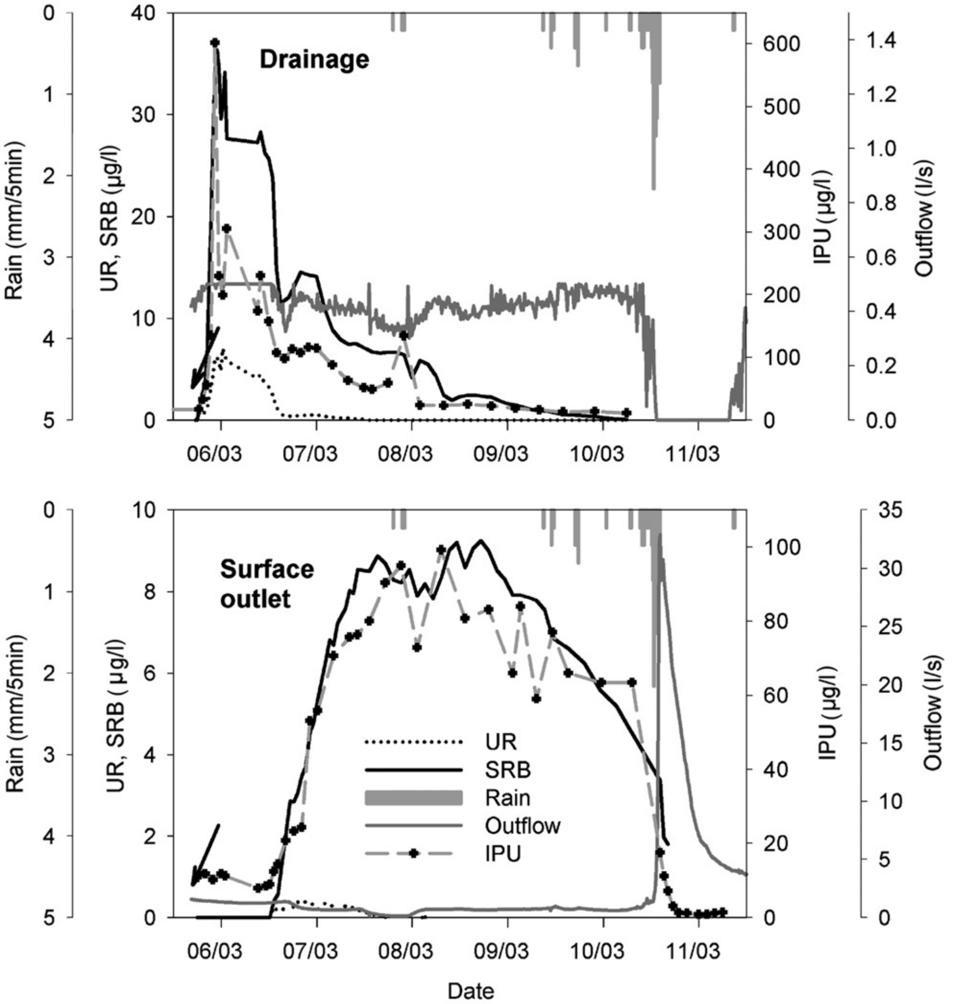

Figure 4. Tracer and IPU breakthroughs at SFW3 for drainage outflow (upper graph) and surface outlet (lower graph). Arrows denote tracer injection.

3.2 *Comparison among wetland types*

NaCl- and NaBr-breakthrough curves were used to calculate normalised RTD functions (Figure 6) and hydraulic parameters (Table 3). Where no salt was injected, the fluorescence tracer with the highest recovery was used instead (SFW1: UR; SFW3: SRB) and the recovered tracer mass was used instead of the injected to calculate t_{50}. The long breakthroughs at SFW2 and SFW3 increased τ and σ^2, while the 30 min breakthrough at SFW4 yielded highest $E(t)$ values. Intermittent flow rates caused outliers which were most prominent in SFW2 (Figure 3). Also at SFW3 a time period of reduced inflow became visible at 0.8τ (Figure 6). Both vegetated ditches SFW5 and SFW6 were characterised by unimodal and smooth RTD functions. Non-steady flow conditions and relatively low average outflow rates resulted in low λ and ε values for SFW1 and SFW2 (Table 3).

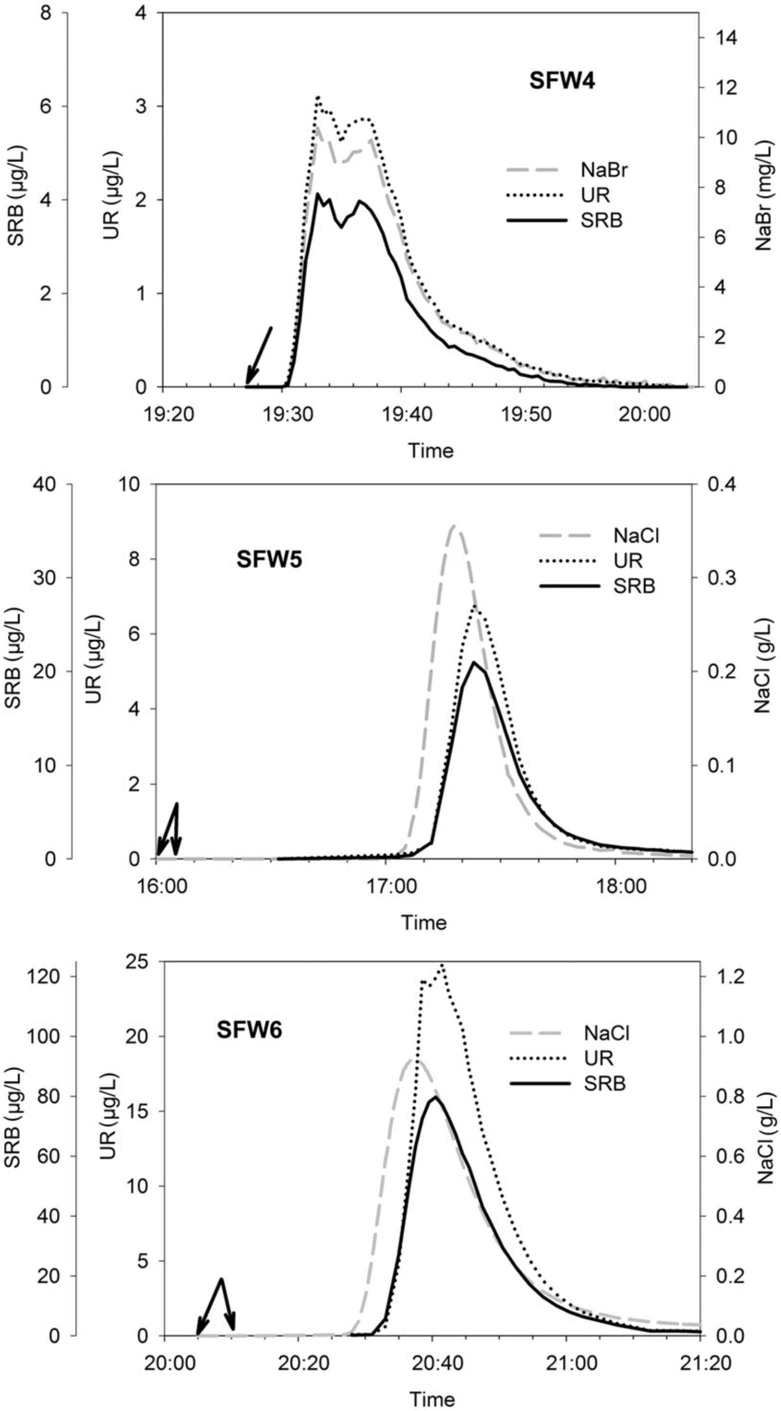

Figure 5. Tracer breakthroughs measured at SFW4-6. Arrows denote tracer injection. Axes are scaled according to injected tracer mass. Note that NaCl was injected 5 min prior to UR and SRB at SFW5 and SFW6.

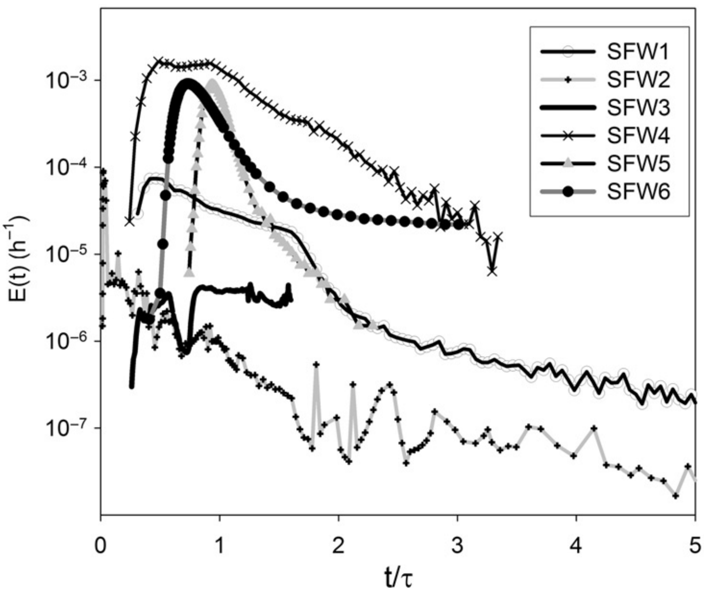

Figure 6. Normalised RTD functions.

Table 3. Parameters for hydraulic comparison; t_1: time of first tracer appearance; v_{max}: maximum flow velocity; t_P: time of peak concentration; t_{50}: time when 50% of the injected tracer has passed the outlet; v_{mean}: mean flow velocity; τ: mean detention time; t_N: nominal residence time; σ^2: variance of the RTD; λ: hydraulic efficiency; ε: effective volume ratio.

	t_1 (h)	v_{max} (m min)$^{-1}$	t_P (h)	t_{50} (h)	v_{mean} (m min)$^{-1}$	τ (h)	t_N (h)	σ^2 (h^2)	λ	ε
SFW1	1.5	0.78	2.00	3.75	0.32	4.83	13.1	19.86	0.15	0.28
SFW2	0.90	0.43	1.25	13.5	0.03	58.2	55.6	19273	0.02	0.23
SFW3	18.8	0.18	62.3	73.5	0.05	71.9	113	643	0.55	0.65
SFW4	0.04	4.00	0.08	0.15	1.11	0.17	0.32	0.01	0.26	0.47
SFW5	1.03	6.66	1.30	1.33	5.18	1.39	1.72	0.05	0.76	0.77
SFW6	0.30	4.44	0.54	0.61	2.19	0.73	1.23	0.13	0.44	0.50

The highest λ and ε were at SFW5 suggesting low dispersion with limited short circuiting and dead zones along the 413 m river reach. Hydraulic efficiency was still satisfactorily at SWF3 but poorer at SFW4 and SFW6. Apart from SFW3 (here the rainstorm event inhibited a complete recording of the breakthrough), τ was generally longer than t_{50}. Regarding the high flow velocities, SFW4 was similar to the vegetated ditches SFW5 and SFW6.

Breakthroughs of UR yielded parameters for mitigation capacities through photolytic decay (Figure 7). Quick tracer passages in SFW4 and SFW6 led to UR recoveries of 100% and zero values for STR and ATR, as photolysis did not occur. When UR remained in the system for a long time, such as in SFW1-SFW3, a higher tracer loss was recorded.

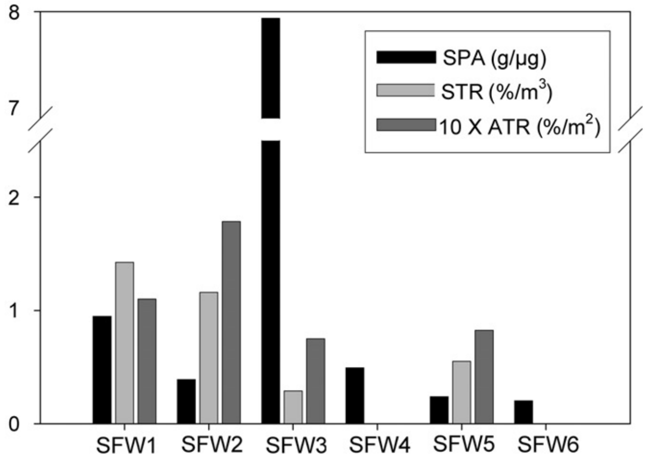

Figure 7. Parameters for SFW comparison using UR, SFW3 excludes underground drainage.

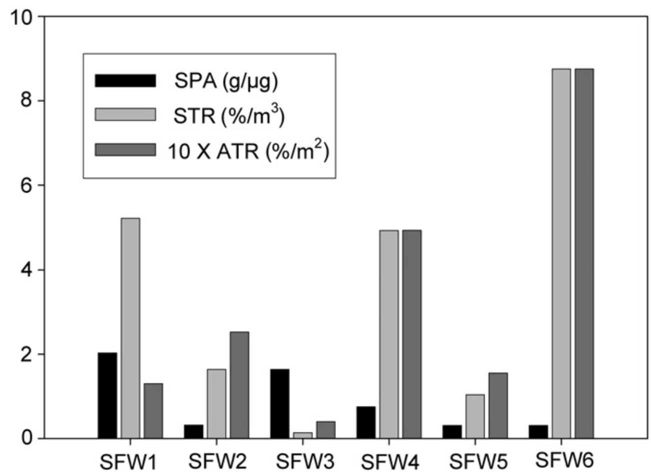

Figure 8. Parameters for SFW comparison using SRB, SFW3 excludes underground drainage.

This was most obvious in SFW3, where peak attenuation (SPA) reached almost $8\,\mu g\,g^{-1}$ when underground drainage was disregarded. The high retention of the non-steady systems was apparently caused by an incomplete flushing of the system, since inflow rates were decreased after 7.5 h (SFW1) and 1.25 h (SFW2) following tracer injection.

Parameters calculated from SRB breakthroughs mainly described sorption capacities (Figure 8). SFW1 had the highest potential for peak attenuation (SPA), followed by SFW3. In SFW3 specific retention (STR, ATR) was marginal. This was mainly due to the large water volume, and incomplete vegetation cover during the tracer experiment. Smaller systems appeared to be more efficient. By far the highest specific SRB retention was observed at SFW6, where large amounts of SRB were retained over a short distance in a relatively small water volume.

4. Discussion

Using breakthrough curves of conservative tracers, normalised RTD-functions may be used to compare internal hydraulics of different wetland systems. Larger systems generally show reduced function values compared to smaller systems. Periods of intermittent flow can be revealed and hydraulic efficiency can be parameterised, e.g. by λ or ε. However, to study mitigation capacities, non-conservative tracers must be used and parameters should quantify losses by e.g. sorption or photolysis. For this purpose the present study uses the fluorescent tracers UR and SRB. Sabatini [30] directly compared the sorption kinetics of both tracers and found that for different mineral media SRB was far more susceptible to sorption than UR, e.g. in limestone material the Freundlich adsorption coefficient was 30 times higher for SRB than for UR. Behrens and Teichmann [31] found that UR can be characterised by a 78 fold loss compared to SRB when exposed to a xenon high pressure lamp. A recent study showed the low toxicity of both tracers making them ideal tracers for environmental studies [32].

IPU was injected in parallel to the fluorescent tracers at two wetland systems (SFW1 and SFW3) to compare the environmental behaviour of tracers and contaminants. Analysis costs limited IPU sampling frequency with single samples deviating from the tracer breakthrough curves. Still, a rather parallel behaviour of IPU and SRB was observed in totally different wetland systems, including underground passage through drainage lines. The behaviour of IPU and SRB was most similar at the surface outlet of SFW3. Similar recovery rates for IPU (SFW1: 21%, SFW3: 70%) and SRB (SFW1: 31%, SFW3: 87%) confirmed this observation. Hence SRB seems to be an appropriate reference tracer to mimic the behaviour of mobile pesticides (low K_{OC}, without degradation) in SFW systems.

In SFW1 an unknown amount of the tracers was only temporally stored in the system and was flushed during a natural flow event three days after tracer injection (Figure 3). Small concentrations of SRB could be detected in three tracer samples collected at the outlet of SFW1 during the rising limb of the rainstorm flood event (10 March 2008), which would result in a relatively large tracer flux. However, for wetland comparison only data up to the storm event was analysed. Hence the obtained retention parameters for SWF1 only represent low flow conditions, and tracers – and therefore contaminants – will be washed out during storm events. Moreover, the different nature of this forest buffer zone (water depth and water volume had to be estimated from soil depth and porosity) permitted only approximate comparisons to permanent wetland systems. Still the order of magnitude obtained showed that these wetland types may be efficient for peak attenuation, while permanent retention capacities seem to be rather limited.

SFW2 represents a densely vegetated surface wetland with a large variation in water storage. These wetland types are often found in detention ponds that primarily serve for flood protection rather than for the treatment of contaminants. The results of the present study suggest that wetland zones in these ponds may also play an important role in contaminant remediation. While peak attenuation is rather limited, tracers and hence contaminants may be stored for long time periods, which may also promote permanent degradation. Among all prototypes, UR-ATR values were largest, indicating favourable conditions for photolytic decay. Also, sorption capabilities were considerable as indicated by the lowest SRB recovery (Table 2). However, stable and non-sorptive substances (in the present case illustrated by NaBr) may also leave these systems a long time after contamination.

Drainage losses in SFW3 caused a quick passage of the tracers and limited retention capacity (Table 2). This is in line with the results of Keefe *et al.* [15] who found smaller tracer removal rates in a leaky than in an impermeable SFW. Additionally, after a 73 h flow through a series of three wetlands, 54% of the injected SRB left SFW3 via the surface outlet. On the contrary, UR was almost completely degraded by photolysis at this time. This highlights the importance of wetland vegetation for the sorption of contaminants. During the experiment vegetation cover was only approximately 10% (Figure 2). Moreover, water depths reached up to 0.77 m. Hence the majority of the tracers travelled freely in the water without any contact to sorbing media.

The remaining SFW types (SFW4–6) had rather small water volumes. The tracers quickly passed the wetlands with only a short time for photolytic decay, evidenced by zero UR retention in SFW4 and SFW6. A clearing of vegetation in SFW5 increased solar radiation and UR losses along the 413 m (1.3 h) passage. Still, remnants of plants inside the river and several pool – riffle sections (Figure 2) increased contact to sediments and vegetation which facilitated considerable SRB losses. SRB recovery was similar for all three wetlands (65–68%, Table 2), but due to smaller water volumes and surface areas STR- and ATR-values were higher in SFW4 and SFW6. In these two SFWs a shallow water depth and a relatively dense vegetation apparently caused the most favourable conditions for SRB sorption. SFW6, with its dense vegetation of *Phragmites australis*, appeared to be the most efficient SRB-trap.

It should be noted the present study is limited to an input/output analysis which treats different SFWs as black boxes. SRB (contaminant) losses by adsorption may be limited to surface chemical phenomena that could either be reversible or irreversible upon the specific pollutant and support media properties. Hence, intense SRB losses inside SFWs should only be regarded as a general affinity to contaminant mitigation. To obtain more detailed information about transformation or biodegradation processes, investigations inside SFWs would be required.

Moreover, it must be recognised that the determined tracer results are only valid for low flow conditions and for the boundary conditions during the various experiments (e.g. flow velocities, vegetation development, flow patterns, etc.). Still, the results suggest that a shallow water depth is a key variable to increase sorption in steady-state wetland systems. This is also in line with Holland *et al.* [16] who found increasing short circuiting and a larger mixing scale with increasing water depth. Large wetlands with deep water bodies - in this study SFW3 – may attenuate concentrations efficiently, but unit retention is more significant in shallow systems, even at much higher flow velocities and shorter contact times. This is facilitated by instantaneous SRB losses, most obvious by the retarded breakthrough in SFW5. Using the unit retention measures STR and ATR, SWF6 (a densely vegetated 80 m ditch) was by far most efficient for SRB sorption. Also Kröger *et al.* [33] documented the importance of in-stream wetland vegetation for contaminant mitigation in drainage ditches.

For flood conditions, a direct comparison of different wetland systems depends on event characteristics. Moreover, it is extremely difficult to determine exact tracer mass balances, because flow rates are high, tracers are diluted and at the same time tracer background concentrations increase. Single tracer samples at the beginning of the flood event at SFW1 indicate a possible washout of tracers - and hence contaminants – during floods. However, the behaviour of wetlands during floods deserves further investigation.

5. Conclusions

In the present study conservative salt tracers were used to study internal hydraulics (e.g. normalised RTD functions, residence times, flow velocities, hydraulic efficiencies) of different types of surface flow wetlands. Non-conservative, fluorescent tracers were used as a surrogate for contaminants.

In different wetland systems a sample contaminant – the highly mobile pesticide isoproturon (IPU) – was found to have similar behaviour as the sorptive fluorescent tracer sulforhodamine-B (SRB). Hence the obtained wetland characteristics for SRB may serve as an indication for pesticide retention. Owing to the properties of IPU, the obtained results should be treated as worst case scenarios for highly mobile contaminants. For photolytic decay no reference contaminant was studied, but the fluorescent tracer uranine (UR) may also serve as a valuable proxy for this process.

In general the proposed parameters, specific peak attenuation SPA and specific tracer retention STR/ATR, facilitated a comparison of completely different wetland types. The present study suggests that wetland systems with intermittent flow may temporally store large amounts of tracers (contaminants). This may lead to an efficient attenuation of peak concentrations. However, when large parts of these systems are flushed by natural storm events, tracers (contaminants) may be re-mobilised.

In steady systems vegetation density and water depth were found to be the most important factors for tracer/contaminant retention. Illustrated by SRB, sorption on sediments and vegetation lead to considerable tracer losses, even at high flow velocities and short contact times. Shallow systems with dense vegetation appeared to be the most efficient SRB/contaminant traps. Thus, limiting the maintenance of small natural water courses (i.e. facilitating natural vegetation growth) may be an efficient and low cost measure to improve water quality at least during low flow conditions.

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