



Research article

Reducing adverse side effects by seasonally lowering nitrate removal in subsurface flow constructed wetlands



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ABSTRACT

Subsurface flow constructed wetlands with wood chips (SSF-CWs) have proven to effectively reduce the loss of nitrogen (N) from agricultural fields to surface water, however in some cases production of negative side effects such as methane and phosphate occur. We examined if these side effects can be avoided by decreasing the hydraulic retention time (HRT) from on average 82 h to 11 h during summer to autumn in two pilot SSF-CWs. Furthermore, we investigated the potential of the SSF-CWs to reduce phosphorus (P) loss from agricultural drainage systems. The influent and effluent concentration of total N (TN), nitrate-N, total P, phosphate-P, suspended sediment, and sulphate were monitored for five years (2013–2017). Methane concentrations were measured during two periods in 2014 and 2017. Flow was measured continuously by electromagnetic flowmeters. The nitrate-N removal was reduced from 98–100% to 27–32% and the sulphate reduction from 32–53% to 1–2% when decreasing HRT. Concurrently this resulted in a considerable decrease in the difference between the effluent and influent concentration of phosphate-P and methane concentration compared to similar periods in the preceding years. The SSF-CWs retained 67–85% of the annual loading of particulate P, but acted as both a sink and source of phosphate-P, thus further initiatives are therefore required to prevent phosphate-P release from SSF-CWs. Although during the entire monitoring period the SSF-CWs retained 29–33% of the total P loading. In summary, this study stresses how important a holistic approach is when implementing and designing new N mitigation measures.

1. Introduction

Subsurface flow constructed wetlands (SSF-CWs) are systems designed to mitigate the high loading of nitrogen (N) from agricultural land via drainage systems to receiving water bodies, however SSF-CWs may create deleterious side effects (Shih et al., 2011; Bruun et al., 2017; Fenton et al., 2016). N and phosphorus (P) loading from agricultural land is one of the pressures of eutrophication of waterbodies in Denmark as well as elsewhere (Kronvang et al., 2009; Rabalais et al., 2001). Since that the 1980s several actions plans have been implemented to decrease the N loading to Danish waterbodies, however further reduction is still required to fulfil the requirements of the EU Water Framework Directive. Therefore a new agricultural regulation has been implemented as of 1 January 2019. This differentiated regulation is based on implementation of more targeted rather than general mitigation measures (NLK, 2013). Accordingly, targeted mitigation measures such as SSF-CWs treating agricultural drainage water are in high demand.

SSF-CWs collect water from subsurface drainage systems draining

agricultural fields into an excavation with filter material such as wood chips. The SSF-CWs are designed to enhance denitrification by ensuring anaerobic conditions, increasing the hydraulic retention time (HRT) and providing carbon (Blowes et al., 1994). A review by Christianson et al. (2012b) showed that SSF-CWs effectively removed NO_3^- -N with removal rates of around 0.38 to $7.76 \text{ g N m}^{-3} \text{ d}^{-1}$ and a relative removal of 12 to 98%. However a limitation in the supply of terminal electron acceptors (TEAs) such as O_2 and NO_3^- may generate a range of negative side effects (Bruun et al., 2017; Bell et al., 2015; Christianson et al., 2012a; Shih et al., 2011).

Generally, microbes use TEAs in a sequential order ($\text{O}_2 > \text{NO}_3^- > \text{Mn (IV)} > \text{Fe (III)} > \text{SO}_4^{2-} > \text{CO}_2$) with preferential use of TEAs yielding the highest energy (Reddy and Delaune, 2008). Thus, when NO_3^- is depleted, phosphate (PO_4^{3-}) can be released if iron (Fe) oxides are reduced (equation (1)), e.g. if Fe oxides are used as TEAs by iron-reducing bacteria (equation (2)) (Reddy and Delaune, 2008).



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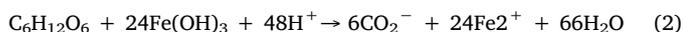
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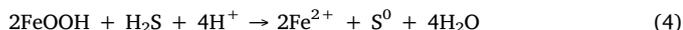
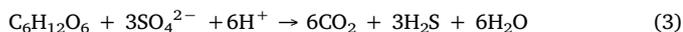
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The process of sulphate reduction (equation (3)) can indirectly mediate PO_4^{3-} release as sulphide (H_2S) produced by sulphate-reducing bacteria (equation (4)) and Fe hydroxides can participate in several reactions releasing PO_4^{3-} (Reddy and Delaune, 2008):



Furthermore, upon depletion of SO_4^{2-} methanogens can take over and produce methane (CH_4) by either acetate fermentation (equation (5a)) or hydrogen fermentation coupled with CO_2 reduction (equation (5b)) (Bubier et al., 1993; Bruun et al., 2017; Reddy and Delaune, 2008). CH_4 is a greenhouse gas with a global warming potential (GWP) 25 times higher than CO_2 (IPCC, 2007).



Although various management strategies to solve these occasional problems of SSF-CWs have been proposed, only few studies have investigated how to avoid these adverse side effects in practice (Christianson et al., 2017; Shih et al., 2011). One strategy would be to ensure, that conditions for complete NO_3^- -N reduction does not occur. Thus, the TEA supply must always exceed the TEA consumption. The hydraulic loading rate (HLR) mainly controls the TEA supply, while TEA consumption is strongly affected by temperature and HRT (Hoffmann et al., 2018). The present study aimed at investigating whether it was possible to reduce the adverse side effects by increasing HLR and thereby decreasing HRT. Specifically the objective was to assess if the side effects following TEA exhaustion in SSF-CWs can be minimised by decreasing HRT during the low drainage discharge season. We hypothesised that the decrease of HRT would lead to lower NO_3^- and SO_4^{2-} reduction rates, ensuring the presence of more energetically favourable TEAs and thereby lowering the PO_4 -P release and CH_4 production. In order to investigate the P retention potential of SSF-CWs designed for N mitigation, we monitored the annual water and P balance.

2. Material and methods

2.1. Study site and design

The study site was located in the River Gjern catchment (114 km²) situated in central Jutland, Denmark (UTM, ZONE 32, ETRS 89, x, y: 546104, 623014). The study was conducted in two pilot SSF-CWs (CW1 and CW2) with horizontal flow that are part of an experimental plant with six independent SSF-CWs, each measuring 10 m × 10 m × 1 m (only the data from CW1 and CW2 was relevant for this study). The joint inlet pond of the experimental plant received water from a tile drainage system covering an agricultural catchment of 78 ha, thus the

wetland:catchment (W:C) ratio was 0.07%. The drainage water was distributed equally among the six SSF-CWs by individual inlet wells (Fig. 1). Each SSF-CW was lined with a 1 mm thick watertight membrane (Junifold PE HD GEO MEMBRANE; Millag APS, Denmark). The matrix of the filter beds consisted of willow wood chips (size 8–60 mm; Ny Vraa bioenergy I/S, Denmark) mixed with crushed mussel shells (size 2–4 mm; Danshells ApS, Denmark) in volume ratios of 50:50 in CW1 and 75:25 in CW2, as recommend by Bruun et al. (2016a). The total porosity of CW1 and CW2 was 0.64 m³ m⁻³. In the inlet and outlet zones of the filter bed, a distribution layer consisting of coarse seashells (Danshells ApS, Denmark) ensured homogeneous infiltration. Upon establishment in 2012, *Phragmites australis* was planted in CW1, while CW2 was unvegetated. However, shortly after establishment, both CWs were dominated by *Phragmites australis*, *Typha latifolmis*, *Bidens tripartite*, *Epilobium hirsutum* and *Salix* sp. A PVC pipe (Ø 150) connected the filter bed of each SSF-CW with an outlet well, which was connected with another outlet well to reoxidise the water (Fig. 1). More details on the study site and the design of the SSF-CWs are given by Hoffmann and Kjaergaard (2015) and Hoffmann et al. (2018), and additional details about the physical parameters of the filter matrix can be found in Bruun et al. (2016b).

2.2. Instrumentation and sampling

Instrumentation and sampling have been described in previous papers (Bruun et al., 2016b; Hoffmann et al., 2018) and summarised here. Each outlet well was equipped with an electromagnetic flow-meter (Ø 100 mm; Waterflux 3070, Krohne, Germany) connected with a data logger (Campbell CR10X, Logan, USA) that recorded the flow velocity as a mean every 10 min (first outlet well from the left in Fig. 1). From 03/04/2015 to 05/31/2015, the CWs were used for bromide tracer experiments and this period was therefore excluded from the study. As the inflow was not monitored it was assumed to equal the outflow, and given the small size of the SSF-CWs the contribution of precipitation and evaporation was minor; around 0–1% according to Hoffmann et al. (2018). The water level and temperature of each CW were measured from October 2013 using a pressure transducer (Level 2000, Madgetech, Warner, New Hampshire, USA) placed in a piezometer in the center of the filter bed. The water level of the filter bed was fixed, despite varying HLR, and the water level meter was only installed to investigate if ponding occurred during precipitation events. However in 2015 the water level was decreased by 20 cm. There was no bypass flow throughout the monitoring period.

Water samples were taken from the joint inlet pond and the separated individual outlet wells every third hour by a time proportional sampler (ISCO 6700 FR Samplers ISCO, Lincoln, Nebraska, USA) (Fig. 1). In the period 01/01/2013 to 06/30/2015 and 05/30/2017 to 12/31/2017 samples were subsequently collected according to flow, and the composite samples represented periods of 1 to 22 days. In the period 06/30/2015 to 05/30/2017, the composite samples represented 2 to 6 weeks.

Water samples for analysis of dissolved CH_4 were taken as grab

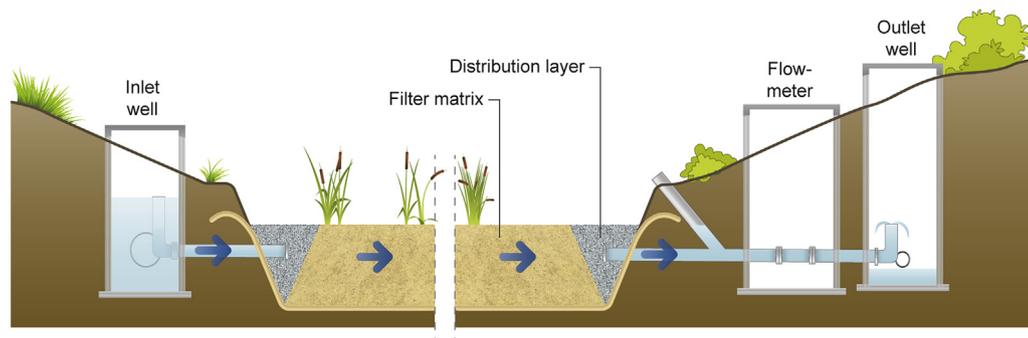


Fig. 1. Conceptual sketch of subsurface flow constructed wetlands (SSF-CWs) with horizontal flow, including inlet well, distributions pipes, distribution layer (seashells), filter matrix (willow woodchips and seashells), membrane, outlet well with flow-meter and outlet well with effluent sampling and aeration of the effluent water. The blue arrows indicate the direction of the water flow. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

samples in the inlet pond and outlet well every third week at two sampling events: 12/11/2013 to 04/15/2015 and 06/22/2017 to 31/12/2017. The water samples were transferred with a gas-tight syringe (20 ml) and tubing (TygonTM) into a glass vial (12 ml exetainer; Labco, High Wycombe, UK), allowing overflow. The samples were preserved by adding bactericide (400 µl, 50%, w/v, ZnCl₂) to each vial, which contained a glass ball.

In the field O₂, temperature, conductivity and pH were measured every third to sixth week using a multimeter (YSI Professional Plus, Xylem Analytics, Ohio, USA) in the piezometer pipe located in the center of the filter bed.

Redox potentials were measured at the same sampling events and with the same frequency as for dissolved CH₄ by connecting a portable microprocessor pH meter (WTW, PH 96) with a double junction calomel reference electrode (E21M001, Radiometer Analytical, Vaulx-en-Velin, France), which was installed permanently 2.5, 5.0 and 7.5 m from the inlet side in each CW at 50 cm depth. The measured values were converted to standard hydrogen electrode potentials (Eh) by adding 245 mV. The Pt electrodes were tested for accuracy prior to installation using a hexacyanoferrate II/III pH 7 redox buffer (BS870, Radiometer, Denmark).

2.3. Analytical methods

Immediately after sampling, the samples were transported to the laboratory where they were filtered through a 0.45 µm mixed cellulose ester membrane filter (ADVANTEC, Frisenette ApS, Knebel, Denmark) and stored dark and cold (3–5 °C) until analysis the following day. Ammonium (NH₄⁺-N), total P (TP) and PO₄-P were measured colorimetrically on a spectrophotometer (Shimadzu 1700, Shimadzu Corp., Kyoto, Japan) according to the Danish/European standard methods (DS/EN 11732, 2005) for NH₄⁺ and DS/EN ISO 6878 (2004) for TP and PO₄³⁻-P. NO₃⁻-N, nitrite (NO₂⁻-N) and SO₄²⁻ were analysed according to DS/EN ISO 10304 (2009) by ion chromatography (Dionex ICS-1500 IC-system) with an anion Micro Membrane Suppressor (AMMS III 4 mm) as basic eluent. The system was equipped with a guard column (IonPac AG22) and a separator column (IonPac AS22). The eluent was a mixture of 4.5 mM Na₂CO₃ and 1.4 mM NaHCO₃. All samples for ion chromatography were filtered through a double-layered 0.22 µm glass fibre filter (SNY2225, Frisenette ApS, Knebel, Denmark). Total organic carbon (TOC) and TN were both measured on a TOC-L analyser equipped with a TNM-L module (Shimadzu, Kyoto, Japan) at a temperature of 720 °C using DS/EN ISO 1484 (1997) and DS/EN 12260 (2003), respectively. Dissolved CH₄ was analysed by creating 3 ml of headspace in each vial with gaseous helium (He). Vials were shaken to allow the gases to equilibrate between headspace and liquid phases and then analysed on a gaschromatograph (GC 7890A, Agilent Technologies ApS, Santa Clara, US).

2.4. Hydraulic retention time

In 2013 and 2014, the hydraulic loading from the drainage system was distributed almost equally among the six parallel pilot SSF-CWs. During three periods in 2015–2017, the incoming drainage water was only distributed to CW1 and CW2, while the remaining four SSF-CWs received no influent water. This corresponded to a decrease of the W:C ratio to app. 0.02% from app. 0.07% and a reduction of HRT. The three periods with decreased HRT were from 07/01/15 to 10/20/15, from 09/24/16 to 10/25/16 and from 07/01/2017 to 09/13/2017.

2.5. Calculations and statistics

The theoretical daily HRT was calculated by the following equation:

$$\text{HRT} = (\text{volume} \cdot \text{porosity}) / \text{inflow} \quad (6)$$

where the unit of HRT is hour, the volume of CW is m³, porosity is m³

m⁻³ and inflow m³ hour⁻¹.

During dry periods, inflow/outflow rates close to 0 resulted in very long HRTs (> 300 h) and since there is no detection limit or uncertainty provided for the flow meter when flow rates are close to 0, we determined the lower limit by calculating the maximum curve of inflow rates (m³ hour⁻¹) plotted against HRT for each CW. The maximum curvature occurred at an HRT of 192 h, thus an HRT greater than 192 was assumed to be 192 h.

The percentage removal of NO₃⁻-N and SO₄²⁻ (in section 3.3) was calculated by the following equation:

$$\% \text{ reduction} = ((\text{Ci} - \text{Ce}) / \text{Ci}) * 100 \quad (7)$$

where Ci and Ce are the in mg L⁻¹ in influent and effluent water.

The annual percentage removal of the measured parameters (TN, TP ect.) (in section 3.6) was calculated by:

$$\% \text{ removal} = ((\text{load} - \text{loss}) / \text{load}) * 100 \quad (8)$$

where load and loss are g m⁻³ CW yr⁻¹.

For mass balance calculations we used composite samples, however grab samples were included if composite samples were not available, and linear interpolation was applied for the few periods where composite measurements or grab samples did not exist. Mass balances were generated using SAS[®] software 9.4 (SAS Institute Inc., 2013). For statistical analysis, data was only used if a sample of both influent and effluent water covering the same sampling period was available. On four occasions, composite samples of influent and effluent water of uneven length were compared. If composite samples were not taken, grab samples of influent and effluent water were used instead.

The influence of decreased HRT was evaluated by comparing periods with decreased HRT in 2015 and 2017 (07/01–09/13) with corresponding periods in 2013 and 2014 without decreased HRT. The data from 2016 was omitted as HRT was only decreased for one month (September to October). The difference between the periods was tested using a Wald test (Harrell, 2001) and included an autoregressive process of first order to adjust for auto correlation (Diggle, 1990). Statistical analysis was performed using SAS 9.4 (SAS Institute Inc., 2013).

3. Results

3.1. Hydrological and chemical characteristics of influent and effluent water

The SSF-CWs received drainage discharge during all seasons, although it was characterised by strong seasonal variations with high HLR in winter. The HLR during winter, spring, summer and autumn corresponded to 50, 21, 14 and 16% of the annual HLR in 2013 and 2014. The annual average temperature of the influent water was 9.2 ± 2.9 °C (Table 1), fluctuating seasonally with peak temperatures in August to September (12.8 to 14.7 °C) and minimum temperatures in January to February (1.1 to 1.3 °C) (Fig. 2 a). The pH of the influent water was on average slightly acid to neutral (6.5 to 7.2), while the pH of the effluent water was generally higher (7.4 to 7.5) (Table 1). The water leaving the CWs was oxygen depleted (on average 0.5 to 0.8 mg L⁻¹), while the oxygen content of the water entering the CWs ranged from 4.8 to 13.3 mg L⁻¹, with an average of 9.5 mg L⁻¹. The flow-weighted TN concentration of the influent was on average 11 mg N L⁻¹, while the effluent concentration was 6.5 mg N L⁻¹. The flow-weighted TP concentration of the influent water amounted to 0.12 mg P L⁻¹, while the effluent concentration was 0.09 mg P L⁻¹.

3.2. Nitrate and sulphate reduction

The daily percentage removal of influent NO₃⁻-N covaried with HRT and temperature (Fig. 2 a, c), being almost complete (> 98%) from early spring to autumn during the first two years of the monitoring period where HRT ranged from 25 to 192 h and effluent water

Table 1

Hydraulic retention time (HRT), temperature (Temp), oxygen content (O₂), flow-weighted total nitrogen (TN) concentration and flow-weighted total phosphorus (TP) concentration of inlet and outlet of CW1 and CW2.

	HRT	Temp	O ₂	pH	TN	TP
	hour	°C	Mg L ⁻¹		mg L ⁻¹	mg L ⁻¹
Inlet	–	9.2 ± 2.9	9.5 ± 2.9	6.9 ± 0.4	11.0 ± 0.8	0.12 ± 0.02
Outlet CW1	49 ± 35	9.3 ± 3.8	0.8 ± 1.2	7.4 ± 0.3	6.5 ± 1.5	0.09 ± 0.02
Outlet CW2	47 ± 32	9.4 ± 3.9	0.5 ± 0.6	7.5 ± 0.3	6.5 ± 1.4	0.09 ± 0.03

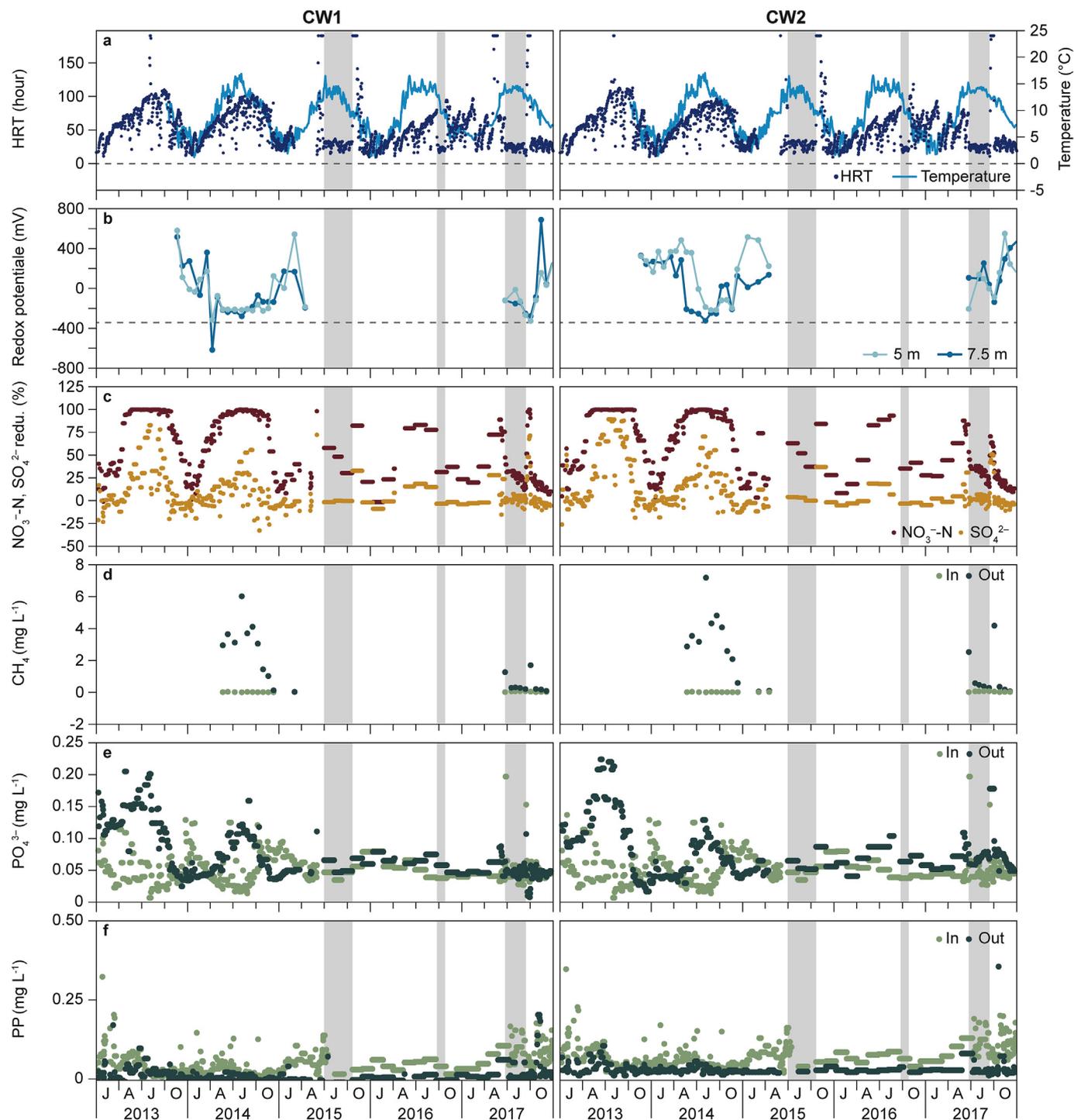


Fig. 2. Time series of hydraulic retention time (HRT) and water temperature measured in the filter beds of CW1 and CW2 (a), redox potential measured 5.0 and 7.5 m from the inlet well (b), nitrate-N (NO₃⁻-N) and sulphate (SO₄²⁻) reduction (c), methane CH₄ (d), concentration of phosphate-phosphorus (PO₄³⁻-P) (e), particulate P (PP) (f) in influent and effluent water of CW1 and CW2. Grey areas indicate the periods with decreased HRT.

temperature varied from 10.0 to 16.7 °C (Fig. 2 a, c). These periods were associated with low redox potentials (−184 to −324 mV) (Fig. 2 b) and reduction of SO_4^{2-} , which peaked in July (Fig. 2 c). In the winter months, when temperatures (1.6 to 9.6 °C) and HRT (5 to 91 h) were lower, the daily NO_3^- -N reduction rate ranged from 0 to 76%, and SO_4^{2-} reduction rarely occurred. The redox potentials (−67 to 639 mV) were mainly positive during winter. In 2015–2017, when the HRT was decreased by increasing HLR periodically, the percentage NO_3^- -N reduction ranged from 12 to 52% even though temperatures were 11 to 14 °C (grey areas in Fig. 2). The NO_3^- -N concentration of effluent water varied from 3.9 to 7.7 mg L^{−1}. In 2017 the redox potential was positive in CW2 (40 to 253 mV), but low in CW1 (−85 to −277 mV).

3.3. Methane in influent and effluent water

The effluent concentration of CH_4 was profoundly higher than the influent concentration from May to October 2014 and peaked in August where effluent concentration was 6.0 to 7.2 mg L^{−1} higher than influent (Fig. 2 d). In December, the effluent CH_4 concentration was only slightly higher than the influent. The effect of decreasing the HRT is clearly seen from Fig. 2d, by the higher CH_4 concentration in the effluent water just before and immediately after the HRT was decreased (grey areas in Fig. 2d). During the period with decreased HRT the difference between influent and effluent water was very small (0.1 to 0.5 mg L^{−1}), although the effluent CH_4 concentration was still slightly higher than the influent.

3.4. Phosphate in influent and effluent water

The difference between the influent and effluent concentration of $\text{PO}_4\text{-P}$ was greater and more variable in 2013 and 2014 than throughout the rest of the monitoring period. The effluent concentration of $\text{PO}_4\text{-P}$ was higher than the influent concentration during spring to autumn in both 2013 and 2014, the most notable difference was recorded in August 2013 (0.21 mg L^{−1}) (Fig. 2e). The influent concentration of $\text{PO}_4\text{-P}$ exceeded the effluent from October to February/March in 2014 and 2015, however only shortly in 2016 (November to January). In the periods with decreased HRT, the effluent $\text{PO}_4\text{-P}$ concentration was only 0 to 0.05 mg L^{−1} higher than the influent concentration, and on a few occasions the influent concentration was higher than the effluent. The concentration of PP was considerable higher in the influent water than in the effluent water during the major part of the study period. However on a few occasions in warm periods with long HRT (mid-June to August 2013 and September to October 2017) effluent PP concentration exceeded the influent (Fig. 2f).

3.5. Effects of decreasing hydraulic retention time

In order to evaluate the effects of decreasing the HRT, periods from 2015 to 2017 of equal length (07/01 to 09/13) were compared with similar periods in 2013 and 2014. The NO_3^- -N reduction was significantly lower in the periods with decreased HRT, however the temperature was also lower (in average 1.0 °C) (Table 2). According to the models developed in (Hoffmann et al., 2018) predicting the NO_3^- -N removal from HRT and temperature, this temperature difference would only affect NO_3^- -N removal by a few percentage (3 to 5%). Both the percentage SO_4^{2-} reduction and the difference in $\text{PO}_4\text{-P}$ concentration between the influent and effluent water were significantly lower in the periods with decreased HRT compared to the periods with long HRT (Table 2). The low sampling frequency of CH_4 measurements prevented statistical analysis; however, the difference between the influent and effluent concentrations of CH_4 was 13–21 times lower in the periods with decreased HRT compared with the periods in 2013 and 2014.

3.6. Annual efficiency and mass balances for nitrogen

The annual loading rates of TN to the CWs varied between 1454 to 2510 g N m^{−3} CW^{−1} yr^{−1}. In general, the annual TN loading rate was slightly higher to CW2 compared to CW1 due to generally higher HLR to CW2, except in 2016 (Table 3). The annual removal rates were around 689 to 938 g N m^{−3} CW^{−1} yr^{−1}. The TN loading during winter, spring, summer and autumn corresponded to 47, 24, 13 and 15% of the annual TN loading in 2013 and 2014. The percentage removal of N showed that the CWs were most efficient in 2013 and 2014 (53 to 54%) declining to 29 to 40% in years with decreased HRT (2015 and 2017). Of the total TN load to the CWs, 81 to 91% occurred as NO_3^- -N and only 0.5 to 2.9% as NH_4^+ . The NO_3^- -N removal rate varied between 611 to 804 g N m^{−3} CW^{−1} yr^{−1} (Table 3). The average daily NO_3^- -N removal rate was around 1.6 ± 1.1 to 2.4 ± 1.6 g N m^{−3} CW^{−1} d^{−1} and was slightly lower in 2017. The relative NO_3^- -N removal efficiency showed the same pattern as TN.

3.7. Annual efficiency and mass balances for phosphorus

The loading of TP to the CWs was around 14.9 to 34.4 g m^{−3} CW^{−1} yr^{−1}, peaking in 2017 (32.6 to 34.4 g P m^{−3} CW^{−1} yr^{−1}) (Table 3). The annual removal rate of TP ranged from 1.0 to 15.9 g P m^{−3} CW^{−1} yr^{−1} (0.003 to 0.044 g P m^{−3} CW^{−1} day^{−1}), except in CW1 in 2013 where a net TP release of −1.9 g P m^{−3} CW^{−1} yr^{−1} (0.005 g P m^{−3} CW^{−1} day^{−1}) was observed. The TP loading during winter, spring, summer and autumn corresponded to 61, 20, 8 and 11% of the annual TP loading in 2013 and 2014. The relative annual removal was highest in 2017 (46 to 48%) and lowest in 2013 (−10 to 5%). PP constituted 37 to 67% of the incoming annual load of TP. The absolute PP retention varied between 4.0 and 19.8 g P m^{−3} CW^{−1} yr^{−1} and was considerably higher in 2017 than in earlier years (Table 3). The annual PP removal varied from 67 to 85%, with no pronounced difference between years with and without decreased HRT. Of the incoming TP, 30 to 60% was in the form of $\text{PO}_4\text{-P}$. In contrast to PP, there was a net annual release of $\text{PO}_4\text{-P}$ in 2013, 2016 and 2017 from both CW1 and CW2 (Table 3), however in 2014, 2015 net retention ranged from 0.5 to 1.5 g P m^{−3} CW^{−1} yr^{−1}.

4. Discussion

4.1. Effects on nitrate, sulphate and methane by decreased hydraulic retention time

During the first two years of the study, the SSF-CWs generated adverse side effects such as CH_4 during warm periods with low flow (Bruun et al., 2017). These periods were associated with complete NO_3^- -N removal and SO_4^{2-} reduction. To avoid the generation of such side effects, HRT was decreased (July to September) in 2015 and 2017. As expected, this led to a significant reduction of percentage NO_3^- -N removal, and concomitantly a significant reduction of the percentage SO_4^{2-} reduction (equation (3)) and CH_4 production (equation (5a) and (5b)). This is in agreement with a study on a SSF-CW receiving glass-house waste water, revealing negligible production of dissolved CH_4 due to high concentrations of NO_3^- (Warneke et al., 2011). Studies of other systems e.g. rice fields have also shown that the presence of NO_3^- suppresses CH_4 production (Klüber and Conrad, 1998). It should also be emphasised, though, that we only investigated dissolved CH_4 exported via effluent water, which according to Bruun et al. (2017) comprised 37 to 45% of the total annual CH_4 emission (direct + indirect) at our experimental site. Although this aspect was not investigated in our study, we expect direct emission to be lower considering the presence of NO_3^- and SO_4^{2-} , as Bruun et al. (2017) found a negative correlation of CH_4 emission with HLR and SO_4^{2-} concentration in effluent water. Additionally, the water level of the filter bed was lowered, to promote oxidation of CH_4 . Thus, our study demonstrated that indirect

Table 2

Temperature (Temp) and hydraulic retention time (HRT), and statistical analysis of the percentage reduction of the load of nitrate-N (NO_3^- -N) and sulphate (SO_4^{2-}), difference between influent and effluent concentration of phosphate-P (PO_4^{3-} -P) and methane (CH_4) in periods with decreased HRT (IH) (07/01 to 09/13 in 2015 and 2017) and without decreased HRT (CH) (07/01 to 09/13 in 2013–2014) for CW1 and CW2. * indicate if the difference was significant.

CW1		CW2									
		n (CH, IH)	Mean (CH)	Mean (IH)	χ^2	p	n (CH, IH)	Mean (CH)	Mean (IH)	χ^2	p
Temp ^{Inlet}	°C	75, 149	13.5 ± 0.9	12.5 ± 0.4			75, 149	13.5 ± 0.9	12.5 ± 0.4		
Temp ^{Outlet}	°C	75, 149	14.5 ± 1.4	13.7 ± 0.9			75, 149	14.3 ± 1.4	13.6 ± 0.8		
HRT	hour	150, 150	82 ± 25	11 ± 4			150, 150	78 ± 19	11 ± 6		
NO_3^- -N	%	25, 26	99.0 ± 1.2	25.2 ± 7.6	1749	*	26, 26	98.8 ± 2.0	30.9 ± 7.6	281	*
SO_4^{2-}	%	25, 26	32.3 ± 24.8	0.9 ± 3.9	35	*	26, 26	52.5 ± 25.8	1.50 ± 3.9	86	*
PO_4^{3-} -P	$\mu\text{g L}^{-1}$	25, 26	-94 ± 36	-1 ± 30	65	*	26, 26	-91 ± 41	-21 ± 3	27	*
CH_4	mg L^{-1}	3, 3	-4.27 ± 1.54	-0.20 ± 0.05			3, 3	-4.86 ± 2.07	-0.36 ± 0.10		

Table 3

Average annual temperature (Temp), hydraulic retention time (HRT) and outflow of water and annual loading, loss, absolute and percentage removal (of load) of total nitrogen (TN), nitrate-N (NO_3^- -N), ammonium-N (NH_4^+ -N), total phosphorus (TP), particulate P (PP), suspended sediment (SS) and phosphate-P (PO_4^{3-} -P) during 2013–2017 in CW1 and CW2.

		CW1					CW2				
		2013	2014	2015 ^a	2016	2017	2013	2014	2015 ^a	2016	2017
Temp	Outlet °C	–	9.6 ± 4.1	9.0 ± 3.5	9.2 ± 4.3	9.5 ± 3.3	–	9.7 ± 4.0	9.2 ± 3.5	9.2 ± 4.4	9.6 ± 3.7
HRT	Outlet hour	60 ± 30	56 ± 25	45 ± 52	38 ± 19	48 ± 47	59 ± 31	53 ± 24	40 ± 47	41 ± 21	42 ± 36
Water	Outlet $\text{m}^3 \text{m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	1391	1422	1776	2071	2043	1446	1518	1905	1928	2093
TN	Inlet $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	1454	1462	1884	2510	2360	1513	1558	2005	2341	2415
	Outlet $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	686	686	1196	1572	1684	694	715	1223	1403	1631
	Removal $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	768	776	689	938	676	819	843	781	938	784
	Removal %	53	53	37	37	29	54	54	39	40	32
NO_3^- -N	Inlet $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	1377	1325	1633	2047	2128	1431	1413	1742	1910	2179
	Outlet $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	621	592	1021	1271	1530	626	616	1069	1146	1475
	Removal $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	2.1 ± 0.9	2.0 ± 0.8	2.2 ± 1.7	2.1 ± 1.6	1.6 ± 1.1	2.2 ± 0.9	2.2 ± 0.9	2.4 ± 1.6	2.1 ± 1.5	1.9 ± 1.3
	Removal %	756	733	611	776	598	804	797	673	764	704
	Removal %	55	55	37	38	28	56	56	39	40	32
NH_4^+ -N	Inlet $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	11	9	32	18	8	11	10	35	17	8
	Outlet $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	8	10	18	13	6	8	13	9	5	5
	Removal $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	3	–1	15	5	1	3	–3	26	11	3
	Removal %	25	–10	45	27	18	29	–32	75	68	42
TP	Inlet $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	18.2	14.9	20.0	22.1	32.6	19.2	16.0	21.9	20.4	34.4
	Outlet $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	20.1	10.3	12.2	16.6	17.0	18.2	10.4	13.0	15.4	18.5
	Removal $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	–1.9	4.6	7.8	5.5	15.6	1.0	5.6	8.9	5.0	15.9
	Removal %	–10	31	39	25	48	5	35	41	24	46
PO_4^{3-} -P	Inlet $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	8.1	9.0	10.5	11.7	9.9	8.5	9.6	11.3	10.8	10.1
	Outlet $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	15.8	8.2	10.0	13.5	10.0	14.4	8.1	10.7	12.9	14.2
	Removal $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	–7.7	0.8	0.5	–1.8	–0.2	–5.9	1.5	0.6	–2.1	–4.1
	Removal %	–95	9	5	–16	–2	–70	16	5	–20	–40
PP	Inlet $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	8.9	5.5	8.4	9.6	21.7	9.4	5.9	9.3	8.8	23.2
	Outlet $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	2.9	1.5	1.3	2.3	6.1	1.9	1.5	1.4	1.5	3.4
	Removal $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	6.0	4.0	7.2	7.3	15.6	7.5	4.4	8.0	7.3	19.8
	Removal %	67	73	85	76	72	80	75	85	83	85
SS	Inlet $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	1512	958	1400	1994	5492	1597	1037	1499	1843	5967
	Outlet $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	202	133	130	237	710	173	136	133	508	521
	Removal $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	1310	825	1270	1758	4782	1424	902	1365	1335	5446
	Removal %	87	86	91	88	87	89	87	91	72	91
SO_4^{2-}	Inlet $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	3530	3630	4345	4846	5153	3664	3869	4637	4516	5285
	Outlet $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	3269	3444	4267	4721	5072	3141	3541	4715	4475	5216
	Removal $\text{g m}^{-3} \text{CW}^{-1} \text{yr}^{-1}$	262	187	78	125	80	523	328	–78	42	69
	Removal %	7	5	2	3	2	14	8	–2	1	1

^a Measurements from spring 2015 was omitted, due to a tracer experiment conducted by Bruun et al. (2016b).

production of CH_4 via effluent water can be suppressed considerably by ensuring that more energetically favourable TEAs, such as NO_3^- or SO_4^{2-} are not completely removed.

Despite that the NO_3^- -N effluent concentrations was above 3.4 mg N L^{-1} in these periods, SO_4^{2-} reduction and CH_4 production still occurred, although at a somewhat low rate. The concurrent NO_3^- -N and SO_4^{2-} reduction and CH_4 production in our study might be facilitated by non-equilibrium solute transport, which takes place in these SSF-CWs as documented by Bruun et al. (2016b). The consequence of non-equilibrium solute transport is a spatial distribution in solute residence time, as the solute transport between woodchips is

characterised by dispersion-convection, while diffusion controls the solute exchange between the woodchips and the voids within the woodchips (Van Genuchten and Wierenga, 1977; Van Genuchten and Wierenga, 1976). In other studies of SSF-CWs SO_4^{2-} reduction only occurred when the reactors were NO_3^- -N depleted (Robertson and Merkley, 2009; Christianson et al., 2012a). More specifically, Robertson and Merkley (2009) found that SO_4^{2-} reduction was inhibited when the NO_3^- -N concentrations of the filter material of in-stream reactors exceeded 0.5 mg N L^{-1} . A possibly explanation of these divergent observations, might be the degree of non-equilibrium solute transport in the SSF-CWs, as hydraulic design differed. Other studies of SSF-CWs

have found that models taking non-equilibrium flow into account describe the NO_3^- -N transportation well (Jaynes et al., 2016; Herbert, 2011). More research is needed on the non-equilibrium flow in SSF-CWs as it seems that non-equilibrium flow has considerable impact on the N transportation and the potential side effects.

4.2. Effects on phosphate by decreased hydraulic retention time

The difference between effluent and influent PO_4 -P concentrations was significantly lower in periods with decreased HRT than in similar periods with longer HRT. However, the effluent PO_4 -P concentration was still slightly higher than the influent concentration. In wetlands, P can be retained by immobilization, plant uptake, adsorption, precipitation and sedimentation, and released by decomposition/mineralisation, desorption and dissolution. Since the various transformation processes inside the filter bed are unknown in this study, it is difficult to assess the underlying reason for the lower difference between effluent and influent concentrations. In addition, the interactions between the different processes acting in the filter bed may change over time, rendering between-year comparisons uncertain when using a black box approach.

Thus, the smaller difference between effluent and influent PO_4 -P concentration is either a result of lower release of P (e.g. mineralisation rates decreasing over time) or a higher retention of P (e.g. incoming sorption sites, plant uptake), or a mixture.

Theoretically, the decrease of HRT should lower the release of redox sensitive PO_4 -P, either by suppression of Fe reduction (equation (1) and (2)) due to the presence of TEAs or lowering of the SO_4^{2-} reduction leading to a reduced production of H_2S , which can mediate the Fe-bound P release (equation (4)) (Lamers et al., 1998; Roden and Edmonds, 1997). Another potential consequence of low redox conditions is release of PP, which we observed at a few occasions. Even though sedimentation is considered one of the long-term retention processes in wetlands (Reddy et al., 1999; Howard-Williams, 1985), the deposited PP can be transformed to soluble forms, for instance under low redox conditions. However, when HRT was decreased, PP release was not observed.

4.3. Annual N removal rates and efficiencies

The daily N removal rates of 1.6 to 2.4 $\text{g N m}^{-3} \text{ CW}^{-1} \text{ day}^{-1}$ recorded in this study are within the lower range of removal rates (0.4 to 7.8 $\text{g N m}^{-3} \text{ CW}^{-1} \text{ day}^{-1}$) reported in a review of SSF-CWs receiving water from drainage systems (Christianson et al., 2012b). Comparisons of absolute N removal rates across studies are rather ambiguous as they often differ in hydraulic design, hydrological regime, microbial community composition, climate, filter material etc. although, the removal N rate is primarily depended temperature and HRT (Christianson et al., 2012b). Thus, the seasonal variation in HLR and temperature might explain why our removal efficiency is in the lower end of the range, as approximately half of the annual N loading occurred in the winter months (December–February). During winter the conditions for denitrification were not optimal due to low temperature and short HRT. In order to deal with both peak flow and short HRT during winter, storage basins have to be added to the newly established SSF-CWs (Hoffmann and Kjærsgaard, 2017). The active decrease of HRT during summer to autumn in 2015 and 2017 led to an annually lower relative TN removal efficiency, which was expected since periods with 100 %TN removal did not occur in these years. The absolute removal rate was lower by in average 126 $\text{g N m}^{-3} \text{ CW}^{-1} \text{ yr}^{-1}$, which we consider a low “price” for reduction of negative side effects. However, the cost in terms of removal efficiency might be higher as the periods should preferably have been slightly longer in order to avoid CH_4 emission in spring and autumn.

4.4. Annual phosphorus removal efficiencies

The pilot SSF-CWs were primarily designed to optimise N removal, but as P loss from agriculture may cause eutrophication in P-limited systems, such as lakes, streams and estuaries (in spring), P will most likely be an object of intensified management concern in the coming years. The potential of P removal in SSF-CWs with woodchips is less studied than the removal of N. In our study, the P balance might be more uncertain in the periods (mid-2015 to mid-2017) where time proportional sampling was applied, as the influent P concentration is depended on the prevailing flow. However, we reckon that the high temporal sampling frequency ensured a representative concentration. The two SSF-CWs used in this study acted as efficient PP traps, if periods with very long HRT (> 192 h) was avoided. Annually, they retained 57 to 88% of the incoming PP. However with respect to PO_4 -P, the SSF-CWs acted as both sink and source. The net release of PO_4 -P was especially high during the first year, which might be due to PO_4 -P leaching from the woodchips, as the SSF-CWs were not in contact with soil. It therefore seems that the current design is not an optimal solution for PO_4 -P removal. Thus, to mitigate PO_4 -P leaching from agricultural drainage water, SSF-CWs should be used in combination with an amendment added directly to the woodchips or a separate P filter, as suggested in other studies (Christianson et al., 2017; Ballantine and Tanner, 2010). Although during the entire monitoring period, the SSF-CWs retained 29–33% of the total TP loading.

4.5. Concluding remarks

The seasonal decrease of HRT to 11 h on average during summer to autumn in 2015 and 2017 led to a considerable lower NO_3^- -N and SO_4^{2-} percentage reduction than in preceding years where HRT was 82 h on average. Concurrently this resulted in a considerable decrease in the difference between the effluent and influent concentration of PO_4 -P and CH_4 concentrations compared to preceding years. For CH_4 this was most likely due to suppression of methanogens, but with respect to PO_4 -P the underlying reason cannot be assessed. Even though more energetically favourable TEAs such as NO_3^- -N were present SO_4^{2-} reduction and CH_4 production still occurred, which could potentially be ascribed to non-equilibrium transport in the filter beds. Our study emphasises the importance of the design of SSF-CWs treating agricultural drainage water in order to diminish the deleterious side effects during warm periods with low flow. Thus, the treatment capacity of the SSF-CWs should be adjustable according to specific needs, for instance by using inlet and outlet control structures or designing individual SSF-CWs in series or in parallel. The specific needs and the actions required will be depended on the site and the seasonal variation in run off.

The N removal rate and efficiency observed in our study were comparable with results reported from other SSF-CWs. Our SSF-CWs showed a relatively high potential for PP retention in the absence of periods with long HRT (> 192 h). However, with respect to PO_4 -P, both net annual release and retention appeared. Therefore, to obtain a higher PO_4 -P removal efficiency and avoid SSF-CWs acting as P sources, the SSF-CWs should be combined with a separate P filter. Over five years the SSF-CWs retained 29–33% of total TP loading. Our study clearly demonstrated that complete NO_3^- -N removal in SSF-CWs should be avoided in order to minimise the generation of adverse side effects. Accordingly, the management and design of SSF-CWs require a holistic approach to take into consideration the various negative side effects associated with SSF-CWs.

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STØTTET AF

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