

## Research article

## Pilot-scale hybrid constructed wetlands for the treatment of cooling tower water prior to its desalination and reuse

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## ABSTRACT

Cooling towers are responsible for a large part of the industrial fresh water withdrawal, and the reuse of cooling tower water (CTW) effluents can strongly lower industrial fresh water footprints. CTW requires desalination prior to being reused, but various CTW components, such as total organic carbon (TOC), conditioning chemicals and total suspended solids (TSS) hamper physico-chemical desalination technologies and need to be removed from the CTW. A cost-efficient and robust pre-treatment is thus required, which can be provided by constructed wetlands (CWs). The present study is the first study that determined the CTW pre-treatment efficiency of hybrid-CWs and the impact of winter season and biocides in the CTW on the pre-treatment efficiency. The most efficient CW flow type and dominant removal mechanisms for CW components hampering physico-chemical desalination were determined. Subsurface flow CWs removed  $\text{PO}_4^{3-}$ , TSS and TOC as a result of adsorption and filtration. Vertical subsurface flow CWs (VSSF-CW) excelled in the removal of benzotriazole as a result of aerobic biodegradation. Horizontal subsurface flow CWs (HSSF-CW) allowed the denitrification of  $\text{NO}_3^-$  due to their anaerobic conditions. Open water CWs (OW-CWs) did not contribute to the removal of components that hamper physico-chemical desalination technologies, but do provide water storage options and habitat. The biological removal processes in the different CW flow types were negatively impacted by the winter season, but were not impacted by concentrations of the biocides glutaraldehyde and DBNPA that are relevant in practice.

For optimal pre-treatment, a hybrid-CW, consisting of an initial VSSF-CW followed by an OW-CW and HSSF-CW is recommended. Future research should focus on integrating the hybrid-CW with a desalination technology, e.g. reverse osmosis, electrodialysis or capacitive ionization, to produce water that meets the requirements for use as cooling water and allow the reuse of CTW in the cooling tower itself.

## 1. Introduction

Human intervention in water catchments has severely aggravated downstream fresh water scarcity over the last 40 years (Veldkamp et al., 2017) and especially delta areas around the globe experience significant fresh water stress (Yao et al., 2015; Mekonnen and Hoekstra, 2016). Delta areas are hotspots for the industry because of the good connection between sea and hinterland, and these industries are responsible for a substantial part of the fresh water withdrawal in industrialized delta areas. A large part of this fresh water is used for process cooling in

cooling towers. After the cooling tower water (CTW) reaches a mineral concentration threshold, the CTW is generally discharged to the surface water without further treatment, and new fresh 'make-up' water is taken in. The treatment and reuse of CTW in the cooling tower could prevent water scarcity and unwanted environmental problems and lower the fresh water footprint of cooling towers (Pan et al., 2018).

To reuse the CTW, it needs to comply with various water quality requirements, such as limited concentrations of  $\text{PO}_4^{3-}$ , total organic carbon (TOC) and total suspended solids (TSS) (Groot et al., 2015; Pan et al., 2018). In addition, the electric conductivity (EC) of the CTW needs

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to be lowered, and therefore desalination of the CTW is required. However, the desalination of CTW is hindered by the presence of different constituents in the CTW, such as TOC, TSS,  $\text{PO}_4^{3-}$  and conditioning chemicals, for instance by fouling of reverse osmosis membranes (Groot et al., 2015; Löwenberg et al., 2015). Proper pre-treatment of discharged CTW could significantly improve the desalination efficiency of physico-chemical desalination technologies, and several pre-treatment methods have been reviewed recently (Löwenberg and Wintgens, 2017; Pramanik et al., 2017; Wagner et al., 2018). Constructed wetlands (CWs) could be a suitable nature-based pre-treatment option for CTW (Wagner et al., 2018).

CWs are man-made wetland systems in which natural removal mechanisms remove contaminants from water, such as biodegradation, adsorption, photodegradation and plant uptake, (Garcia et al., 2010). The water flow type of the CW determines the contribution of the various removal mechanisms. A distinction can be made between surface flow CWs, in which photodegradation and biodegradation are the dominant removal mechanisms (Jasper and Sedlak, 2013) and subsurface flow CWs, in which adsorption, plant uptake and biodegradation prevail (Garcia et al., 2010). A combination of CWs with different water flow types in so-called hybrid-CWs has shown to perform well for the treatment of wastewater streams containing contaminants with differing characteristics, such as CTW, as a result of the simultaneous functioning of the different removal mechanisms (Avila et al., 2015). In addition to the removal of components that hinder physico-chemical CTW desalination, CWs provide additional benefits: CWs provide a natural habitat that can increase the local biodiversity and CWs enable the storage of large volumes of fresh water that could be used in periods when fresh water is less available.

The use of CWs for CTW-treatment to lower the cooling tower fresh water footprint has not been described in the scientific literature before. The present study is the first to study CTW treatment in CWs and the pre-treatment efficiency of CWs before physico-chemical desalination. In previous studies, we investigated the potential of different separate CW removal mechanisms for the removal of CTW conditioning chemicals (Wagner et al., 2020a, 2020b; 2020c). The main goal of the present study is to determine the efficiency of the combination of these mechanisms in hybrid-CWs for the pre-treatment of CTW in the temperate sea-climate of Western-Europe. Therefore, pilot-scale hybrid-CWs were constructed and fed with synthetic CTW. With this set-up, we aimed to answer the following research questions: i) Do hybrid-CWs remove CTW fractions that hamper physico-chemical desalination? ii) What are the dominant removal mechanisms responsible for removing these fractions? iii) What is the influence of the winter season in the temperate marine climate of Western-Europe on the removal efficiency (RE) of the hybrid-CW? iv) What is the influence of biocides in the CTW on the RE of the hybrid-CW? v) Is there an optimal sequence of CWs with different water flow types in a hybrid-CW set-up for the pre-treatment of CTW?

## 2. Materials & methods

### 2.1. Chemicals

$\text{NaNO}_3$  (>99%),  $\text{CaCl}_2$  (>94%),  $\text{Na}_2\text{SO}_4$  (>99%),  $\text{KH}_2\text{PO}_4$  (>99%), humic acid (sodium salt) (45–70%), benzoic acid (>99.5%) and benzotriazole (>99%) for the preparation of synthetic CTW were obtained from Carl Roth GmbH (Karlsruhe, Germany). DBNPA, glutaraldehyde, methanol (UHPLC-grade), formic acid and acetic acid (100%) were obtained from Sigma-Aldrich (Zwijndrecht, The Netherlands).

### 2.2. Hybrid constructed wetlands

Six hybrid-CWs consisting of three CW compartments each were placed in three 12 m<sup>2</sup> polyethylene (PE) basins that were dug into the ground next to the Department of Environmental Technology of Wageningen University and Research (Wageningen, The Netherlands)

(Fig. 1). Each PE basin contained two different hybrid-CWs, and each hybrid-CW consisted of a vertical subsurface flow CW (VSSF-CW), horizontal subsurface flow CW (HSSF-CW) and an open water flow CW (OF-CW). All six possible hybrid-CWs orders were tested (Fig. 1). The current set-up allowed for both obtaining sound insights into the contribution of different removal mechanisms in the different CW flow types in the duplicate first compartments, and determining the removal efficiency of the total hybrid-CW.

The VSSF-CW was 96 × 143 × 97 cm and contained a water collection basin of 20 × 20 × 96 cm where the pump was placed. Water was pumped from this basin to the next compartment. The collection basin was connected to the CW with a drainage tube. The bottom of the VSSF-CW was filled with 16–32 mm gravel until it completely covered the drainage tube. Sand with a diameter >250 µm was placed on top. Subsequently, the system was covered with 16–32 mm gravel to prevent sand blow out and planted with *Phragmites australis*. The VSSF-CWs were batch-fed and the water was distributed over the top of the CW by perforated tricoflex tubing.

The HSSF-CW was 145 × 145 × 39 cm. The collection basin was 20 × 145 × 39 cm and was connected with the CW by a drainage tube. Gravel with a size of 16–32 mm was placed at the collection side of the horizontal flow CW until the drainage tube was covered. The rest of the compartment was filled with sand with a diameter >250 µm and covered with 16–32 mm gravel. The HSSF-CWs were planted with *Phragmites australis*. The influent was distributed at the influent side of the HSSF-CW with perforated tricoflex tubing.

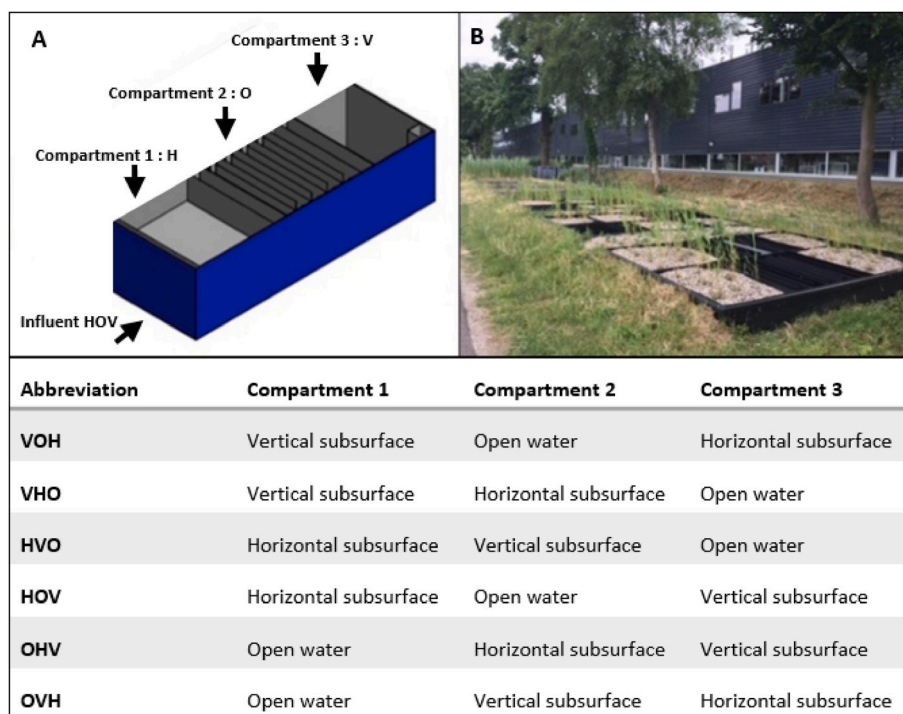
The open water flow CW (OW-CW) was 145 × 145 × 30 cm and the collection basin was 20 × 145 × 30 cm. The water flow was guided by PE baffles. No sediment was placed on the bottom of the open OW-CW. However, natural deposition of plant remains on the bottom occurred, also providing space for microorganisms to grow.

The hybrid-CWs were constructed in November 2016. *Phragmites australis* was planted in December 2016. The invasion of other plant species was not prevented. Synthetic fertilizer was added in spring 2017. The hybrid-CWs were allowed to develop during 2017, solely fed on rain water. In January 2018, the separate compartments were interconnected by pond pumps that were connected to LOGO! automation software (Siemens, Amersfoort, the Netherlands) that determined the pumping frequency and time of each pump. After the water distribution system and pumps were installed, the hybrid-CWs were connected to tap water and the pumping regime was installed in LOGO! and tested. After the pumping regime was under control, evidenced by the absence of water overflow and the continuous presence of water in the collection basins, the hybrid-CWs were fed with synthetic CTW (paragraph 2.3) from August 8th, 2018 until June 18th, 2019. The system was allowed to adjust to the CTW by providing it with a CTW which was diluted twice for the first 14 days.

### 2.3. Synthetic cooling tower water

The composition of the synthetic CTW (Table 1) was based on the composition of CTW that is discharged by the cooling towers of the ELSTA power generation facilities (Terneuzen, The Netherlands) and which has been described before by Löwenberg et al. (2015) and Groot et al. (2015).

The synthetic CTW was prepared in tap water. A 5x concentrated stock solution was prepared in a 3 m<sup>3</sup> tank stored outdoors. Fresh concentrated synthetic CTW was made every 7 days. This concentrated solution was pumped into a dilution tank where it was diluted 5x with tap water. Each hybrid-CW received approximately 160 L of CTW daily. From the dilution tank, it was pumped into the first compartment of each hybrid-CW at a continuous rate of 110 mL/min for the OW-CWs and HSSF-CWs. The VSSF-CW was batch fed 4x/d with 40 L each time at a rate of 1368 mL/min. The second and third compartment of the hybrid-CW were fed by the pond pumps. The VSSF-CWs were batch-fed 4x/d with 40 L per episode. The HSSF-CWs were semi-continuously fed



**Fig. 1.** Design of the six different hybrid constructed wetlands (CW) with a combination of a vertical subsurface flow CW (V), horizontal subsurface flow CW (H) and open water flow CW (O). The schematic figure (A) provides an example of the HOV hybrid-CW, while picture (B) gives an overview of all 6 hybrid-CWs at location.

**Table 1**  
Characteristics of synthetic cooling tower water.

| Composition                     |           | General water quality parameters |             |
|---------------------------------|-----------|----------------------------------|-------------|
| Na <sub>2</sub> SO <sub>4</sub> | 1660 mg/L | Temperature                      | 15 °C       |
| CaCl <sub>2</sub>               | 830 mg/L  | pH                               | ~7.2        |
| NaNO <sub>3</sub>               | 83 mg/L   | EC                               | ~3200 µS/cm |
| KH <sub>2</sub> PO <sub>4</sub> | 10 mg/L   | TSS                              | ~121 mg/L   |
| Humic acid                      | 50 mg/L   | TDS                              | ~2300 mg/L  |
| Benzoic acid                    | 50 mg/L   | TOC                              | ~15 mg/L    |
| Benzotriazole                   | 1 mg/L    | PO <sub>4</sub> <sup>3-</sup>    | ~4 mg/L     |
|                                 |           | NO <sub>3</sub> <sup>-</sup>     | ~40 mg/L    |

24x per day with 8.3 L per episode. The OW-CWs were batch-fed 8x/d with 20 L per episode.

#### 2.4. Experimental phases

To answer our five research questions, the experimental period was divided in four phases (Table 2).

The hydraulic retention time (HRT) of the hybrid-CWs was estimated using the breakthrough of the EC after the influent of the hybrid-CWs was switched from tap water with an EC of  $\pm 500$  to the twice diluted CTW with an EC of  $\pm 1600$  µS/cm. The HRT was defined by the time for the effluent EC to reach an value of 1100 µS/cm. Samples for EC determination were taken from the influent and the 18 different compartments at t (hour): 0, 22, 28, 46, 52, 72, 96, 118, 124, 142, 148, 166, 172, 192, 216 and displayed in the supplementary information (SI) (Fig. S1). The HRT of the 6 hybrid-CWs was between 120 and 166 h (Fig. S1). The pumps in hybrid-CW HOV, OHV, OVH and VHO were adjusted to match the HRT of  $\pm 120$  h of hybrid-CW VOH and HVO. In addition to the HRT of the complete hybrid-CW, the HRTs of the compartments could be determined. These were  $\pm 40$  h for the VSSF-CW,  $\pm 35$  h for the HSSF-CW and  $\pm 55$  h for the OW-CW (Fig. S1).

After the HRT-determination, the baseline REs for the parameters mentioned in Table 2 were determined during late summer and autumn. On the 4th of December, 2018, the vegetation in the CWs was cut and

**Table 2**  
Overview of different experimental phases.

| Phase  | Period (start – end)                       | Parameters analysed  |
|--|--|--|
| Acclimatization to cooling tower water and HRT <sup>a</sup> determination  | August 8th, 2018<br>September 18th, 2018   | EC   |
| Baseline removal efficiency  | September 19th, 2018<br>December 3rd, 2018 | EC, pH, TOC, TSS, TDS, PO <sub>4</sub> <sup>3-</sup> , NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , turbidity, benzotriazole, benzoic acid              |
| Winter season  | December 4th, 2018<br>March 25th, 2019     | EC, pH, TOC, TSS, TDS, PO <sub>4</sub> <sup>3-</sup> , NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , turbidity, benzotriazole, benzoic acid              |
| The impact of biocides   | March 26th, 2019<br>June 19th, 2019        | EC, pH, TOC, PO <sub>4</sub> <sup>3-</sup> , NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , turbidity, benzotriazole, benzoic acid, glutaraldehyde, DBNPA |
| <ul style="list-style-type: none"> <li>• 5 mg/L glutaraldehyde</li> <li>• 1 mg/L DBNPA</li> <li>• 5 mg/L glutaraldehyde + 1 mg/L DBNPA</li> <li>• 50 mg/L glutaraldehyde</li> <li>• 10 mg/L DBNPA</li> <li>• 50 mg/L glutaraldehyde + 10 mg/L DBNPA</li> </ul> |  |  |

<sup>a</sup> Hydraulic retention time.

left on top of the CW for isolation. This marked the start of the winter season (Table 2). After the winter season, the impact of a low (5 mg/L) and high (50 mg/L) concentration of the biocides glutaraldehyde and DBNPA and their mixture on the RE of the hybrid-CWs was determined during spring (Table 2). Therefore, the biocides were added to the CTW that was fed to the hybrid-CWs twice per week. Biweekly addition of the biocide-containing CTW to the hybrid-CW was performed to represent the shock-dosing of biocides during cooling tower operation (Klaine et al., 1996), which leads to periods with and without biocides in the CTW. This biweekly feeding of biocide-containing CTW was performed with 25% of the daily volume of CTW that the hybrid-CWs received.

## 2.5. Sampling

Liquid grab samples were manually collected every Monday in 50 mL polypropylene tubes. Samples were taken from the influent, the concentrated CTW and from every collection basin of the hybrid-CWs. After collection, samples were immediately prepared for various analyses (section 2.6). During the determination of the impact of biocides on the hybrid-CWs, samples were taken on day 1, 2, 3 and 4 after biocide addition.

## 2.6. Analyses

### 2.6.1. Weather conditions and general water quality parameters

Temperature and rainfall data were obtained online from a nearby weather station and provided in Figs. S2 and S3. The water temperature, pH and EC were measured with a Radiometer Analytical PHM210 (Villeurbanne Cedex, France) that was calibrated before use. Turbidity was measured by a WTW Turb 550 (Weilheim, Germany). TSS and TDS were measured gravimetrically by filtration over a 0.2 µm polycarbonate filter (Merck, Darmstadt, Germany) and subsequent evaporation at 105 °C during the first 22 experimental weeks for the effluent of the total hybrid-CW. TOC was measured on a TOC-L<sub>CPH</sub> analyser connected to an ASI-L autosampler (Shimadzu, 's Hertogenbosch, The Netherlands). A 680 °C catalytic oxidation – non dispersive infrared detection method was used. Data acquisition and analysis were performed in Shimadzu TOC-Control.  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$  were measured by ion chromatography (IC) on an ICS 2100 (Dionex, Breda, The Netherlands) equipped with a Dionex IonPac AS19 column (4 × 250 mm) using a hydroxide gradient. Prior to IC analysis, samples were filtered over 0.2 µm polyethersulfone (PES) filters.

### 2.6.2. Benzotriazole, benzoic acid and glutaraldehyde

All samples were filtered over 0.2 µm PES filters. Samples for benzotriazole analysis were diluted 100x and analysed by HPLC-MS/MS as described by Wagner et al. (2020a). Samples for benzoic acid analyses were acidified with 1% (v: v) acetic acid and analysed by HPLC-DAD as described by Wagner et al. (2020b). Samples for glutaraldehyde were analysed by colorimetry as described by Wagner et al. (2020b). Samples for DBNPA analysis were analysed on the HPLC-MS/MS that was used for benzotriazole, using the same mobile phases and a 4.5 min gradient elution method with an increase from 10% B to 100% B in 2 min, 100% B for 2 min and a decrease from 100% B to 10% B in 0.5 min. DBNPA was identified by multiple reaction monitoring using fragment ions 241/198 and 241/119.

## 2.7. Data analysis

The cumulative removal efficiency of each compartment of the hybrid-CWs was calculated by comparing the average effluent concentration of each compartment ( $C_{\text{out}}$ ) with the average influent concentration during the experimental period ( $C_{\text{in}}$ ) according to equation (1) (Eq. (1)).

$$\text{Removal efficiency (\%)} = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100 \quad (1)$$

Technical malfunction resulted in non-representative influent and effluent concentrations in weeks 7, 23, 24 and 37. The influent and effluent concentration from these weeks were omitted from the data analysis.

## 3. Results and discussion

### 3.1. Baseline removal efficiency

The effluents of the all the compartments of the hybrid-CWs were analysed for EC,  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , TOC, TSS, TDS, turbidity, benzoic

acid and benzotriazole because these are critical CTW components that could hamper physico-chemical desalination and re-use of CTW in the cooling tower. The EC is the most important reuse parameter for potential make-up water and should be below 1000 µS/cm for the water to be suitable for direct reuse in the cooling tower (Groot et al., 2015). However, the EC of the CTW did not change after any of the hybrid-CW pre-treatments (Fig. 2). The EC followed the influent fluctuations throughout all six hybrid-CWs (Fig. S4), which justifies its use as HRT tracer as described in section 2.4.1. The EC is the result of the salts contained in the CTW, and since the salts made up a large part of the TDS, the TDS trend followed the EC trend during the first 22 weeks of operation (Fig. S5). Hence, CWs are not suitable as stand-alone treatment for the desalination of CTW and physico-chemical desalination of the CTW is still needed. However, several components that hinder physico-chemical desalination of the CTW were removed during pre-treatment by the hybrid-CWs, such as  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{PO}_4^{3-}$ , turbidity, TSS, benzoic acid and benzotriazole (Fig. 2).

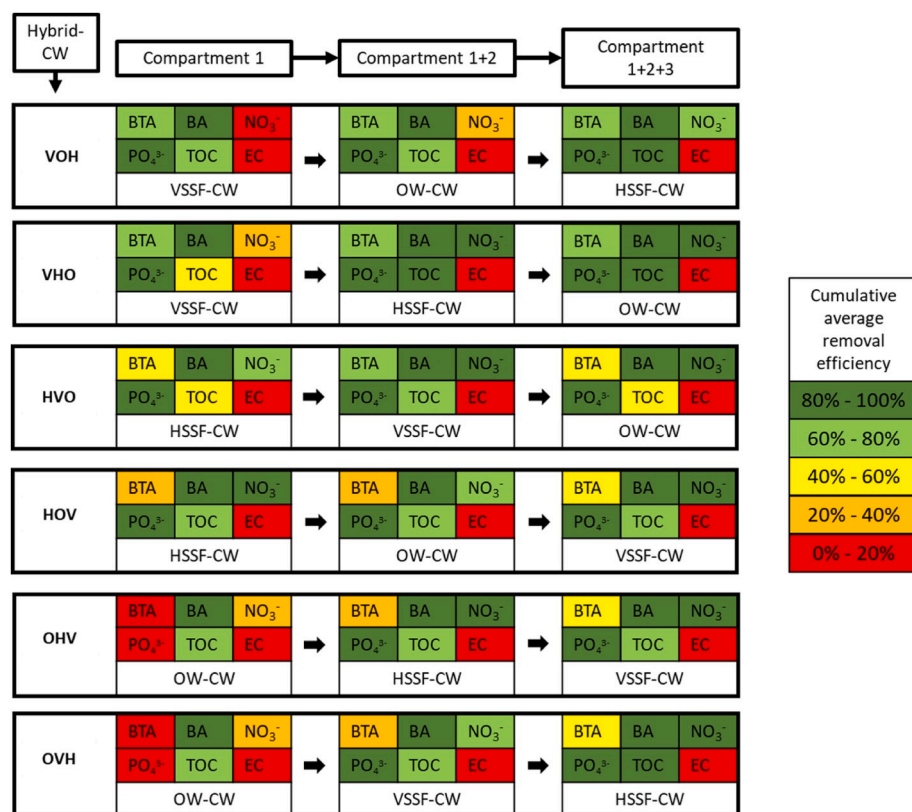
$\text{NO}_3^-$  was completely removed in all hybrid-CWs, as can be deduced from the RE of compartment 1 + 2+3 of each hybrid-CW, which equals the RE of the complete hybrid-CW (Fig. 2 and S6). The REs in the duplicate VSSF-CW, HSSF-CW and OW-CW first compartments of the hybrid-CWs allow the determination of the CW flow-type with the highest RE. The  $\text{NO}_3^-$  RE in the first compartments of the hybrid-CWs was the highest in the HSSF-CWs (Fig. 2 and S6) and these HSSF-CWs completely removed all  $\text{NO}_3^-$  (Fig. S6). The  $\text{NO}_3^-$  removal in the OW-CW was higher than in the VSSF-CW (Fig. 2 and S6). The removal of  $\text{NO}_3^-$  is mainly the result of denitrification by denitrifying microorganisms and plant uptake (Vymazal, 2007; Garcia et al., 2010; Dotro et al., 2017). Denitrification and plant uptake result in the complete removal of  $\text{NO}_3^-$  from the CW system instead of the transformation to other N-forms. Denitrification in subsurface-flow CWs is possible both in anaerobic and anoxic conditions (Reinhardt et al., 2006; Hu et al., 2016) and aerobic conditions (Coban et al., 2015) in the presence of organic carbon as electron donor. The higher  $\text{NO}_3^-$  removal in the HSSF-CWs than in the VSSF-CWs indicates that anaerobic denitrification is a more relevant removal mechanisms for  $\text{NO}_3^-$  from CTW than aerobic denitrification in our hybrid-CWs.

Denitrification converts  $\text{NO}_3^-$  in  $\text{NO}_2^-$  and ultimately to  $\text{N}_2$ . Periodically,  $\text{NO}_2^-$  was present in the influent as a result of denitrification in the influent tank (Fig. S7). This is also the cause of the fluctuating  $\text{NO}_3^-$  influent concentration (Fig. S6).  $\text{NO}_2^-$  was almost completely removed in the subsurface flow CWs, but not in the OW-CW (Fig. S7). The removal of  $\text{NO}_2^-$  is likely due to denitrification, as also described by others (Vymazal, 2007; Garcia et al., 2010).

$\text{PO}_4^{3-}$  was completely removed in all hybrid-CWs (Fig. 2 and S8). A single subsurface flow CW, either HSSF-CW or VSSF-CW, was enough to completely remove  $\text{PO}_4^{3-}$  (Fig. S8). The removal of  $\text{PO}_4^{3-}$  in the subsurface flow CW is the result of adsorption to the sediment, plant uptake, microbial activity and chemical precipitation (Drizo et al., 1999; Chung et al., 2008). However, the most dominant removal mechanism for  $\text{PO}_4^{3-}$  could not be determined while determining the CWs baseline REs.

More than 80% removal of TOC was observed in all hybrid-CWs (Fig. 2 and S9). A large fraction of the TOC was removed in the HSSF-CWs and the VSSF-CWs, while the OW-CW removed a smaller fraction (Fig. 2 and S9). A large part of the TOC consisted of particulate organic matter, since the humic acids, which is the main TOC fraction in real CTW (Löwenberg et al., 2015), did not completely dissolve in the synthetic CTW. Hence, physical removal mechanisms, such as sedimentation and filtration, were responsible for a large part of TOC removal. This might have resulted in an overestimation of the CWs TOC removal capacity, since dissolved humic acids are typically considered as recalcitrant to biological transformation (Almendros and Dorado, 2001), which is one of the main removal mechanisms for dissolved TOC (Imfeld et al., 2009). The turbidity and TSS of the CTW were the result of the presence of humic acids. Sedimentation and filtration in the subsurface flow CWs were also responsible for a decrease of both the turbidity





**Fig. 2.** The cumulative average BTA, BA,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , TOC and EC removal efficiency per compartment of the six different hybrid constructed wetlands VOH, VHO, HVO, HOV, OHV and OVH during the baseline removal efficiency determination. VOH = a hybrid constructed wetland starting with V = vertical subsurface flow constructed wetland (VSSF-CW), followed by O = open water flow constructed wetland (OW-CW) and H = horizontal subsurface flow constructed wetland (HSSF-CW) and vice versa. BTA = benzotriazole; BA = benzoic acid;  $\text{NO}_3^-$  = nitrate;  $\text{PO}_4^{3-}$  = phosphate; TOC = total organic carbon; EC = electrical conductivity. The removal efficiency is the average removal efficiency of 11 samples taken over a time-period of 13 weeks.

(Fig. S10) the TSS (Fig. S11).

Benzoic acid removal was already observed in the dilution tank, providing highly variable benzoic acid influent data varying between 0 and 35 mg/L (Fig. S12). Despite this varying influent concentrations, benzoic acid was always completely removed in all CW compartments (Fig. 2 and S12). Benzoic acid is easily degradable by CW microorganisms within the HRT of our hybrid-CWs (Wagner et al., 2020b). Hence, benzoic acid can represent the fraction of easily degradable organic conditioning chemicals, and residual benzoic acid concentrations in the effluent of the hybrid-CW can be evidence for the disturbance of the microbial activity.

The removal of benzotriazole was the highest in the VSSF-CWs (Fig. 2 and S13), and the removal of benzotriazole in hybrid-CWs starting with an OW-CW was lower than that of hybrid-CWs starting with a VSSF-CW or HSSF-CW (Fig. 2 and S13). The VSSF-CW has the highest benzotriazole RE because of simultaneous aerobic biodegradation and adsorption (Wagner et al., 2020a). The design of the hybrid-CW did not allow determination of the redox conditions by measuring the dissolved oxygen concentration of the CW effluent because the effluent was in contact with air in the collection compartment (section 2.2). Nevertheless, the combined higher benzotriazole RE and lower  $\text{NO}_3^-$  RE in the VSSF-CW compared to the HSSF-CW confirm our hypotheses of prevailing aerobic redox conditions in the VSSF-CW and anaerobic redox conditions in the HSSF-CW. Aerobic conditions in the VSSF-CW are the result of air re-entering the VSSF-CWs after each feeding episode, as demonstrated by others as well (Fan et al., 2012).

Interestingly, the removal of benzotriazole in a VSSF-CW that is not the starting compartment of the hybrid-CW is lower than that of a VSSF-CW that is the starting compartment of the hybrid-CW. This could be due to a longer HRT (Fig. S1), since a longer HRT positively influences the RE in a CW (Headley and Kadlec, 2007). In addition, the lower removal in the second or third compartment might be because the aerobic biodegradation that is responsible for part of the benzotriazole removal is probably a co-metabolic process by microorganisms that are

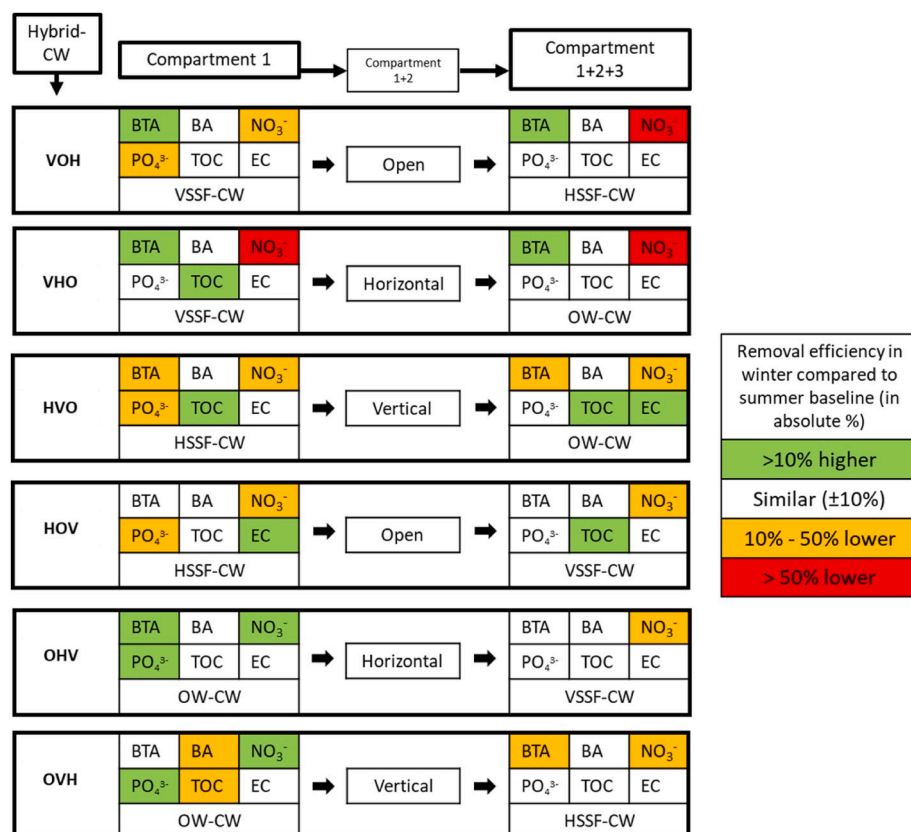
degrading other carbon and nitrogen sources (Herzog et al., 2014; Shi et al., 2019). Herzog et al. (2014) showed that the presence of nitrogen-containing compounds was crucial for benzotriazole removal, and hence the extent of removal of benzotriazole in the second and third compartment of the hybrid-CW might be lower because part of the nitrogen-containing compounds and other organics are already removed in earlier compartments.

The high removal of nutrients in the first subsurface flow planted compartment also had an effect on the *Phragmites australis* growth in the second planted compartment. The plants in the second planted compartment were visibly more yellow as result of leaf chlorosis than the plants in the first planted compartment for all six hybrid-CWs (Fig. S14), most likely as a result of a nutrient deficiency. Another potential cause for leaf chlorosis could be an iron deficiency, as a result of the formation of iron-oxide precipitates that are immobilized under aerobic conditions and a neutral pH because of their low solubility (Weedon, 2014; Butterworth et al., 2016; Wu et al., 2019). This phenomenon was observed previously in the second stage of a two-stage French VSSF-CW-system (Weedon, 2014) and in aerated CWs (Butterworth et al., 2016; Wu et al., 2019). However, although the pH of typically 7–8 in our hybrid-CWs enables iron precipitation (Fig. S15), the occurrence of plant yellowing in the anaerobic HSSF-CWs in our hybrid-CW system is an indication that the leaf chlorosis is the result of a nutrient deficiency.

### 3.2. Winter season

The impact of the winter season was determined from December 10th onwards, after the *Phragmites australis* was cut and left on the hybrid-CWs, and the average temperature reached 5 °C (Fig. S2). The REs of the hybrid-CWs during winter are provided in Fig. S16. Fig. 3 provides a comparison of the REs during the summer baseline period and the winter.

Winter has the highest negative impact on the  $\text{NO}_3^-$  removal, with



**Fig. 3.** The absolute difference in cumulative average BTA, BA,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , TOC and EC removal efficiency for compartment 1 and the total hybrid constructed wetland (compartment 3) of the six different hybrid constructed wetlands VOH, VHO, HVO, HOV, OHV and OVH during winter compared to the baseline removal efficiency. VOH = a hybrid constructed wetland starting with V = vertical subsurface flow constructed wetland (VSSF-CW), followed by O = open water flow constructed wetland (OW-CW) and H = horizontal subsurface flow constructed wetland (HSSF-CW) and vice versa. BTA = benzotriazole; BA = benzoic acid;  $\text{NO}_3^-$  = nitrate;  $\text{PO}_4^{3-}$  = phosphate; TOC = total organic carbon; EC = electric conductivity. The removal efficiency is the average removal efficiency of 14 samples taken over a time-period of 16 weeks.

more than 50% reduction of the  $\text{NO}_3^-$  RE in the VOH, VHO, HVO, HOV and OVH compartments (Fig. 3 and S6). The average of the minimum and maximum temperatures decreased from 9.7 during the baseline period to 5.0 during winter season (Fig. S2). A significantly lower  $\text{NO}_3^-$  removal in CWs during lower temperatures is in agreement with values reported in the literature (Spieles and Mitsch, 1999; Kuschek et al., 2003). As discussed in section 3.1,  $\text{NO}_3^-$  removal in CWs is mainly the result of denitrification by microorganisms and plant uptake. Denitrification is a microbial process that is strongly influenced by the temperature, with significantly lower denitrification rates at temperatures below 5 °C (Vymazal, 2007). Kuschek et al. (2003) already observed lower denitrification rates below 15 °C. In addition to a lower microbial removal, the removal of the vegetation resulted in a net removal of the  $\text{NO}_3^-$  already taken up from the hybrid-CW system, but reduced and almost stopped the plant uptake of  $\text{NO}_3^-$  during the period that the shoots were dormant.

The  $\text{PO}_4^{3-}$  removal was reduced by the winter season in the first compartment of hybrid-CWs starting with subsurface flow CWs (Fig. 3 and S8). A lower  $\text{PO}_4^{3-}$  removal during lower temperatures was observed previously in HSSF-CWs by Akrotas and Tsihrintzis (2007). Seasonal changes in  $\text{PO}_4^{3-}$  REs can give indications about the contribution of the different removal mechanisms (Kadlec and Wallace, 2008), and this was also possible in our pilot-scale hybrid-CW set-up. The reduced RE during winter in the subsurface flow CWs indicates that biological processes rather than chemical or physical processes are responsible for at least part of the  $\text{PO}_4^{3-}$  removal, since microbial- and plant uptake of  $\text{PO}_4^{3-}$  are negatively influenced by low temperatures and vegetation removal. However, the contribution of abiotic removal processes, such as  $\text{PO}_4^{3-}$  adsorption, is substantial, since two subsurface flow CWs are still capable of removing all the  $\text{PO}_4^{3-}$  during winter (Fig. S8). Nevertheless, the substantial contribution of abiotic removal pathways implies that the  $\text{PO}_4^{3-}$  removal will decrease over time, since adsorption sites for  $\text{PO}_4^{3-}$  will become saturated.

Benzoic acid was completely removed during the largest part of the

winter (Fig. S12). Only on the 21st of January, when day temperatures were below 0 °C and night temperatures reached −10 °C (Fig. S2), benzoic acid effluent concentrations of >5 mg/L in the first compartment of the HOV, HVO, OHV and OVH hybrid-CW were measured. Apparently, the microbial activity of the HSSF-CWs and OW-CWs was inhibited by the low temperatures, while the temperature in the deeper VSSF-CW was high enough for maintaining microbial activity.

The influence of the winter season on the removal of benzotriazole was significantly different between the VSSF-CWs and the HSSF-CWs (Fig. 3 and S13), and between the VSSF-CWs as first or subsequent compartment of the hybrid-CW (Fig. S13). The winter season reduced the RE of benzotriazole in the HSSF-CW, likely as a result of the removal of the *Phragmites australis* that provided the required oxygen for aerobic biodegradation of benzotriazole. The VSSF-CW does not depend on oxygen input by *Phragmites australis* for aerobic conditions, and the VSSF-CW of the VHO and VOH hybrid-CWs showed an increased benzotriazole removal during winter (Fig. S13). This increase is probably not an effect of the winter season but more likely the result of maturation of the CW-system and the adaptation of the microbial community towards degrading benzotriazole. A similar increasing benzotriazole RE, also during winter, was observed in VSSF-CWs by Brunsch et al. (2018). In contrast to the VSSF-CWs as first compartment of the hybrid-CW, the VSSF-CWs in the HVO, HOV, OVH and OHV hybrid-CWs had a reduced benzotriazole RE during winter (Fig. S13). This could be due to the temperature of 15 °C of the CTW when it entered the hybrid-CWs, which then dropped during treatment in the first compartment, resulting in a lower microbial activity in subsequent compartments. The temperature of industrial CTW is often similar to or higher than that of the synthetic CTW used in the present study (Wagner et al., 2018). Hence, an increase of the benzotriazole biodegradation due to the relatively high temperature can be expected when large volumes of CTW are treated in large-scale CW-systems.

The TOC removal is not impacted during winter (Fig. 3 and S9)

because physical removal mechanisms, such as sedimentation, are hardly influenced by the temperature.

### 3.3. Biocide addition

Biocides, such as glutaraldehyde and DBNPA, are commonly used in cooling towers to prevent microbial fouling, a process that lowers the heat transfer efficiency (Klaine et al., 1996). Previous batch experiments of our group with microorganisms from CWs have shown that these biocides affect the biodegradation of benzoic acid (Wagner et al., 2020b). To study their influence on the RE of hybrid-CWs, glutaraldehyde and DBNPA were dosed to the hybrid-CWs twice a week in different concentrations corresponding to levels used in practice in CTW.

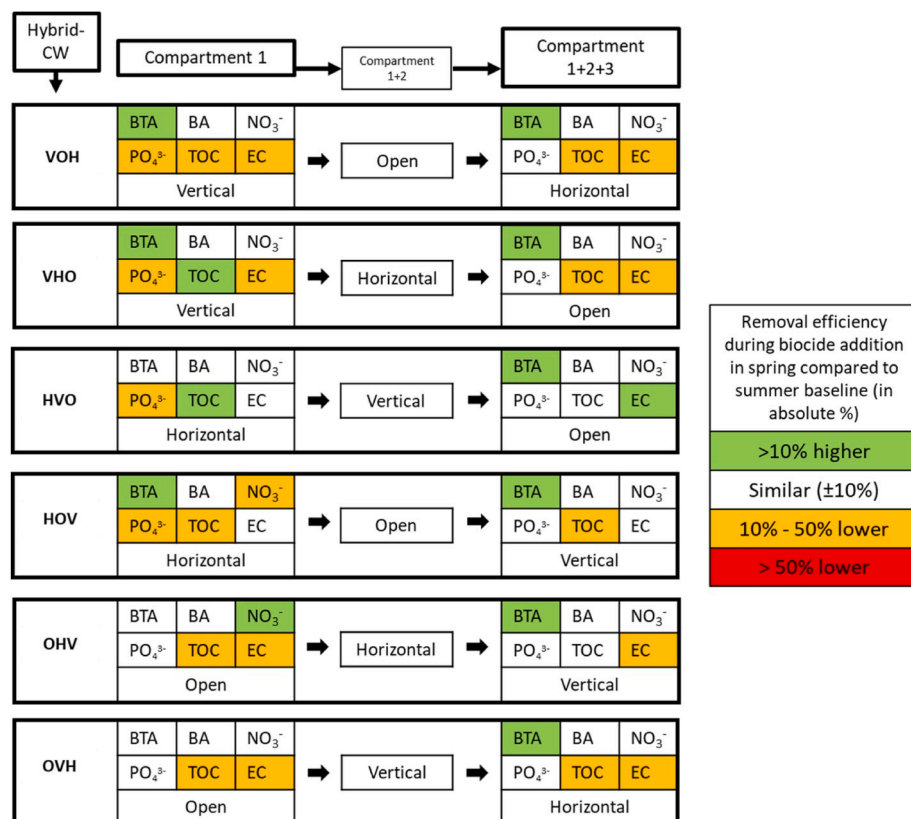
None of the tested doses (glutaraldehyde concentration of 5 mg/L or 50 mg/L, DBNPA concentration of 1 or 10 mg/L and a mixture of 5 mg/L glutaraldehyde and 1 mg/L DBNPA, or 50 mg/L glutaraldehyde and 10 mg/L DBNPA) had an apparent effect on the RE of the hybrid-CWs (Fig. 4 and S17). The RE of chemicals that are degraded biologically, such as  $\text{NO}_3^-$ , benzoic acid and benzotriazole, was not reduced by the addition of biocides. This is in contrast with the findings in our batch experiments (Wagner et al., 2020b), where the biodegradation of benzoic acid was reduced by levels of 0.5–5 mg/L of glutaraldehyde and DBNPA. In addition, the absence of an reduced RE as result of biocide addition was in contrast to the findings of Rogers et al. (2017), who observed that a 50 mg/L glutaraldehyde concentration completely inhibited the biodegradation of hydraulic fracturing compounds by aquifer microorganisms. To compensate for the unstable benzoic acid influent concentrations (section 3.1), benzoic acid was added separately to the CTW with biocides (section 2.4.3). In addition, sampling occurred daily to avoid missing temporary effects of the biocides. However, no effect of biocides on the RE for compounds that are biologically removed was observed.

A likely reason for the limited effect of the biocides is the reactivity of

the biocides. Glutaraldehyde was quickly removed during biotic and abiotic batch experiments with CW sediment (Wagner et al., 2020b). The glutaraldehyde concentrations in the effluent of the first compartments of the hybrid-CWs were monitored, and concentrations up to 4 mg/L were only found during the first feeding episode with the addition of 5 mg/L glutaraldehyde (Fig. S19). These concentrations were not observed during the addition of 50 mg/L glutaraldehyde or the mix with DBNPA in high and low concentrations (Fig. S19). This could be an indication that the microbial communities in the hybrid-CWs adapted to the presence of glutaraldehyde, as described by Campa et al. (2018), and were able to biodegrade it.

No DBNPA was observed in the effluent of the first compartment of the hybrid-CWs (data not shown). Although DBNPA is instable and cannot be quantified (Wagner et al., 2020b), DBNPA was present in the influent samples, and thus it can be concluded that DBNPA was removed in the HSSF-CW, VSSF-CW and OW-CW. DBNPA quickly transforms to different transformation products in CTW (Wagner et al., 2020c), and the transformation rate and route is influenced by the CW sediment and photodegradation (Wagner et al., 2020b, 2020c).

DBNPA and glutaraldehyde were added during spring, when the *Phragmites australis* and other invasive plant species started growing again and the temperatures rose to a maximum of 31 °C (Fig. S2). This led to a recovery of the winter  $\text{NO}_3^-$  RE to summer baseline values for the total hybrid-CW (Figs. S6 and 4). The  $\text{NO}_3^-$  removal of the OW-CW of the OHV sequences increased, probably as the result of the development of free floating vegetation, such as *Lemna minor*, that can take up these nutrients (Adhikari et al., 2015). The  $\text{PO}_4^{3-}$  RE in the hybrid-CWs with a subsurface flow CWs as a starting compartment only returned to its baseline values in the last weeks of the experimental period at the end of May, when significant plant growth had occurred (Fig. S18). The late recovery of the vegetation resulted in average REs similar to the winter REs for the VOH, HVO and HOV sequences (Fig. S8). A difference in plant growth between the VSSF-CWs and HSSF-CWs was observed, with a more dense coverage, higher plant growth and less invasive species in



**Fig. 4.** The absolute difference in cumulative average BTA, BA,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , TOC and EC removal efficiency for compartment 1 and the total hybrid constructed wetland (compartment 3) of the six different hybrid constructed wetlands VOH, VHO, HVO, HOV, OHV and OVH during the addition of biocides compared to the baseline removal efficiency. VOH = a hybrid constructed wetland starting with V = vertical subsurface flow constructed wetland (VSSF-CW), followed by O = open water flow constructed wetland (OW-CW) and H = horizontal subsurface flow constructed wetland (HSSF-CW) and vice versa. BTA = benzotriazole; BA = benzoic acid;  $\text{NO}_3^-$  = nitrate;  $\text{PO}_4^{3-}$  = phosphate; TOC = total organic carbon; EC = electric conductivity. The removal efficiency during biocide addition is the average removal efficiency of 11 samples taken over a time-period of 11 weeks.



the HSSF-CWs (Fig. S18), probably as a result of its more saturated water conditions.

The recovery of the vegetation resulted in higher benzotriazole REs for the HSSF-CWs compared to winter (Figs. S13, 3 and 4), as a result of the oxygen input by the plant roots. The removal of benzotriazole in the VSSF-CWs further increased compared to the summer baseline and the winter season, resulting in the nearly complete removal of benzotriazole at the end of the experimental period (Fig. S13). This is higher than benzotriazole REs from treated domestic wastewater in the conventional VSSF-CWs of 63% reported by Kahl et al. (2017), 19–82% by Brunsch et al. (2018) and 62% by Nivala et al. (2019). This higher benzotriazole RE can be a result of the composition of the CTW, which is low in easy degradable organics, possibly forcing the microbial community to adapt towards the use of benzotriazole as a carbon source.

The TOC removal of the hybrid-CWs decreased by 12–18% compared to the summer baseline (Fig. S9). This could possibly be the result of the decay of plant material that entered the sampling compartment, or a loss of filter capability as result of clogging of the sediment.

In summary, with the current experimental set-up, we were able to determine the most important removal mechanisms and CW-designs for the removal of various fractions from CTW (Table 3).

### 3.4. Implications for future constructed wetland design

Our study tested the applicability of different CW designs for the treatment of brackish CTW prior to its reuse, and elucidated the CW removal mechanisms for CTW fractions that hinder its direct reuse, such as conditioning chemicals.

Physico-chemical desalination of the CTW is needed prior to its reuse in the cooling tower, since the EC did not reach the threshold of 1000  $\mu\text{S}/\text{cm}$  (Groot et al., 2015) as a result of hybrid-CW treatment (Table 4). Several processes, such as dilution by rainfall and evapotranspiration do result in fluctuating EC values between 3000 and 4000  $\mu\text{S}/\text{cm}$ , but the *Phragmites australis* was able to cope with these fluctuations. The pH of CTW is generally kept between 7 and 9 to prevent processes that lower the heat transfer efficiency, such as fouling and scaling (Wagner et al., 2018). The pH of the CTW in our study did not change except in the hybrid-CWs ending with an OW-CW, where it increased from  $\pm 7.2$  to  $\pm 7.5$  (Fig. S15). These values still meet the pH requirement for its use as make-up water (Table 4).

The threshold concentration for  $\text{PO}_4^{3-}$  in make-up water is 1 mg/L (Table 4), since high  $\text{PO}_4^{3-}$  concentrations result in  $\text{PO}_4^{3-}$  mineral scale formation and  $\text{PO}_4^{3-}$  forms a source of nutrients for microorganisms (Li et al., 2011; Groot et al., 2015). Physico-chemical desalination technologies, such as electrodialysis and capacitive deionization, are not able to meet this  $\text{PO}_4^{3-}$  threshold, while the required EC can be reached (Groot et al., 2015). Reverse osmosis is able to meet the required EC and

$\text{PO}_4^{3-}$  thresholds, but requires pre-treatment to avoid membrane fouling (Groot et al., 2015; Wagner et al., 2018). Pre-treatment by a single HSSF-CW or VSSF-CW is able to meet the  $\text{PO}_4^{3-}$  threshold during summer (Table 4; Fig. S8), but this threshold concentration was not reached in the OW-CW (Fig. S8). During winter, two subsurface flow CWs are needed to meet the  $\text{PO}_4^{3-}$  threshold concentration (Table 4). A part of the  $\text{PO}_4^{3-}$  removal is because of finite capacity processes, such as adsorption (section 3.2). However, low  $\text{PO}_4^{3-}$  REs as result of substrate saturation or seasonality can be overcome by using unplanted sacrificial  $\text{PO}_4^{3-}$  retention filters (Dotro et al., 2017) using locally available media with high  $\text{PO}_4^{3-}$  sorption capacity, such as steel slag aggregates (Blanco et al., 2016), clay minerals (Yin et al., 2017) or oyster shell (Wang et al., 2013), that are periodically replaced. The impact of these materials on subsequent physico-chemical desalination technologies should be considered, since residuals from coagulation as pre-treatment can cause severe reverse osmosis membrane fouling (Löwenberg et al., 2015).

A 5 mg/L threshold concentration for  $\text{NO}_3^-$  was estimated, since threshold concentrations are not provided in the literature, but high concentrations of  $\text{NO}_3^-$  could form a nutrient source for microorganisms, ultimately leading to biofouling. The HSSF-CW is capable of removing  $\text{NO}_3^-$  during periods of plant growth, while the VSSF-CW and the OW-CW do not sufficiently remove  $\text{NO}_3^-$ . However, the HSSF-CW does not remove  $\text{NO}_3^-$  during winter, and thus a subsequent physico-chemical desalination technique that does remove  $\text{NO}_3^-$  would be beneficial for the treatment of CTW.

The TOC threshold of <15 mg/L cannot be obtained by electrodialysis or capacitive deionization, but can be obtained by reverse osmosis, where the TOC does cause membrane fouling (Löwenberg et al., 2015). Hybrid-CW treatment was able to lower the TOC concentration of the CTW in all the hybrid-CW compartments throughout every season. However, the influent TOC concentration was lower than in the CTW described by Groot et al. (2015). In addition, the removal seemed mainly caused by physical processes, such as sedimentation and filtration, which may be less relevant when the TOC of the CTW is well dissolved. Sedimentation and filtration are also responsible for lowering the TSS, but not consistently below the 1 mg/L threshold (Fig. S11; Groot et al., 2015). However, electrodialysis, capacitive deionization and reverse osmosis are able to meet this threshold value (Groot et al., 2015).

A reduction of the concentration of conditioning chemicals in treated CTW, such as benzotriazole, is important to prevent accumulation of these compounds as result of CTW reuse, resulting in operational problems with physico-chemical desalination technologies (Löwenberg et al., 2015). The VSSF-CW removed sufficient benzotriazole during its first summer in operation, and its RE steadily increased over time leading to complete benzotriazole removal, probably as a result of an adapting microbial population (Table 4; Fig. S13). The increase of the biological removal capability of CWs for conditioning chemicals is beneficial for CTW treatment, but does imply that the CW system needs time to develop and deliver the required pre-treatment efficiency.

The most optimal CW system for CTW treatment is a hybrid-CW containing a VSSF-CW and a HSSF-CW system. An OW-CW system neither contributes to nor negatively affects the pre-treatment efficiency of the hybrid-CW system. However, the OW-CW could provide buffer capacity for large volumes of water and opportunities for biodiversity and educational and recreational purposes. In a hybrid-CW, it is recommended to opt for a VSSF-CW as the initial stage, since this system does not remove nutrients, such as  $\text{NO}_3^-$  that are needed for the vegetation in subsequent subsurface flow CWs. In addition, the VSSF-CW is more robust during winter season, allowing year-round removal of conditioning chemicals such as benzotriazole. If an OW-CW is used, it should not be used as last stage in the hybrid-CW, to prevent discharge of solids. Hence, the preferred final stage in a hybrid-CW is a HSSF-CW that removes remaining nutrients anaerobically.

**Table 3**

Dominant removal mechanisms and constructed wetland designs for cooling tower water components that hamper the desalination of cooling tower water.

| Cooling tower parameter | Dominant removal mechanisms                          | Optimal constructed wetland design |
|-------------------------|--|------------------------------------|
| Total suspended solids  | Sedimentation  | VSSF-CW and HSSF-CW                |
| Turbidity               | Sedimentation  | VSSF-CW and HSSF-CW                |
| $\text{PO}_4^{3-}$      | Microbial uptake, plant uptake, substrate adsorption | VSSF-CW and HSSF-CW                |
| $\text{NO}_3^-$         | Denitrification                                      | HSSF-CW                            |
| Benzotriazole           | Aerobic biodegradation                               | VSSF-CW                            |
| Benzoic acid            | Biodegradation                                       | VSSF-CW and HSSF-CW                |
| DBNPA                   | Abiotic degradation, photodegradation                | VSSF-CW, HSSF-CW, OW-CW            |
| Glutaraldehyde          | Abiotic degradation, adsorption, biodegradation      | VSSF-CW, HSSF-CW, OW-CW            |



**Table 4**

Threshold water quality parameters for use as make-up water in cooling towers and the capability of different constructed wetland flow types to meet this thresholds during summer and winter season.

|                    | Threshold value                          | VSSF-CW Summer | HSSF-CW Summer | OW-CW Summer | VSSF-CW Winter | HSSF-CW Winter | OW-CW Winter |
|--------------------|--|----------------|----------------|--------------|----------------|----------------|--------------|
| EC                 | <1000 $\mu\text{S}/\text{cm}^{\text{a}}$ | X              | X              | X            | X              | X              | X            |
| pH                 | 7–9 <sup>b</sup>                         | ✓              | ✓              | ✓            | ✓              | ✓              | ✓            |
| $\text{PO}_4^{3-}$ | <1 mg/L <sup>a</sup>                     | ✓              | ✓              | X            | X              | X              | X            |
| TOC                | <15 mg/L <sup>a</sup>                    | ✓              | ✓              | ✓            | ✓              | ✓              | ✓            |
| TSS                | <1 mg/L <sup>a</sup>                     | X              | X              | X            | X              | X              | X            |
| $\text{NO}_3^-$    | <5 mg/L <sup>b</sup>                     | X              | ✓              | X            | X              | X              | X            |
| Benzotriazole      | <0.25 mg/L <sup>b</sup>                  | ✓              | X              | X            | ✓              | X              | X            |

<sup>a</sup> Groot et al. (2015).

<sup>b</sup> Own estimation.

#### 4. Conclusions

The present study is the first report of the pre-treatment of cooling tower water (CTW) by constructed wetlands (CWs) prior to physico-chemical desalination. CWs can remove components present in CTW that could hamper its physico-chemical desalination. In this way, CTW desalination can be optimized so that discharged CTW can be reused in the cooling tower itself. In the present study, the most efficient CW design and dominant removal mechanisms for nutrients, conditioning chemicals and general water quality parameters were determined. Subsurface flow CWs removed  $\text{PO}_4^{3-}$ , total suspended solids and total organic carbon as result of adsorption and filtration. Vertical subsurface flow CWs (VSSF-CWs) excelled in the removal of benzotriazole as result of aerobic biodegradation. Horizontal subsurface flow CWs (HSSF-CWs) allowed the denitrification of  $\text{NO}_3^-$  because of their anaerobic conditions. Open water CWs (OW-CWs) do not contribute to the removal of CTW fractions that hinder its desalination, but allow the storage of large volumes of water, and additionally contribute to the local biodiversity. While the biological removal processes in the different CW designs appeared to be negatively impacted by the winter season, the biocides glutaraldehyde and DBNPA did not have an impact on the removal efficiencies. For optimal pre-treatment of CTW before its desalination, a hybrid-CW, consisting of an initial VSSF-CW followed by an OW-CW and HSSF-CW is recommended. Future studies should focus on integrating CWs with a desalination technology to be selected from either reverse osmosis, electrodialysis or capacitive ionization, to produce water that meets the EC,  $\text{PO}_4^{3-}$ , TOC and TSS requirements and allow the reuse of the CTW in the cooling tower itself.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### CRediT authorship contribution statement

**Thomas V. Wagner:** Conceptualization, Methodology, Validation, Investigation, Data curation, Writing - original draft, Visualization, Project administration. **Vinnie de Wilde:** Conceptualization, Methodology, Writing - review & editing. **Bert Willemsen:** Methodology. **Muhamad Mutaqin:** Investigation, Data curation, Writing - review & editing. **Gita Putri:** Investigation, Data curation, Writing - review & editing. **Julia Opdam:** Investigation, Data curation, Writing - review & editing. **John R. Parsons:** Conceptualization, Methodology, Writing - review & editing, Funding acquisition. **Huub H.M. Rijnaarts:** Conceptualization, Methodology, Writing - review & editing, Funding acquisition. **Pim de Voogt:** Conceptualization, Methodology, Writing - review & editing, Funding acquisition. **Alette A.M. Langenhoff:** Conceptualization, Methodology, Writing - review & editing, Supervision, Funding acquisition.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2020.110972>.

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