



## Benzotriazole removal mechanisms in pilot-scale constructed wetlands treating cooling tower water

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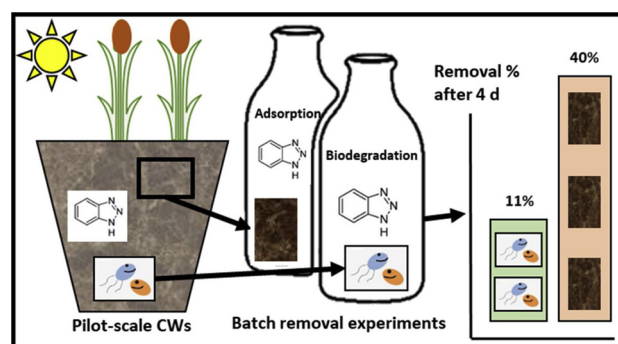
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### GRAPHICAL ABSTRACT



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### ABSTRACT

The reuse of discharged cooling tower water (CTW) in the cooling tower itself could reduce fresh water intake and help mitigating fresh water scarcity problems. However, this requires desalination prior to its reuse, and hindering fractions, such as conditioning chemicals, should be removed before desalination to obtain a higher desalination efficiency. Constructed wetlands (CWs) can provide such a pre-treatment. In this study, the mechanisms underlying the removal of conditioning chemical benzotriazole (BTA) in CWs was studied using an innovative approach of differently designed pilot-scale CWs combined with batch removal experiments with substrate from these CWs. By performing these combined experiments, it was possible to determine the optimal CW design for BTA removal and the most relevant BTA removal processes in CWs. Adsorption yielded the highest contribution, and the difference in removal between different CW types was linked to their capability to aerobically biodegrade BTA. This knowledge on the main removal mechanisms for BTA allows for a CW design tailored for BTA removal. In addition, the outcomes of this research show that performing batch experiments with CW substrate allows one to determine the relevant removal mechanisms for a given compound which results in a better understanding of CW removal processes.

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## 1. Introduction

Reuse of saline industrial waste-water can significantly reduce the industrial fresh water withdrawal, and can contribute in preventing future fresh water scarcity problems. Enormous volumes of fresh water are used in cooling towers worldwide (dos Santos et al., 2015). In recirculating cooling towers, the non-evaporated fraction of this cooling tower water (CTW) is discharged when it reaches a mineral concentration threshold. The reuse of this CTW in the cooling tower itself lowers the pressure on external fresh water sources. However, the CTW requires physico-chemical desalination prior to reuse, and fractions of the CTW that hinder physico-chemical desalination, such as conditioning chemicals (CCs), should be removed to obtain a higher desalination efficiency (Wagner et al., 2018). Pre-treatment of the CTW prior to physicochemical treatment is therefore required.

A potential pre-treatment method for CTW is the use of constructed wetlands (CWs) (Wagner et al., 2018). CWs are man-made wetland systems in which natural contaminant removal mechanisms are responsible for the removal of pollutants from waste-water streams. The main mechanisms facilitating the successful removal of contaminants in CWs are biodegradation, photodegradation, plant-uptake and transformation and adsorption (Brix, 1993; Garcia et al., 2010; He et al., 2018). The susceptibility of a chemical to be removed by one of the processes in a CW is the result of its physical-chemical properties, such as its chemical structure,  $\log K_{ow}$  and  $\log K_{oc}$ .

Many of the CCs possess polar characteristics. In general, these polar chemicals hardly adsorb to common constructed wetland substrates consisting of sandy material with < 5% organic matter. In addition, some polar CCs cannot be biodegraded completely within often used CW hydraulic retention times of 1–7 d. Furthermore, they might not be susceptible to UV-light and not taken up by plants. Hence, some CCs are currently not completely removed by conventional CW systems, and a method to determine the most relevant removal mechanisms for a given CC allows a better understanding of the CW system and the design of a CW tailored to the removal of this CC and the water it receives.

Benzotriazole (BTA) is a polar CC with a low  $\log K_{ow}$  value of 1.23 that is commonly used as corrosion inhibitor in cooling towers. Commonly applied BTA concentrations in cooling towers range between 2.5 and 5 mg/L (Koeman-Stein et al., 2016). BTA is present in surface water throughout the whole of Europe (van Leerdam et al., 2009, Alotaibi2015a). Due to this omnipresence, BTA has been proposed as an indicator micropollutant for anthropogenically influenced water (Jekel et al., 2015). Literature shows extreme variation in BTA removal efficiencies in pilot-scale and full-scale CWs from 3%–93% (Matamoros et al., 2010, 2016, 2017; Kahl et al., 2017; Brunsch et al., 2018; Nivala et al., 2019). Biodegradation, adsorption and photodegradation are postulated in these studies as the removal mechanisms responsible for the removal of BTA in CWs. However, the contribution of each mechanism is not clear. A better understanding of the processes responsible for BTA removal could explain the variation in above-mentioned studies and could allow the design of CWs with higher BTA removal efficiencies for CTW treatment.

The objective of this study was to improve our understanding of the fate and removal of BTA in a CW system using an innovative approach of combining differently designed CWs with batch removal experiments using substrate from these CWs. To meet these objectives, surface flow (SF), horizontal subsurface flow (HSSF) and vertical subsurface flow (VSSF) pilot-scale CWs were constructed outdoors to determine their removal of BTA from CTW under realistic climate conditions. In addition, the contributions of biodegradation, photodegradation and adsorption to BTA removal were studied in batch removal experiments with substrate from these pilot-scale CWs under controlled laboratory conditions and the value of performing batch experiments with CW substrate to elucidate relevant CW removal mechanisms for BTA and to predict the CW removal efficiency was determined.

## 2. Materials & methods

### 2.1. Chemicals

Benzotriazole (> 99%) for batch removal experiments, *p*-nitroanisole and pyridine were obtained from Sigma-Aldrich (Zwijndrecht, the Netherlands).  $\text{NaNO}_3$ ,  $\text{CaCl}_2$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{KH}_2\text{PO}_4$ , benzotriazole, benzoic acid and humic acid to prepare synthetic CTW were obtained from Carl Roth GmbH (Karlsruhe, Germany). Methanol and acetic acid were obtained from Sigma-Aldrich (Zwijndrecht, the Netherlands) and were of the highest analytical grade.

### 2.2. Pilot constructed wetlands

Surface flow (SF), horizontal subsurface flow (HSSF) and vertical subsurface flow (VSSF) pilot-scale CWs were built from polyethylene (PE) in duplicate for the treatment of synthetic CTW. The pilot-scale CWs were located outdoors, next to the laboratory of the Environmental Technology department of Wageningen University & Research (51.986114 N, 5.658782 E) (Fig. S1). The SF-CWs had a surface of 2.1 m<sup>2</sup> and the water flow was guided by PE baffles. The HSSF-CWs had a surface of 2.1 m<sup>2</sup> and a depth of 39 cm. They were filled with sand with a diameter of > 250  $\mu\text{m}$ , with a 5 cm layer of gravel (16–32 mm) on top. This gravel was also used at the distribution and collection side. The VSSF-CWs had a surface of 1.37 m<sup>2</sup> and a depth of 97 cm. They consisted of a 10 cm bottom layer of 16–32 mm gravel, 75 cm sand with a diameter of > 250  $\mu\text{m}$  and a 5 cm top layer of 16–32 mm gravel. Both the HSSF-CWs and VSSF-CWs were planted with *Phragmites australis*. The CWs were allowed to develop for 1.5 y solely fed by rainwater, before feeding them with synthetic CTW. The composition of the synthetic CTW was based on a real CTW (Groot et al., 2015) and consisted of  $\text{NaNO}_3$  (83 mg/L),  $\text{CaCl}_2$  (830 mg/L),  $\text{Na}_2\text{SO}_4$  (1660 mg/L),  $\text{KH}_2\text{PO}_4$  (10 mg/L), humic acid (50 mg/L), benzoic acid (50 mg/L) and 1 mg/L of BTA. This composition results in an EC of  $\pm 3600 \mu\text{S/cm}$ , a pH of  $\pm 7.2$ , a  $\text{NO}_3^-$  concentration of  $\sim 25 \text{ mg/L}$ , a TOC concentration of  $\sim 15 \text{ mg/L}$  and  $\sim 4 \text{ mg/L PO}_4^{3-}$ . The CWs were acclimatized to the CTW for 3 w after the development period of 1.5 y by using a CTW with 50% of the final concentration before sampling started. The SF and HSSF were continuously fed with 158 L per d. The VSSF-CWs were fed 158 L in batch mode with 4 batches per d. The hydraulic retention time (HRT) was determined according to the breakthrough of the electric conductivity (EC) of the CTW (Fig. S2). An EC of 1100  $\mu\text{S/cm}$  was used as a proxy for the HRT, since this was the average of the starting EC of 400  $\mu\text{S/cm}$  and the EC of the CTW during acclimatization of 1800  $\mu\text{S/cm}$ . This resulted in a HRT of approximately 55 h for the SF-CWs, 40 h for the HSSF-CWs and 35 h for the VSSF-CWs. Weekly samples for BTA analysis were taken from the influent and effluent of all CWs for a period of 14 w from September until December 2018. These samples were filtered over a 0.2  $\mu\text{m}$  polyethersulfone filter. These filters were tested for their capacity to retain BTA, which they did not. After filtration, the samples were diluted 100x with Milli-Q water (Millipore, Burlington, U.S.) and stored in 1.5 ml glass LC vials at  $-20^\circ\text{C}$  until analysis. The *Phragmites australis* was harvested in wk 12. The weather data was obtained from both a nearby weather station located at 1 km from the pilot CWs, as well as our own weather station (Davis Vantage Pro 2 logged with Davis WeatherLink 6.0.4 (Hayward, USA)), that was installed next to the CWs halfway the experimental period (Fig. S3).

### 2.3. Biodegradation experiments

Biodegradation experiments with a BTA starting concentration of 1 mg/L and three different microbial inocula were performed based on the experimental set-up described in Wagner et al. (2019). The three different inocula consisted of 'Pilot0', HSSF-Pilot5' and 'VSSF-Pilot5'. 'Pilot-0' was taken from the sediment of both the vertical flow and horizontal flow pilot-scale CWs described in paragraph 2.2 before

feeding with synthetic CTW, mixed and stored at 4 °C until use. 'VSSF-Pilot5' was taken from the pilot-scale VSSF-CWs and 'HSSF-Pilot5' was taken from the pilot-scale HSSF-CWs after 5 mo of feeding the synthetic CTW containing 1 mg/L BTA. Samples of 2 ml were taken at t (d) 0, 3, 7, 14, 21 and 28 and processed as described in paragraph 2.2

Abiotic controls were performed as described in Wagner et al. (2019). In addition, biotic controls to ensure microbial activity of the inoculum were performed with 50 mg/L benzoic acid in a similar way as the experiments with BTA. Benzoic acid was analysed as described in Wagner et al. (2019).

#### 2.4. Photodegradation experiments

Direct photodegradation experiments were performed outdoors and in a controlled laboratory environment. The experiments were performed in triplicate in 100 ml glass cylindrical reactors that were covered with a quartz-glass cover to prevent evaporation or dilution. A volume of 30 ml ultrapure water with a BTA concentration of 1 mg/L was used. Samples of 2 ml were taken after 0, 17, 23, 47, 65 and 71 h and processed as described in paragraph 2.2.

The outdoors experiments were performed in May 2018 in a week with  $\pm$  9 h sunshine per d and an average temperature of 16.4 °C. The indoors experiments were performed in a cabinet with 3 160 W D3-UV basking lamps (Arcadia, Cambridgeshire, United Kingdom). The wavelength distribution of sunlight and the lamps were measured with an USB4000 spectrophotometer and SpectraSuite software (Ocean Optics, Largo, United States) (Fig. S4).

Each photodegradation experiment had a corresponding dark control and positive control. The dark control was similar to the photodegradation experiments, but covered in aluminium foil. *p*-Nitroanisole was used a positive control for photodegradation. *p*-Nitroanisole – pyridine is commonly used as chemical actinometer (Laszakovits et al., 2016) since the photodegradation rate of *p*-nitroanisole depends on the concentration of pyridine. A *p*-nitroanisole starting concentration of 10 mg/L was used with a corresponding pyridine concentration that was 1000 times higher. *p*-Nitroanisole was analysed on the analytical set-up used for benzoic acid analysis as described in Wagner et al. (2019), but with acetonitrile instead of methanol as organic solvent and an elution method starting at 60% acetonitrile.

Indirect photodegradation was assessed in the pilot-scale CWs.

#### 2.5. Adsorption experiments

##### 2.5.1. Constructed wetland substrates

The substrate from the pilot-scale CWs, 'CW-Pilot', was tested for its adsorptive capacity. CW-Pilot was obtained from the both the pilot-scale HSSF-CWs and VSSF-CWs (see paragraph 2.2.) after 5 mo of feeding with synthetic CTW containing BTA. The substrate was mixed, dried in an oven at 105 °C for 48 h and LOI-analysis showed that it had an OM-content of  $\pm$  1% in weight.

##### 2.5.2. Granular activated carbon

Preliminary adsorption experiments with different GACs revealed that BTA strongly adsorbed to GAC type F400 (Chemviron Carbon, Feluy, Belgium). F400 has a size of 0.55-0.75 mm, a mean particle diameter of 1.0 mm and a total surface area of 1100 m<sup>2</sup>/g according to its supplier. GAC was used as delivered by the supplier.

##### 2.5.3. Experimental set-up

Adsorption experiments with the 'CW-Pilot' substrate were performed in 125 ml serum bottles. The serum bottles were wrapped in aluminium foil to prevent photodegradation and stored at a shaker at 120 rpm and 20 °C. A liquid:substrate ratio of 1:2 (w:w) was used. No chemicals were used to inhibit the microbial activity in addition to the thermal inhibition described in section 2.5.1, thus excluding the influence of chemical inhibitors on the adsorption process. In biological tests

with sodium acetate as easily biodegradable chemical, no biological activity was observed within 96 h. Hence, this was also not expected for the more difficult to biodegrade BTA. The influence of GAC-amendment was determined in separate serum bottles by adding 0.1% GAC in weight.

The liquid phase consisted of ultra-pure water (UPW) and CTW (see paragraph 2.2.) A BTA concentration of 10 mg/L was used. Desorption experiments to test the desorption of BTA from the 'CW-Pilot' substrate were performed similarly as the adsorption experiments, but without spiking of BTA. Samples were taken after 0, 6, 24, 48, 72 and 96 h. T<sub>0</sub>-samples were taken before the addition of GAC. These samples were processed as described in paragraph 2.2, except a 1000x instead of a 100x dilution.

#### 2.6. Benzotriazole analysis

BTA was analysed by LC–MS/MS. The sample injection volume was 20  $\mu$ l. Chromatographic separation was achieved with a Shim-pack XR-ODSIII C18-column (50 x 2 mm with a particle size of 1.6  $\mu$ m) (Shimadzu, 'S-Hertogenbosch, the Netherlands) installed in a Prominence LC consisting of two LC-20AD XR pumps, a SIL-20AC XR auto-sampler and a CTO-20AC column oven. The mobile phase consisted of solvent A: H<sub>2</sub>O with 0.1% acetic acid and solvent B: methanol. An 4.5 min gradient elution method was used with an increase from 10% B to 100% B in 2.5 min, 100% B for 1.5 min and a decrease from 100% B to 10% B in 0.5 min. The flow rate was 0.3 ml/min and the column temperature 35 °C. The system was allowed to equilibrate for 2.5 min prior to each sample injection. Mass spectrometry was performed on a 4000 QTRAP MS/MS system (AB Sciex, MA, USA) coupled to an ESI interface operating in positive mode. Data acquisition and analysis was performed with AB Sciex Analyst software (version 1.5.1, AB Sciex, USA). BTA was identified and quantified by multiple reaction monitoring (MRM) using fragment ions 120/65 and 120/92 and an 11-point external calibration line (0.1–20  $\mu$ g/L). The lowest point of the calibration line (0.1  $\mu$ g/L) corresponded with the limit of quantification for BTA.

#### 2.7. Determination of removal rate constants

Zero and first order rate constants for aerobic biodegradation,  $k_{\text{biodegradation}}$ , adsorption,  $k_{\text{adsorption}}$  and photodegradation,  $k_{\text{photodegradation}}$ , were determined by fitting the experimental data of the batch removal experiments to Eq. (1) for zero order rate constants and Eq. (2) for first order rate constants.

$$C = C_0 - kt \quad (1)$$

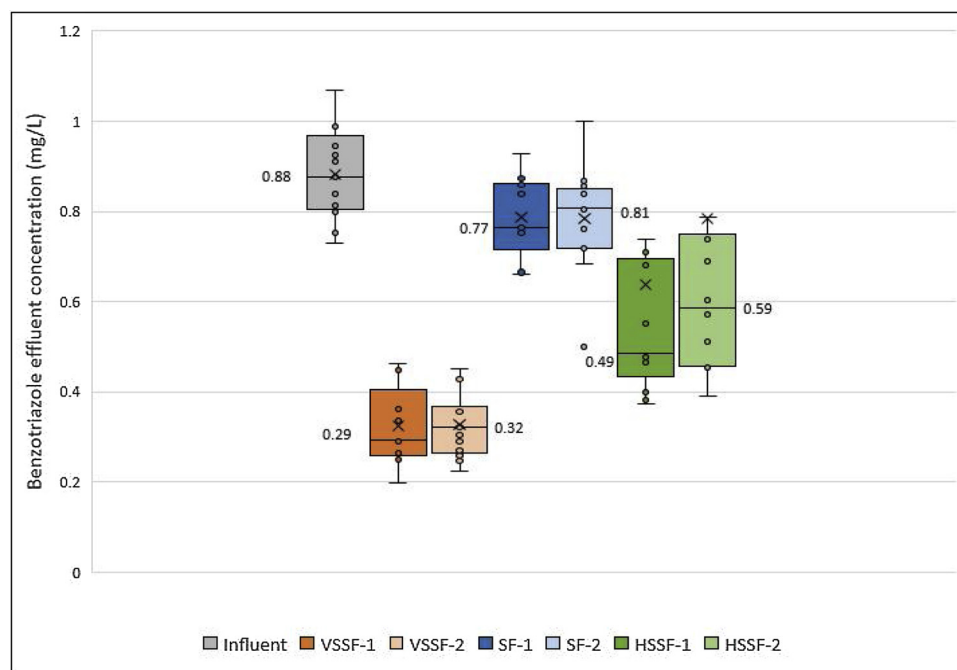
$$C = C_0 * e^{-kt} \quad (2)$$

Where  $C$  is the concentration of BTA,  $C_0$  is the concentration of BTA at  $t$ , time, 0 and  $k$  is the rate constant in  $\text{mg BTA} * t^{-1}$  for zero order rate constants and  $t^{-1}$  for first order rate constants. Eqs. 1 and 2 were subsequently used to predict the removal efficiency in the pilot-scale CWs using the obtained rate constants from the batch experiments and the HRT of the pilot-scale CWs. We did not apply a temperature correction factor, since the temperature inside the pilot-scale CWs was not measured.

### 3. Results & discussion

#### 3.1. BTA removal in pilot scale constructed wetlands

The VSSF-CWs showed the highest BTA removal, followed by the HSSF-CWs and the SF-CWs (Fig. 1). The difference in BTA removal between the VSSF-CWs and HSSF-CWs suggests that aerobic biodegradation could be responsible for part of the removal, since the VSSF-CW has more aerobic redox conditions than the HSSF-CW due to the



**Fig. 1.** Benzotriazole influent and effluent concentrations of the subsurface flow (VSSF) (orange boxplots), surface flow (SF) (blue boxplots) and horizontal subsurface (HSSF) (green boxplots) pilot-scale constructed wetland duplicates. The horizontal line with corresponding number shows the median concentration. The mean concentration is given by 'x'. The boxes show the first and third quartile, while the whiskers show 1.5 times the interquartile range. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

batch-wise feeding of CTW, which allows the penetration of oxygen in the system after each feeding episode. The redox conditions in the pilot-scale CWs are illustrated by the removal of  $\text{NO}_3^-$  (Fig. S5).  $\text{NO}_3^-$  denitrification requires anaerobic conditions in combination with organic carbon as electron donor (Vymazal, 2007), and the significantly higher  $\text{NO}_3^-$  removal in the HSSF-CWs compared to the VSSF-CWs illustrates the more anaerobic redox conditions in the HSSF-CW. The difference in BTA removal is most likely not influenced by difference in substrate or vegetation, since the substrate of the HSSF-CWs and VSSF-CWs theoretically possessed similar adsorption capacities and both CWs are planted with the same plant species. Photodegradation probably played a minor role in BTA removal considering the low removal in the SF CWs. In addition, this low extent of BTA removal in the SF-CW could also be attributed to biodegradation by microorganisms living in the water phase and on the bottom (Jasper et al., 2014).

The BTA effluent concentration in the VSSF-CWs decreased over the experimental period, while the effluent concentration in the HSSF-CWs increased (Fig. S6). The decrease in BTA effluent concentration over time in the VSSF-CWs could be an indication that the microbial community adapts towards the biodegradation of BTA. The increase in BTA effluent concentration in the HSSF-CWs coincides with a decrease in the temperature (Fig. S3). The *Phragmites australis* in the CWs started to decolour, die off and was harvested. The *Phragmites australis* behaved similarly in both the VSSF-CWs and HSSF-CWs, so it is unlikely that the die-off resulted in differences in BTA uptake by the *Phragmites australis* between both CWs. It is more likely that a lower removal efficiency is observed due to a lower input of oxygen and/or nutrients by the *Phragmites australis*, resulting in more anaerobic conditions in the HSSF-CW and less aerobic BTA biodegradation.

The extent of removal in our VSSF-CWs is comparable with the removal of BTA observed in the VSSF-CWs used by Brunsch et al. (2018) after two growing seasons. In these VSSF-CWs planted with *Phragmites australis*, the removal increased from 25% in the summer of 2014 to 82% in the winter of 2017. Although this removal was attributed to biodegradation, no distinct difference between performance in summer and winter was observed. A 6–17 times higher absolute removal %/cm substrate was observed in VSSF-CW layers high in organic matter (OM) or amended with biochar or GAC (Brunsch et al., 2018) during start-up, indicating that adsorption might be a relevant removal mechanisms for BTA.

The average removal of BTA in our HSSF-CWs of 38% is higher than the removal in the HSSF-CWs studied by Matamoros et al. (2016; 2017). A removal of  $5 \pm 7\%$  in warm season and  $1 \pm 32\%$  in cold season was found by Matamoros et al. (2016) in HSSF-CWs planted with *Phragmites australis* with an HRT of 4–6 d. Approximately  $9 \pm 13\%$  BTA was removed in the 10 y old HSSF-CWs planted with *Phragmites australis* that functioned as tertiary treatment for a conventional WWTP receiving urban and industrial wastewater (Matamoros et al., 2017). The authors hypothesized that the removal was the result of biodegradation, since a correlation was found with biological  $\text{NH}_4\text{-N}$  removal (Matamoros et al., 2016).

The mutual differences in removal between the various CW flow types in this study are consistent with other studies in which multiple CW flow types were compared. The high removal in VSSF-CWs compared to CWs with different flow types is consistent with Matamoros et al. (2010), who found approximately 90% removal in a VSSF-CW, while 50% removal was observed in a SF-CW consisting of deep and shallow parts planted with *Typha latifolia* and *Phragmites australis* and a HRT of 1 mo. The removal in the SF-CW in the present study was substantially lower than in the SF-CW in Matamoros et al. (2010). Phytodegradation, photodegradation and biodegradation were considered to be the main BTA removal mechanisms in the SF-CW, while biodegradation and phytodegradation were responsible for the BTA removal in the VSSF-CW (Matamoros et al., 2010). Kahl et al. (2017) found 63% BTA removal in VSSF-CWs compared to 19% in HSSF-CWs, and this removal was attributed to biodegradation. Both CWs were planted with *Phragmites australis* and were in operation for 5 y. In the same study, a higher removal of BTA was found in aerated VSSF-CWs and HSSF-CWs under low  $\text{CBOD}_5$  and high oxygen availability conditions (Kahl et al., 2017). Nivala et al. (2019) followed up on the study by Kahl et al. (2017) and found similar BTA removal efficiencies in the CWs as those observed by Kahl et al. (2017). Higher BTA removal, linked to aerobic biodegradation, was found in CWs with a measurable effluent dissolved oxygen (DO) concentration (Nivala et al., 2019). In conclusion, the BTA removal in our and the abovementioned studies was mostly attributed to biodegradation and a higher BTA removal was observed in VSSF-CWs than in HSSF-CWs as result of the predominantly aerobic conditions.

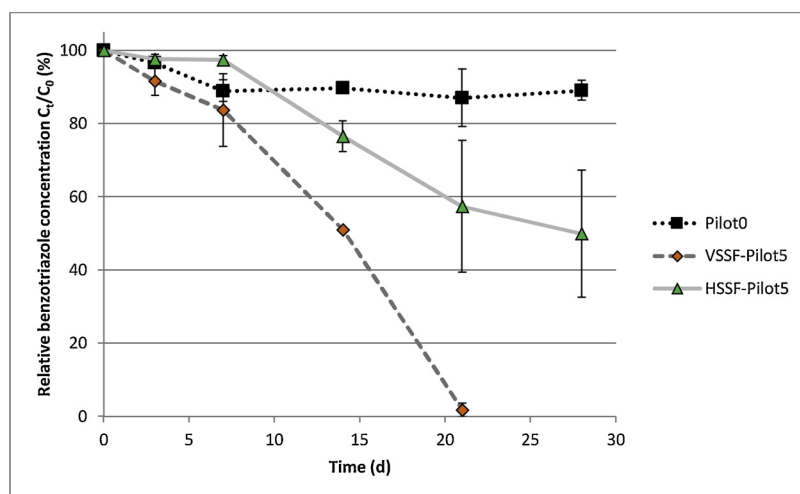


Fig. 2. Relative concentration of benzotriazole over time in batch biodegradation experiments for the Pilot0 inoculum (black squares), VSSF-Pilot5 inoculum (orange diamonds) and HSSF-Pilot5 inoculum (green triangles). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

### 3.2. BTA removal in batch experiments

#### 3.2.1. Biodegradation

Batch experiments with substrate from the pilot-scale CWs were performed to elucidate the contribution of biodegradation, adsorption and photodegradation in the pilot CWs. In the biotic biodegradation experiments with the 'Pilot0' inoculum, 8% of the BTA was removed within 28 d (Fig. 2). The VSSF-Pilot5 inoculum, obtained from the pilot-scale VSSF-CWs after 5 mo of feeding CTW containing BTA showed almost 100% BTA removal within 21 d (Fig. 2). The HSSF-Pilot5 inoculum, obtained after 5 mo of feeding the pilot-scale HSSF-CW resulted in 50% removal in 28 d (Fig. 2). The HSSF-Pilot5 inoculum showed a 7 d lag-period, after which BTA was gradually removed. The abiotic experiments showed that there was little removal in the absence of a living microbial community (Fig. S7), and thus the removal observed in Fig. 2 can be attributed to aerobic biodegradation.

The BTA half-life of  $\pm 14$  d calculated from the VSSF-Pilot5 batch experiment is lower than that found in previous BTA batch aerobic biodegradation studies. Liu et al. (2011a) reported a half-life of 114 d for biodegradation by a non-adapted activated sludge inoculum and a similar BTA starting concentration of 1 mg/L. In non-adapted aquifer material, a half-life of 43 d under similar experimental conditions was found (Liu et al., 2013). However, the 14 d half-life obtained in our experiments is substantially higher than the half-lives of 44 h for a non-adapted activated sludge inoculum (Mazioti et al., 2015a) and 24 h for a non-adapted activated sludge inoculum (Huntscha et al., 2014).

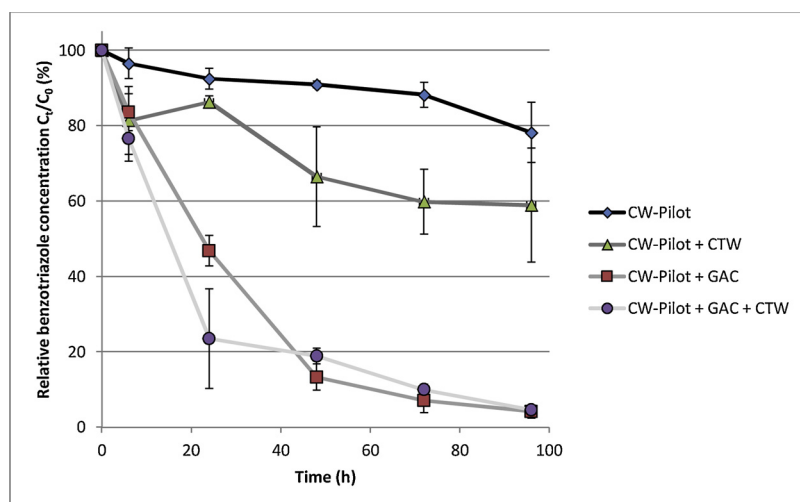
BTA biodegradation is considered to be a co-metabolic process by micro-organisms using different carbon sources as nutrients (Huntscha et al., 2014; Mazioti et al., 2015a, b; Ulrich et al., 2017). However, Herzog et al. (2014) showed that the presence of nitrogen was more important than the presence of carbon sources. Similarly, Matamoros et al. (2016) found a significant correlation between  $\text{NH}_4\text{-N}$  removal and BTA removal. Given the differences in biodegradation capacity between the inoculum obtained at the start of the experimental period and the inocula obtained after 5 mo (Fig. 2) and the earlier mentioned differences in literature half-lives (Liu et al., 2011a, 2013; Huntscha et al., 2014; Mazioti et al., 2015a), growth-linked biodegradation as result of microbial adaptation (Poursat et al., 2019) seems to play an important role in BTA biodegradation. It was apparent that the inoculum obtained from the VSSF-CWs was better adapted to biodegrade BTA than the inoculum from the HSSF-CWs, and that the removal rate in the pilot-scale VSSF-CWs increased over time (Fig. S6). This is likely the result of the aerobic conditions in the VSSF-CWs, allowing better development of a microbial community that is capable of aerobic BTA biodegradation. Similar faster biodegradation after microbial adaptation was observed by Herzog et al. (2014). However, no defined BTA

degrading microorganisms are described thus far (Shi et al., 2019).

#### 3.2.2. Photodegradation

In the aquatic environment, both direct and indirect photodegradation occurs (Schwarzenbach et al., 2003). In the present study, direct photodegradation of BTA did not occur in ultrapure water, neither in the outdoor nor the indoor photodegradation experiments (Fig. S8). The concentration of BTA in the outdoor experiments even increased slightly, likely as result of evaporation of water. The photodegradation set-up was tested by using p-nitroanisole (PNA) as a positive control and this control showed that the indoor photodegradation set-up did photodegrade PNA, albeit slower than in outdoor experiments (Fig. S9). This was expected because the lamps of the indoor experiment provided the full solar wavelength spectrum, but with a different intensity per wavelength than real sunlight (Fig. S4). Nevertheless, this confirms that these lamps are suitable for photodegradation experiments.

In contrast to our findings, BTA is considered to be photodegradable in the environment (Matamoros et al., 2010; Janssen et al., 2015; Bianco et al., 2016; Felis et al., 2016; Weidauer et al., 2016). However, BTA has been shown to adsorb light mainly in the 250–300 nm region (Borin et al., 2003; Bianco et al., 2016), which is environmentally less relevant since this wavelength does not reach the earth's surface (Fig. S4). Thus, a distinction has to be made between photodegradation studies relevant for the natural environment, with lamps that properly mimic sunlight, and studies in which benzotriazole photodegrades at wavelengths not occurring in nature, such as 254 nm (Andreozzi et al., 1998; Liu et al., 2011b; Benitez et al., 2013; Bahnmüller et al., 2015), which are relevant for man-made photoreactors for water treatment. Furthermore, also the lamp intensity is important. Felis et al. (2016) used a lamp emitting the full solar spectrum and observed 26% removal after 660 min of irradiation with an intensity of  $1000 \text{ W/m}^2$ , which is about ten times higher than the average solar intensity in Northwestern-Europe (Bishop and Rossow, 1991). A similar high intensity of  $784 \text{ W/m}^2$  with a 290–800 nm spectrum resulted in a BTA half-life of 24.2 h in Weidauer et al. (2016). Janssen et al. (2015) observed a direct photochemical half-life for BTA of 1.8 d without DOM under 300 W Xe lamps emitting the full light spectrum. This half-life decreased to 1.4 d in the presence of dissolved organic matter (DOM) in the form of standardized Suwannee River Fulvic Acid, as result of indirect photodegradation. However, the CTW fed to the pilot-scale CWs and real CTW (Löwenberg et al., 2015) contains DOM in the form of humic acids. In contrast to fulvic acids, humic acids have shown to inhibit micro-pollutant photodegradation by light-screening (Chen et al., 2017). The pH of the CTW could also influence the photodegradation of BTA, since a difference has been found in the photodegradation of the



**Fig. 3.** Relative concentration of benzotriazole over time in batch adsorption experiments for the pilot constructed wetland substrate in ultra-pure water (purple diamonds), pilot constructed wetland substrate in cooling tower water (green triangles), pilot constructed wetland substrate mixed with granular activated carbon in ultra-pure water (red squares) and pilot constructed wetland substrate mixed with granular activated carbon in cooling tower water (purple circles). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

anionic and neutral form of BTA (Bianco et al., 2016) that is depending on the  $pK_a$  of BTA, which is 8.3 (Hart et al., 2004). In their experiments with lamps emitting 300–500 nm, the estimated half-lives of BTA varied from d to m depending on the experimental conditions (Bianco et al., 2016). CTW could have a pH that is in the range of the  $pK_a$  (Wagner et al., 2018) and, as a consequence, the combination of the pH and the buffer capacity of any constructed wetland could result in local differences in BTA photodegradability in the CW.

### 3.2.3. Adsorption

The batch adsorption experiments showed that adsorption to the substrate of the pilot-scale CWs is a relevant removal mechanisms for BTA. Approximately 20% of BTA was adsorbed to the substrate of the pilot-scale CWs in 96 h in ultra-pure water (Fig. 3). The main process responsible for sorption of ionizable N-heterocyclic compounds, such as BTA, is cation exchange (Bi et al., 2007). However, BTA is mainly present in its neutral form in both the experiments in UPW and CTW, according to BTA's  $pK_a$  of 8.3 (Hart et al., 2004) and the average CTW pH of 7.15, so no cation exchange is expected. The sorption of BTA in neutral form is the result of van der Waals interactions with the functional groups of the soil organic matter (SOM) (Hart et al., 2004; Bi et al., 2007; Jia et al., 2007; Yu et al., 2009; Rhodes-Dicker and PASSESport, 2019). As result of the weak bonding, Rhodes-Dicker and PASSESport (2019) observed increasing desorption hysteresis with increasing concentrations of BTA in bioretention soil filter material, suggesting that only low amounts of BTA are irreversibly adsorbed to SOM. Similar reversible sorption of BTA was observed by Yu et al. (2009). However, in our study, no desorption of earlier adsorbed BTA was observed in desorption experiments with the substrate of the pilot-CWs after 5 mo of feeding BTA containing CTW (data not shown).

In the actual CTW, more than 40% of BTA was adsorbed within 96 h (Fig. 3), highlighting the importance of the role of the nature of the water matrix in batch adsorption experiments. The increased sorption observed in the experiments with the CTW matrix is not likely the effect of pH differences and subsequent ionization of BTA, since the pHs in the experiments with UPW and CTW were similar and did not reach the  $pK_a$  of BTA. The increased sorption of BTA could be the result of the higher  $Ca^{2+}$  content of the CTW compared to ultra-pure water. Bi et al. (2007) showed that increasing  $Ca^{2+}$  concentrations led to an increased adsorption of BTA, likely as result of the formation of a BTA +  $Ca^{2+}$  complex that subsequently reacts with mineral surface sites of the sediment. This form of complexation is likely to bind BTA stronger than the interaction of BTA with SOM (Bi et al., 2007).

The interaction of BTA with SOM implies that the sorption capacity of CWs increases as the CW matures and builds up more SOM as a result of natural decay of the biomass. A possibility to enhance this process

and increase the BTA removal efficiency of a CW is to mix the substrate with a substrate that possesses an increased adsorptive capacity, such as biochar or activated carbon (Ulrich et al., 2015, 2017; Brunsch et al., 2018). The addition of 0.1% GAC (w/w) that was mixed with the CW-Pilot substrate indeed resulted in > 95% adsorption of BTA (Fig. 3). Competition for adsorption sites (Zietschmann et al., 2016) in the mixed substrate did not seem to occur in CTW, since the adsorption was not affected by the CTW matrix (Fig. 3). The adsorption rate of the GAC-amended substrate was faster than that of the non-amended substrate. Faster adsorption of BTA is an advantage for CWs with a low HRT, because under those conditions BTA has less time to interact with the substrate.

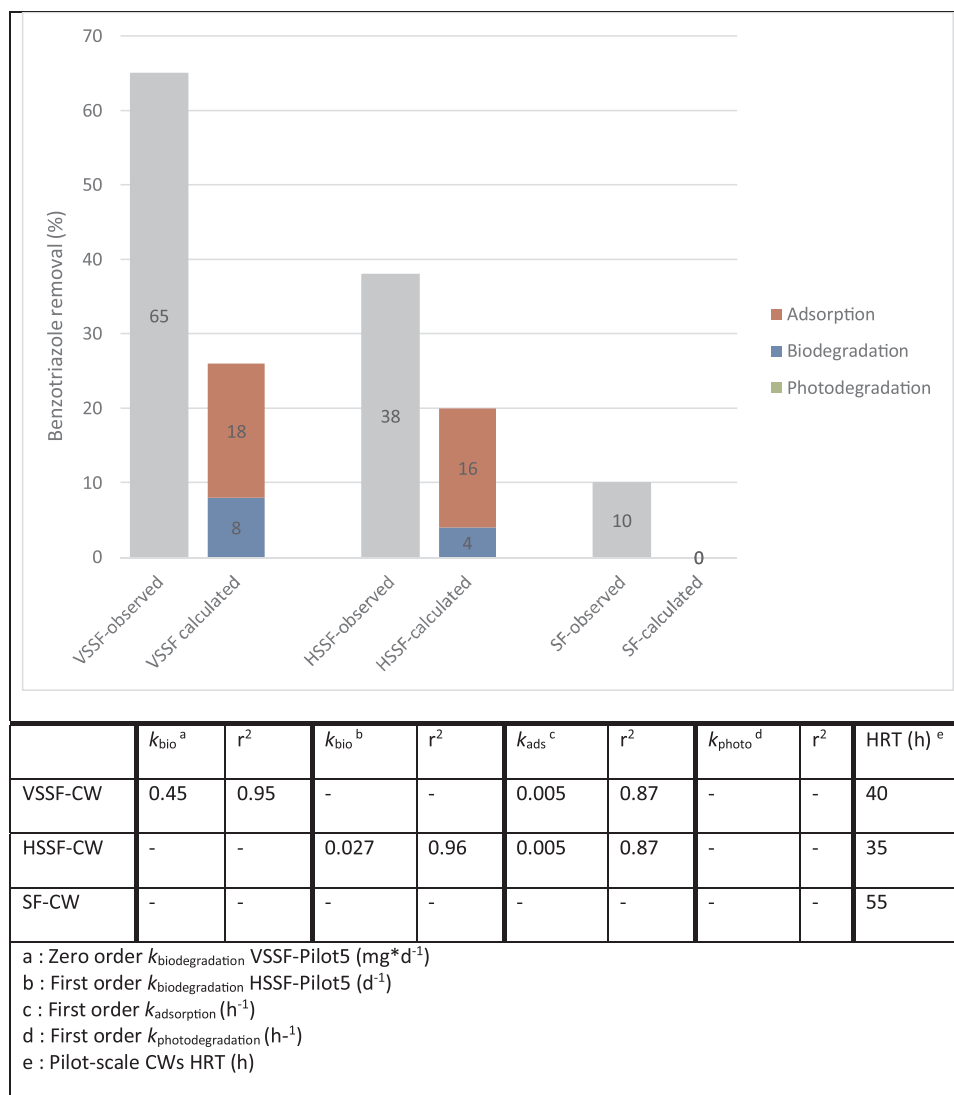
### 3.3. The capability of batch removal experiments to explain the observed removal in experimental constructed wetlands

The predicted removal was compared with the observed removal to evaluate the potential of batch removal experiments to predict the removal efficiency in CWs, and a difference between the observed and calculated removal efficiency was found (Fig. 4). The batch removal experiments were able to predict 40% of the removal observed in the VSSF-CWs and 53% of the removal observed in the HSSF-CWs.

The batch biodegradation experiments showed that the microbial community of the pilot scale VSSF-CWs degraded more BTA than the microbial community of the HSSF-CWs. Combined with the higher HRT of the VSSF-CWs, this partly explains the difference in BTA removal and the different contribution of aerobic biodegradation to the total removal in the two CW flow-types. However, batch biodegradation experiments do not fully mimic the conditions in the CW, since the positive effect of plant exudates in the form of oxygen and nutrients on the microbial activity (Brix, 1994) is lost in batch experiments. In addition, the biodegradation experiments were performed in standardized microbial growth medium, which could result in less co-metabolic BTA biodegradation compared to the CTW. Hence, batch biodegradation experiments likely underestimate the CWs biodegradation potential, giving an explanation for the lower predicted removal with the batch data than the observed removal in the HSSF and VSSF CWs (Fig. 4).

The outcomes of the batch photodegradation experiments are in accordance with the removal found in the pilot-scale CWs. Theoretically, the removal by photodegradation in the pilot-scale SF-CWs could have been the result of direct and indirect photodegradation. Given the low removal in the SF-CWs (Fig. 1), neither of these are relevant for the removal of BTA from CTW. This could either be due to insusceptibility to direct and indirect photodegradation or due to photodegradation inhibition by the humic acids present in the CTW.

The batch adsorption experiments showed that adsorption of BTA is



**Fig. 4.** Calculated removal efficiencies according to removal rates obtained in batch experiments versus the observed removal efficiencies of the pilot scale constructed wetlands for benzotriazole.

a relevant removal process in CWs fed with CTW. Although biodegradation is commonly described as the main removal mechanism responsible for the removal of BTA in CWs (Matamoros et al., 2010; Kahl et al., 2017; Brunsch et al., 2018; Nivala et al., 2019), our experiments show that the contribution of adsorption is higher than that of biodegradation in our pilot-scale CWs. In addition, the contribution of adsorption to the total removal is higher in the HSSF-CWs than the VSSF-CWs due to the lower contribution of aerobic biodegradation. The contribution of adsorption might still be underestimated, since also adsorption to the plant roots can occur in CWs.

In addition to BTA adsorption to the plant roots, BTA might have been taken up by the *Phragmites australis* in the pilot-scale CWs. The uptake and degradation of BTA by this plant species is not described yet, but it is known that BTA is taken up and degraded by plants, such as *Carex praegracilis* (Pritchard et al., 2018), *Lemna minor* (Gatidou et al., 2017), *Arabidopsis thaliana* (Lefevre et al., 2015), and *Helianthus annuus* (Castro et al., 2003). Hence, it would be valuable to perform similar studies with common CW plants as *Phragmites australis* and *Typha latifolia*. However, 95% removal of BTA was observed in unplanted control CW mesocosms versus 97% removal in *Carex praegracilis* planted systems (Pritchard et al., 2018), indicating that other processes, e.g. adsorption in the case of the Pritchard et al. study, are far more relevant for BTA removal than plant uptake.

In conclusion, performing batch removal experiments on biodegradation, photodegradation and adsorption could explain the difference in removal between the various CW flow types, but could not fully predict the observed BTA removal in the pilot-scale CWs. This is most likely due to underestimating the biodegradation capacity of the CW microorganisms in batch experiments. Moreover, since we did not perform plant uptake studies, the possible role of plant uptake could not be incorporated in the prediction.

#### 3.4. Implications for BTA removal from CTW by CWs

Our experiments showed that the VSSF-CWs with its aerobic redox conditions are the most suitable choice for the removal of BTA from CTW prior to its desalination, since simultaneous adsorption and aerobic biodegradation in this CW type results in the highest removal efficiency. The BTA removal efficiency of CWs might be further enhanced by recent technological innovations. A potential way to enhance the BTA removal efficiency is the use of a substrate with enhanced adsorptive capacity. Mixing our sandy CW substrate with GAC has shown to improve the BTA adsorptive removal (Fig. 3). However, long-term pilot-scale experiments with CWs augmented with GAC should be performed to gain a better understanding in the optimal distribution of GAC through the sediment, the time-span of enhanced adsorption,

desorption, and the potential bio-regeneration of the GAC. Furthermore, engineered adsorption materials, such as metal azolate frameworks (Sarker et al., 2017) and calcined Zn-Al layered double hydroxides (Hu et al., 2018) could be tested for their application in CWs.

In addition to enhancing the adsorption, it is possible to create more favourable conditions for aerobic biodegradation. The aerobic conditions in VSSF-CWs can be even further enhanced by artificial aeration, resulting in higher biodegradation rates (Auvinen et al., 2017). Artificial aeration could also enhance the aerobic biodegradation in HSSF-CWs, especially in wintertime when there is less input of oxygen by the vegetation (Ouellet-Plamondon et al., 2006). Aeration has shown to increase the BTA removal in both VSSF-CWs and HSSF-CWs (Kahl et al., 2017). However, it has not been shown that biodegradation of BTA results in its complete mineralization. Various authors have shown that BTA biodegradation leads to BTA transformation products (TPs) with a hydroxylated benzene-ring or methylated triazole ring as result of co-metabolic hydroxylation or methylation (Liu et al., 2011a; Huntscha et al., 2014; Mazioti et al., 2017). Also TPs with both hydroxyl and methyl groups (Huntscha et al., 2014) and oxygenated and carboxylated TPs have tentatively been identified (Huntscha et al., 2014; Mazioti et al., 2017). Their chromatographic behaviour showed that these TPs were more polar than the initial BTA (Mazioti et al., 2017). The behaviour, fate and toxicity of these TPs in CWs is unknown. However, their increased polarity might result in their transport through the CW, after which they end up in the CW effluent. Since this effluent needs to be desalinated prior to its use as make-up water in the cooling tower, it could hamper the functioning of physico-chemical desalination technologies. Hence, increasing the adsorptive capacity of the CW might be the best option for CWs that are treating CTW containing BTA prior to its desalination.

#### 4. Conclusions

An innovative approach using different pilot-scale CWs combined with performing batch experiments with substrate from these CWs made it possible to determine the optimal CW design and the most relevant removal processes for BTA removal in CWs. VSSF-CWs were more efficient in removing BTA from CTW compared to HSSF-CWs and SF-CWs. Batch biodegradation, adsorption and photodegradation experiments showed that the BTA removal in the VSSF-CWs is the result of adsorption and aerobic biodegradation. Adsorption had the highest contribution in the BTA removal in the VSSF-CWs, and the lower removal in the HSSF-CWs was the result of a lower aerobic biodegradation capacity by the microbial inoculum compared to the VSSF-CWs. BTA was not susceptible to photodegradation, and therefore little removal was observed in the SF-CWs. It was not possible to predict the removal efficiency of the pilot-scale CWs by using removal rates obtained in batch experiments, since the biodegradation capacity of CW microorganisms is likely underestimated in batch experiments.

The knowledge on the main removal mechanisms for BTA allows for a CW design tailored for BTA removal from CTW. In addition, the outcomes of this research show that batch experiments with CW substrate provide an insight in and classification of the most relevant removal mechanisms for a given compound and result in a better understanding of the CW removal processes.

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#### Appendix A. Supplementary data

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