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Enhanced dissipation of trace level organic contaminants by floating treatment wetlands established with two macrophyte species: A mesocosm study

Jeong-In Hwang [a], Francisca Ordonez Hinz [a], Joseph P. Albano [b], Patrick Christopher Wilson [a, *]

[a] Soil and Water Sciences Department, University of Florida, Gainesville, FL, 32611, USA
[b] Agricultural Research Service, U.S. Department of Agriculture, Fort Pierce, FL, 34945, USA

HIGHLIGHTS

- Floating treatment wetland (FTW) removed contaminants of emerging concern (CECs).
- FTW mesocosm systems with cannas removed more CECs than sweetflags.
- FTW-planting density did not influence CEC removals.
- The most influential factors for CEC removals were CEC persistency and plant species.
- Canna was the most promising plant species in FTW systems designed for CEC removals.

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ABSTRACT

This study evaluated removal efficiencies of six contaminants of emerging concern (CECs) in floating treatment wetland (FTW) mesocosms established with either Japanese Sweetflag (*Acorus gramineus* Sol. ex Aiton) or canna lilies (*Canna Hybrida* L. 'Orange King Humbert'). The CECs included: acetaminophen (APAP), atrazine (ATZ), carbamazepine (CBZ), perfluorooctanoic acid (PFOA), sulfamethoxazole (SMX), and 17β-estradiol (E2). Each treatment was planted with different numbers of plants (i.e., 0, 10, 15, and 20), and the experiments lasted for 17 weeks. Dissipation of CECs was greater in planted treatments than in non-planted controls, and the planting number had little effect on dissipation of CECs. All residues of APAP and E2 dissipated rapidly within 2 weeks in all planted treatments. At the end of the experiment, residues of ATZ and SMX completely dissipated in the canna treatments, but not in the sweetflag treatments (75.8–87.6% and 96.3–97.1%, respectively). During the 17 week study, moderate dissipation of CBZ was observed in treatments including cannas (79.5–82.6%) and sweetflag (69.4–82.3%), while less dissipation was observed for PFOA (9.0–15.0% with sweetflag and 58.4–62.3% with cannas). Principal component analysis indicates that aqueous persistency of CECs and species of plants used influenced the dissipation of CECs in FTWs. Of the two species evaluated, canna was the most promising plant species for FTW systems designed to remove these CECs from surface water.

1. Introduction

Floating treatment wetlands (FTWs) are an *in-situ* phytoremediation technique used to remove chemical contaminants from surface water using plant-associated processes (Liu et al., 2018). In the FTW system, plants are secured onto buoyant mats that position the shoots above the water surface and the roots below the water surface. The planted mats are floated on the surface of the waterbody in need of remediation. As the plants grow, their roots extend down into the water body where they can contact and remove contaminants through transpiration and sorption, as well as to serve as a substrate to support rhizospheric microflora that can also contribute to contaminant degradation and/or mineralization (Kadlec and Wallace, 2009; Shahid et al., 2018). Since the

* Corresponding author.
E-mail address: pcwilson@ufl.edu (P.C. Wilson).

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first application of FTWs (Hoeger, 1988), they have been utilized as a cost-effective and ecologically-friendly remediation strategy for removing a variety of contaminants from water (Wu et al., 2006; Hijosa-Valsero et al., 2010; Chen et al., 2012; Wang et al., 2015; Xiao et al., 2018). The efficiency of FTWs for contaminant removal may be influenced by the type of plants used and the planting density. However, few studies are available regarding such relationships (Sun et al., 2013; Li et al., 2014). Likewise, to our knowledge no studies are available in the literature evaluating the influence of planting densities on contaminant removal using FTWs.

Trace concentrations of anthropogenic chemicals (for which little is known about their eco-toxicity) are routinely found in aquatic ecosystems (Lecomte et al., 2017) and are referred to as contaminants of emerging concern (CECs) (Pablos et al., 2018). Several CECs include the analgesic/antipyretic, acetaminophen (*N*-(4-hydroxyphenyl)-ethanamide; APAP); the herbicide, atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine; ATZ); the anti-convulsant, carbamazepine (5*H*-dibenzo[*b*,*f*]-azepine-5-carboxamide; CBZ); the industrial surfactant, perfluorooctanoic acid (PFOA); the antibiotic, sulfamethoxazole (4-Amino-*N*-(5-methylisoxazol-3-yl)-benzenesulfonamide; SMX); and the estrogen, 17β-estradiol ((17β)-estra-1,3,5(10)-triene-3,17-diol; E2).

The pharmaceuticals APAP, CBZ, and E2 have been frequently detected in domestic wastewater (Kim et al., 2007; Ekpeghere et al., 2018; Zhang et al., 2019) and have been reported to have adverse effects on humans and ecosystems (Al-Qaim et al., 2018; Zhang et al., 2019). The herbicide ATZ is a relatively old chemical that is frequently detected in water and is regarded as a CEC relative to its potential endocrine disruptor activity (Sass and Colangelo, 2006) and high persistence in water (U.S. EPA, 2007). PFOA is an industrial chemical that was used to make heat-, oil-, and water-resistant coatings on consumer products. These chemicals have hydrophobic and hydrophilic properties and are highly persistent in aquatic ecosystems (Yamashita et al., 2005; Zareitalabad et al., 2013). Moreover, PFOA is classified as “possibly carcinogenic” to humans by the International Agency for Research on Cancer (2017). SMX is the most frequently detected sulfonamide antibiotic detected in municipal wastewater and is of concern due to the emergence of antibiotic-resistant bacterial strains in the environment (Wang et al., 2019).

As reported in many previous studies (Wilson et al., 1999; Lai et al., 2010; He et al., 2013; Basu et al., 2015; Maine et al., 2019; Abdel-Mottaleb and Wilson, 2019), cannas (having broad leaves and densely-developing roots) may be a potential macrophyte species for effectively removing trace concentrations of CECs from contaminated surface water. In addition to their remediation ability, colorful blossoms of canna species can add an aesthetically pleasing element to treatment sites. Sweetflags are another type of macrophytes, having long, narrow, thick grass-like and slightly curved leaves. These macrophytes are often found in wetlands and are also reported to have a high potential for absorbing and accumulating various types of contaminants within their biomass (Wilson et al., 2001; Li et al., 2014; Jiang et al., 2018; Singh et al., 2019). In this study, FTWs were established with two macrophytes species, *Acorus gramineus* Sol. ex Aiton (common name: Japanese sweetflag) and *Canna hybrida* L. ’Orange King Humbert’ (common name: canna), at different planting densities to evaluate removal efficiencies of APAP, ATZ, CBZ, PFOA, SMX, and E2 from contaminated surface water. The most influential factors affecting CEC removal were identified using principle component analysis (PCA).

2. Materials and methods

2.1. Chemicals and reagents

Analytical standards (≥96% purities) of APAP, ATZ, CBZ, PFOA, SMX, and E2 were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). A mixed standard solution of the chemicals was prepared in methanol at the concentrations of 7870 μg mL^{-1} APAP; 136 μg mL^{-1} ATZ; 288 μg mL^{-1} CBZ; 587 μg mL^{-1} PFOA; 116 μg mL^{-1} SMX; and 29 μg mL^{-1} E2. Isotopically-labeled standards with deuterium (APAP-d_4, ATZ-d_5, CBZ-d_{10}, and E2-d_5) or carbon-13 ($^{13}C_8$-PFOA and $^{13}C_6$-SMX) were purchased from Cerilliant Co. (Round Rock, TX, USA) and Cambridge Isotope Laboratories Inc. (Tewksury, MA, USA), respectively. The isotopically-labeled standards were dissolved in methanol to achieve a concentration of 1 μg mL^{-1} for each chemical. This resulting mixture was used as a surrogate standard. Ascorbic acid, hydrochloric acid, sodium azide, formic acid, methyl *tert*-butyl ether (MTBE), and optima high performance liquid chromatography−mass spectrometry (HPLC−MS) grade methanol, and water were purchased from Fisher Scientific, Inc (Fair Lawn, NJ, USA).

2.2. Plant acclimation

For this study, mesocosms were established on the University of Florida campus (29°38′21.3"N 82°21′30.7"W; 2401 Memorial Road, Gainesville, FL 32603, USA). Approximately nine-month old bare root *Acorus gramineus* Sol. ex Aiton (common name: Japanese sweetflag) and three-month old *Canna hybrida* L. ’Orange King Humbert’ (common name: canna) were purchased from Grandiflora Nursery (Gainesville, FL, USA) and Florida Aquatic Nurseries (Davie, FL, USA), respectively. Plant fresh weights and shoot heights were recorded to facilitate selection of uniform individuals. The most uniform plants were transplanted into net cups (225 mL vol., 7.6 cm I.D. × 10.2 cm depth; The Accelerator®, Stuewe and Sons, Inc., Tangent, OR, USA), that were then packed with horticultural-grade perlite. The plants in the net cups were then secured within 7.8 cm diameter holes pre-punched into the floating mats (Beemats, LLC, New Smyrna Beach, FL, USA). The holes were spaced 30 cm (center-to-center) from one another. The Beemats were floated in 378 L (100 gal) commercial stock tanks [90 cm (l) × 130 cm (w) × 66 cm (h); Rubbermaid, Atlanta, GA, USA]. Given the surface dimensions for the tanks, the maximum number of holes in the Beemats was limited to 20 per mat. The tanks were filled with 302 L of water. Water levels in the tanks were calibrated by pouring 18.9 L water repeatedly into each tank and marking the inside of the tank after each addition. Water volumes within the tanks ranged from 264.6 L to 378 L during the study. Water within each mesocosm was fertilized with 3.8 mL of Dyna-Gro Liquid Grow 7-9-5 Plant Food (Richmond, CA, USA) and 4.1 g of calcium nitrate (Southern Agricultural Insecticides, Inc., Palmetto, FL, USA) to achieve environmentally-relevant concentrations of total nitrogen (TN, 4.4 mg L^{-1}) and total phosphorus (TP, 0.7 mg L^{-1}) (Shrestha et al., 2017; Papias et al., 2018).

To evaluate the influence of plant densities, sweetflag or canna plants were established in the mesocosms at 20 plants per mesocosm (100% treatment; T-100), 15 plants per mesocosm (75% treatment; T-75), and 10 plants per mesocosm (50% treatment; T-50). Control mesocosms included non-planted tanks with contaminant treatment and planted (15 plants) tanks without contaminants. All treatments and controls were prepared in triplicate and were randomly assigned to the mesocosms to minimize spatial bias.

During the entire study period, three fungicides (myclobutanil, chlorothalonil, and tebuconazole) were foliar-applied on a weekly

rotation to control the orange rust-causing pathogen, *Puccinia thaliae*. The plants were acclimated for 50 d under these conditions before the CEC were added.

2.3. Mesocosm experiment

One day before CECs were added to the mesocosms, water used during the plant acclimation period was removed and the tanks were scrubbed with fresh tap water. The cleaned tanks were refilled with 302 L of water fertilized with nutrients at the same concentrations as described earlier. A mixed standard solution containing the six CECs was stirred into each tank to achieve initial concentrations of 260 μg L^{-1} APAP, 4.5 μg L^{-1} ATZ, 9.5 μg L^{-1} CBZ, 19.4 μg L^{-1} PFOA, 3.8 μg L^{-1} SMX, and 0.9 μg L^{-1} E2. These concentrations were the highest concentrations previously reported in aquatic ecosystems (Hoa et al., 2011; Slobodnik et al., 2012; Gall et al., 2014; Douglass et al., 2015; Shiwaku et al., 2016; Schaider et al., 2017), except for ATZ. ATZ was added at half of the highest concentration due to concerns about its potential to cause phytotoxicity. Following the addition of nutrients and CECs, the water in the mesocosm tanks was stirred using a polyvinyl chloride (PVC) rod, and samples of the water were collected for analysis of initial CEC concentrations (950 mL) and nutrients (20 mL). After sampling, the Beemats were re-floated on the mesocosm surfaces, and the surfaces were covered with black sheets of polyethylene with holes punched where plants were present in order to prevent the growth of aquatic algae due to light penetration through the non-planted holes and edges between the tanks and mats. The entire mesocosm area was covered with a retractable rain mitigation facility built at a height of 3 m using polyethylene sheets suspended from a wire line running over each set of mesocosms (Fig. S1). The mesocosms were covered on rainy days to prevent them from overflowing, which would result in unaccountable losses of the CECs. To maintain adequate nutrition, half of the initial dose of nutrients was added to both treatments and controls after six weeks of the experiment. Temperature, humidity, and precipitation data in the local area during the study were obtained from the Weather Underground meteorological administration database (https://www.wunderground.com/history/). The entire study was conducted for 17 weeks, from May 31 to October 1, 2018.

2.4. Sampling

Water samples were collected weekly during the first four weeks after the beginning of the experiment, once every two weeks for the following six weeks, and then once after an additional four weeks. Before sampling, the Beemats (including plants) were removed from the tanks and water in the tanks was replenished with tap water up to the initial level (302 L). Once refilled, the water was stirred using a PVC rod and allowed to settle for 3 min. Water samples (950 mL) were collected in 1 L amber glass bottles by submerging each respective bottle 5 cm below the water surface in the middle of each tank. In the same manner, samples for quality assurance/quality control (QA/QC) were collected during each sampling event from a randomly selected treatment tank to evaluate reproducibility in the sampling process (sample duplicate) and from a non-spiked control tank to evaluate the performance of extraction and analysis processes (matrix spike and matrix spike duplicate) based on recoveries and variability (%RSD). All water samples were transported to the laboratory, filtered through syringe filters (0.2 μm, 30 mm I.D., Thermo Scientific Inc., Rockwood, TN 37854), and stored at 4 °C until analysis. In addition to cooling, samples were also preserved by addition of 1 g L^{-1} sodium azide and 50 mg L^{-1} ascorbic acid.

Water samples (20 mL) were also collected for analysis of total nitrogen (TN; sum of nitrate, nitrite, and ammonium) and total phosphorus (TP) as described in Wilson and Albano (2013) and Ordonez-Hinz et al. (2019). Samples for nutrient analysis were filtered through 0.2 μm PTFE syringe filters and stored at −20 °C until analysis. The nutrient analysis was performed at the USDA-ARS (Horticultural Research Laboratory, Fort Pierce, FL, USA). The pH and electrical conductivity (EC) within mesocosms were measured on each sampling day using a YSI 650 Multi-parameter Display system with 600XL Sonde (YSI Inc., Yellow Springs, OH, USA). On the final sampling day, all plants were carefully removed from each treatment and control tank. The plants were dissected into shoots and roots (including tubers), and lengths of each part were recorded. Root lengths were measured from the tuber to the longest primary root tip. Subsequently, the dissected plant parts were individually dried for three months in a 50 °C oven room, after which dry weights were measured.

2.5. Chemical analysis

Prior to CEC analysis, water samples were warmed to ambient temperature and then adjusted to pH 3 using 1 N hydrochloric acid and 1 N sodium hydroxide. Extraction and analysis of samples were based on previously-published methods (Vanderford and Snyder, 2006; Yang et al., 2016). All water samples were spiked with 200 μL of 1 μg mL^{-1} surrogate standard solution. A matrix-spike quality control sample and its duplicate sample were additionally spiked with 100 μL of 1 μg mL^{-1} standard solution of native chemicals for each batch of samples extracted to measure recoveries and %RSD. Samples were extracted using Oasis hydrophilic-lipophilic balance (HLB) solid phase extraction cartridges (6 cm^3, 200 mg; Waters, Milford, MA), placed on a vacuum manifold. The HLB cartridges were pre-activated by washing sequentially with 5 mL of methyl *tert*-butyl ether, 5 mL of methanol, and 5 mL of reagent grade water. The entire volume of water sample was then passed through the cartridges at a flow rate of 10 mL min^{-1}. Cartridges were dried under vacuum for 30 min following sample extraction. CEC residues sorbed onto the HLB media were eluted into a glass tube with 5 mL methanol, followed by 5 mL methanol/MTBE (10/90, v/v). The eluate was then evaporated to about 0.5 mL using a RapidVap system (Model 79000-02, Labconco Co., Kanas City, MO, USA). Methanol was added to adjust the final sample volume to 1 mL before transferring the extract into a 2 mL amber glass vial. CECs in samples were quantified using a Waters Alliance 2695 high pressure liquid chromatograph connected to a Micromass Quattro Ultima tandem mass spectrometer (LC−MS/MS) (Waters Corporation, Milford, MA, USA). A series of calibration standards was analyzed for each CEC (5−2000 ng mL^{-1}) for every batch of 20 samples. All calibration curves were required to have regression correlation coefficients (R^2) of >0.99 for quantification. Details regarding analytical conditions for the LC−MS/MS are provided in Supporting Information. Under the conditions described recoveries were: 116.7 ± 23.4% (APAP); 111.9 ± 3.2% (ATZ); 114.3 ± 18.4 (CBZ); 81.6 ± 1.4% (PFOA); 88.1 ± 15.6% (SMX); 105 ± 12.4% (E2). Instrument detection limits (IDLs) for native and surrogate standards of each CEC were sufficiently low (<5 ng mL^{-1}) to analyze trace CEC residues from water samples collected during the study. Recoveries of CECs in the matrix-spiked quality control samples (100 ng mL^{-1}) were within 80.1−116.7%, with relative standard deviations of <20%.

2.6. CEC dissipation trend characterization

Time-dependent dissipation trends for each CEC in the mesocosms ($C_w(t)$) were simulated using first-order (FO; Eq. (1)) and second-order (SO; Eq. (2)) kinetic models, as well as a double-

exponential (DE) model (Eq. (3); Hwang et al., 2018).

$$C_w(t) = C_0 \times e^{-k_f \times t} \quad (1)$$

$$C_w(t) = C_0/(1 + C_0 \times k_s \times t) \quad (2)$$

$$C_w(t) = C_0 - \left[P_1\left(1 - e^{-k_1 \times t}\right) + P_2\left(1 - e^{-k_2 \times t}\right)\right] \quad (3)$$

where C_0 is the initial concentration of each CEC in water (mg L^{-1}), and k_f and k_s represent first- and second-order dissipation rate constants (d^{-1}), respectively. For the DE model, CEC dissipation curves were divided into two phases (fast and slow) that were divided into proportions of P_1 and P_2 (as percents summing to 100), respectively. The k_1 and k_2 indicate dissipation rate constants for the fast and slow dissipation phases (d^{-1}), respectively. All values of model parameters and half-lives (DT_{50}) were calculated using the Solver Add-in tool in Microsoft Excel™ by minimizing the sum of the square of residuals, which are differences between modeled and measured values.

2.7. Statistical analysis

CEC concentrations between treatments and the controls on each sampling day were subjected to analysis of variance with means comparisons using Duncan's multiple range test method ($P = 0.05$). Likewise, lengths, weights, and leaf numbers of plants measured at the beginning and end of experiment were compared between treatments and the controls using Duncan's multiple range test and Tukey test methods ($P = 0.05$). In addition, principle components analysis (PCA) was conducted using CEC analysis data obtained from the non-planted controls and the T-100 treatments (with both plants) over the 17 week study. From the factor analysis with 18 variables, two principle components (PCs) having the highest eigenvalues were extracted by minimizing the factor–factor covariance with nine time oblique-rotation (including Kaiser normalization) and were used to obtain a pattern matrix, which describes the correlation between PCs and factors. All statistical analysis used the Predictive Analytics Software (PASW) Statistics 18 (International Business Machines Co., Armonk, NY, USA) package.

3. Results and discussion

3.1. Environmental conditions

Weather conditions in the vicinity of the mesocosms during the study are provided in Fig. S2. Temperatures (mean 28.3 ± 5.4 °C) and humidities (mean 75.9 ± 4.5%) were relatively stable throughout the experimental period and were appropriate for supporting plant growth. Although there were 64 rainy days during the entire 119-d study period with 603.3 mm of total precipitation, water levels within the mesocosms never overflowed due to the overhead rain mitigation system. The addition of contaminants did not influence the pH of water in both the mesocosms grown with sweetflag or canna plants and the non-planted mesocosms (Fig. S3A and B). The initial pHs of all treatment and control mesocosms ranged from 7.2 to 8.6. The pH in non-planted controls (6.2–8.8) was relatively stable during the entire study period, except for a slight temporary increase associated with additional nutrient dosing at week 6. The pH in the mesocosms containing sweetflag (5.0–8.0) decreased slightly over time, but the pattern of pH change was similar to that in the non-planted control mesocosm (Fig. S3A). As observed in the non-planted controls, the temporary pH increase at week 6 was also seen in the sweetflag treatments. The pH in mesocosms established with cannas decreased to 3.6 ± 0.3 within the first two weeks and continued to decrease through week 10 (1.8 ± 0.2) (Fig. S3B). Unlike the non-planted controls and sweetflag treatments, the canna treatments showed no momentary pH increase at week 6. Reductions in pH of water associated with floating wetland vegetation has not been reported. Fortunately, the lowered pH did not inhibit canna growth. After week 10, the pH in canna-containing mesocosms increased to 3.5 ± 0.1 by the end of experiment. This increase in pH might be associated with inflow of rain into the mesocosm tanks through tears in the rain mitigation system, which was damaged during a storm by strong winds and heavy rainfall (August 23, 2018). However, despite the inflow of rainwater, the water volumes in the mesocosms were consistently maintained within the calibrated level for estimating total volume. Salinities (0.36–0.87 mS cm^{-1}) recorded in all treatments and controls were below the levels reported to cause salt stress to plants (Karimi et al., 2011) (Fig. S3C and D). Time-dependent trends of ECs in mesocosms were similar between all sweetflag treatments and the non-planted control. However, compared to non-planted controls, the ECs in the canna treatments were lower in weeks 1–2 and higher after week 6.

3.2. Nutrient dynamics

Establishment of plants on the FTWs resulted in a rapid reduction in nutrient concentrations within the mesocosm water during the study (Fig. S4). Concentrations of TN and TP in the water were initially 3.93 ± 0.90 mg L^{-1} and 0.34 ± 0.07 mg L^{-1}, respectively. In non-planted controls, TN concentrations tended to decrease over time following the additions on both the day of treatment and 6 weeks afterwards. This result indicates that nitrogen-consuming microorganisms were present in the non-planted control mesocosms and that nitrogen losses in planted treatments were not solely attributable to plant uptake. Nitrogen resources were depleted within 1–2 weeks following nutrient additions indicating significant removal potential between the plants and microflora in the systems.

Phosphorus resources in non-planted controls barely decreased throughout the entire study period. Although the initial TP concentrations (0.32 ± 0.08 mg L^{-1}) decreased by 25% (0.24 ± 0.09 mg L^{-1}) within 4 weeks, the concentrations after nutrient additions 6 weeks after the study started (0.45 ± 0.08 mg L^{-1}) remained relatively stable through the end of the experiment (0.44 ± 0.08 mg L^{-1}). However, TP concentrations decreased rapidly in all planted treatments, but especially in the canna treatments where most was consumed within 1 week after the initial addition. Phosphorous dissipation was more similar between the two species following the nutrient addition 6 weeks into the study. In both cases, concentrations were <0.2 mg L^{-1} at the end of the study. Plant growth inhibition due to nutrient deficiency was not observed throughout the study.

3.3. CEC dissipation trends

None of the CECs were detected in the controls that were planted, but not spiked. Initial concentrations of CECs in water samples collected immediately after the chemical addition were 184.5 ng mL^{-1} APAP, 3.8 ng mL^{-1} ATZ, 11.8 ng mL^{-1} CBZ, 21.8 ng mL^{-1} PFOA, 3.4 ng mL^{-1} SMX, and 0.8 ng mL^{-1} E2. While initial concentrations of ATZ, CBZ, PFOA, SMX, and E2 were close to nominal target concentrations, measured concentrations of APAP were 1.4 times lower, likely due to its vulnerability to biodegradation by aquatic microorganisms (Lin et al., 2010; Liang et al., 2016). While lower than target, initial APAP concentrations were still high enough for evaluation of its dissipation in water over time.

Measured initial CEC concentrations were used to estimate dissipation of each CEC within each treatment (sweetflag, Fig. 1; canna, Fig. 2) and control after 1, 3, 6, 10, and 17 weeks.

APAP dissipated the most quickly of all CECs evaluated regardless of whether plants were present or not. Concentrations decreased by 18.5% in the non-planted controls within one week and were below detection limits after 2 weeks. While APAP dissipated quickly in all of the planted treatments and controls, the presence of plants (regardless of species or density) accelerated dissipation after one week (Figs. 1 and 2). In the treatments planted with sweetflag, APAP dissipated 2.9–3.6 times more than in the controls after 1 week. Dissipation in the canna treatments was more rapid than with sweetflag, with no APAP being detected after 1 week regardless of planting density. These results are counter to those observed by Abdel-Mottaleb and Wilson (2019) who reported no dissipation of APAP in controls, 100% dissipation in the *A. gramineous* treatments within 14 days, and 64% dissipation in *Canna hybrida* "Orange Punch" treatments using radiolabeled chemicals. This difference is likely due to the more sterile lab testing environment as compared to the field environment where the mesocosms were located, further indicating that other processes (in addition to plant uptake) were involved with the dissipation observed. These results indicate that FTWs established with plants, particularly cannas, can enhance and accelerate the dissipation of APAP in water. Plant density did not influence APAP dissipation with either species.

ATZ dissipation was significantly accelerated in the presence of plants (Figs. 1 and 2). In the non-planted control, ATZ concentrations were relatively stable throughout the 17 week study except for week 1 where little dissipation had occurred. From weeks 1 through 17, concentrations in the non-planted controls decreased by approximately 40%. Less dissipation occurred in mesocosms planted with sweetflag as compared to cannas, which is similar to results from a study using individual plants and radiolabeled ATZ (Abdel-Mottaleb and Wilson, 2019). In this case, 3.1–15.6% of the initial ATZ dissipated within one week, increasing to 75.8–87.6% (nearly 2 × non-planted controls) by the end of the study (Fig. 1). In contrast, dissipation of ATZ was much faster and greater in mesocosms planted with cannas (Fig. 2). ATZ dissipation ranged from 17.2 to 56.3% in the first week, increasing to 87.4–91.0% the following two weeks. ATZ concentrations decreased by 99.7% after 6 weeks. Planting density influenced ATZ concentrations at times (i.e., weeks 6–10 for sweetflag treatments and week 1 for canna treatments), though not consistently. When differences were observed, ATZ dissipation was greater in the treatments including 20 plants.

ATZ dissipation may have occurred through several different pathways, some of which may be related to the study system.

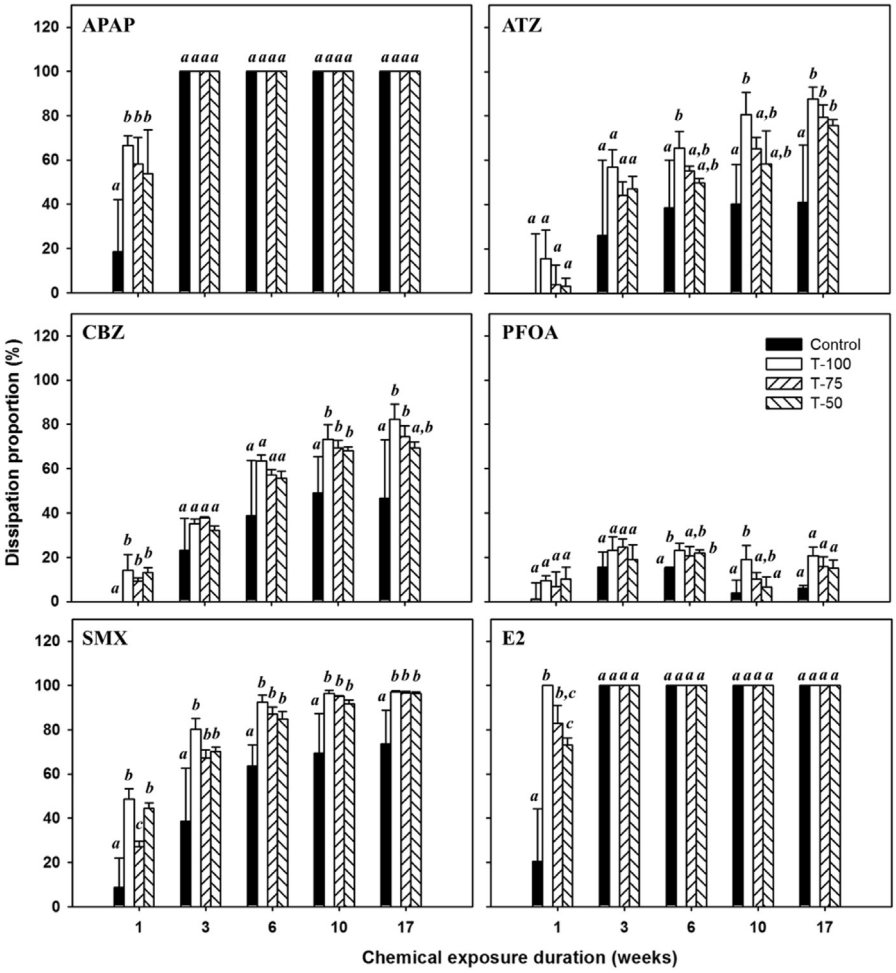

Fig. 1. Dissipation (% of original added) of acetaminophen (APAP), atrazine (ATZ), carbamazepine (CBZ), perfluorooctanoic acid (PFOA), sulfamethoxazole (SMZ), and 17β-estradiol (E2) associated with floating treatment wetlands (FTWs) grown with different densities of *Acorus gramineus* Sol. ex Aiton plants (T-100 = 20 plants, T-75 = 15 plants, and T-50 = 10 plants). Error bars represent standard deviations, and different lower-case letters indicate significant differences between mean values evaluated by Duncan's multiple range test ($p < 0.05$).

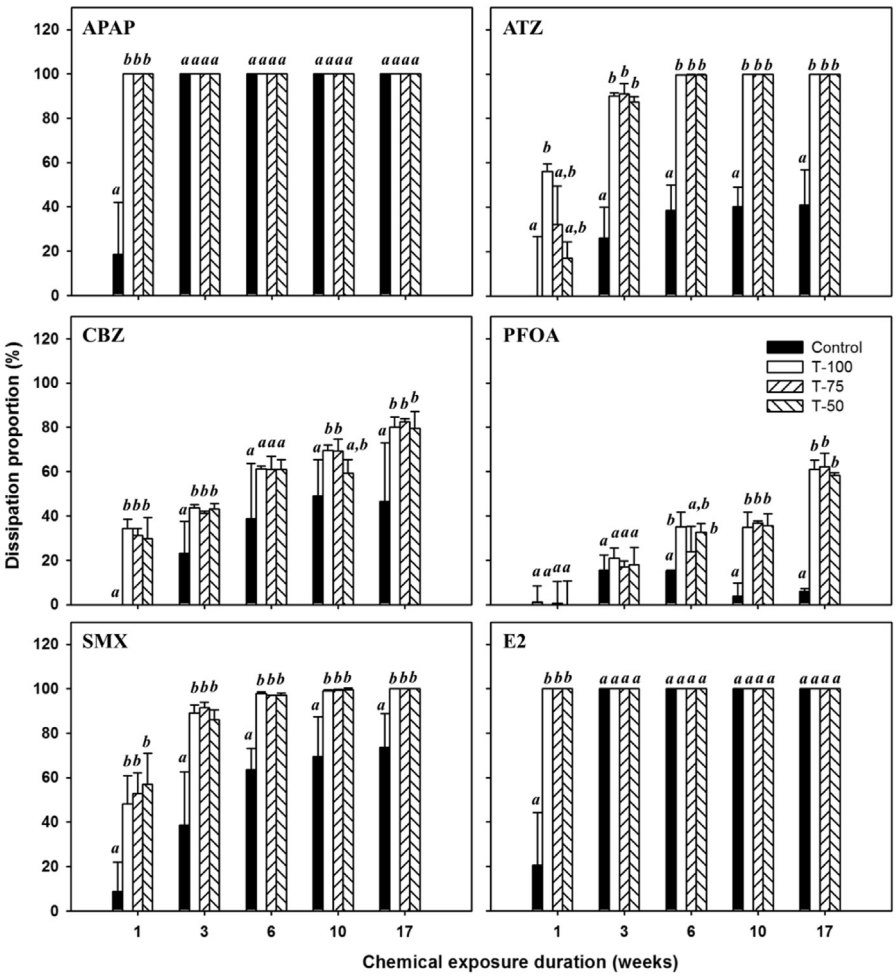

Fig. 2. Dissipation (% of original added) of acetaminophen (APAP), atrazine (ATZ), carbamazepine (CBZ), perfluorooctanoic acid (PFOA), sulfamethoxazole (SMZ), and 17β-estradiol (E2) associated with floating treatment wetlands (FTWs) grown with different densities of *Canna hybrida* L. 'Orange King Humbert' plants (T-100 = 20 plants, T-75 = 15 plants, and T-50 = 10 plants). Error bars represent standard deviations, and different lower-case letters indicate significant differences between mean values evaluated by Duncan's multiple range test ($p < 0.05$).

Uptake of ATZ into plants via the xylem vessels is one potential pathway (Su and Liang, 2011; Albright et al., 2013; Albright and Coats, 2014). Abdel-Mottaleb and Wilson (2019) reported that dissipation of radiolabeled ATZ from spiked solutions was strongly correlated with cumulative transpiration volumes of *Canna hybrida* 'Orange Punch' (R^2 = 0.95) and moderately associated with cumulative transpiration volumes of *A. gramineus* (R^2 = 0.57). Additionally, ATZ can degrade by hydrolysis in strongly acidic and alkaline solutions (Macbean, 2012). While the pH in the canna treatments decreased drastically to <3.6 for several weeks, follow-up in-vitro lab studies where the CECs were incubated in DI water with pH's of 3, 5, and 7 indicated very little dissipation during a 4 week incubation period Fig. S5). Adsorption of ATZ to the roots of plants might account for another dissipation pathway. However, adsorption-relevant dissipation pathways may only be relevant to the canna treatments since ATZ is a weak base (pKa = 1.7) and the adsorption increases with decreasing pH (McGlamery and Slife, 1966; Clay et al., 1988; Liu et al., 1995). Microbial degradation in the rhizosphere might also account for some of the ATZ dissipation observed (Lin et al., 2018).

Similar to results for APAP and ATZ, dissipation of CBZ residues was not influenced by planting densities (Figs. 1 and 2). Although dissipation in the canna treatments was 2.4–3.2 times greater than in the sweetflag treatments after 1 week, dissipation was similar between the sweetflag (9.2–82.3%) and canna (29.7–82.6%) treatments during all subsequent samplings. These results indicate that dissipation of CBZ was not influenced by the type of plants established in the FTWs nor the planting densities. At the end of the study, 69.4–82.6% of the CBZ dissipated in all of the planted treatments and 46.5% dissipated in the non-planted controls. Taken together, only 22.9–36.1% of the total dissipation observed in the planted treatments was associated with the presence of plants. Generally, 22.3–51.0% of CBZ removal in porous-media based artificial wetland systems established with macrophytes has been attributed to plant uptake (Chen et al., 2018). Likewise, Abdel-Mottaleb and Wilon (2019) reported 25.8 and 49.3% removal of CBZ associated with individual *A. gramenius* and *C. hybrida* 'Orange Punch' plants after 2 weeks. Removal was moderately correlated with cumulative transpiration volumes (R^2 values: 0.50 and 0.82). Microbial degradation in the rhizosphere and sorption onto surfaces of plant roots and FTWs might also influence the CBZ dissipation.

The reduced dissipation observed may have been influenced by the stable molecular structure of CBZ. CBZ contains π-bonds in conjugated rings and an electron-withdrawing amide group that can generate electrostatic potentials (Krahn and Mielck, 1989; Hassan et al., 2013). This molecular structure increases the stability of CBZ in aquatic systems, making it resistant to hydrolysis. A

previous study reported that degradation of CBZ residues in water drastically increased at pH < 5 under 254-nm UV irradiation (Wang et al., 2018). Even though acidic pH values have been shown to increase degradation of CBZ, this effect in the current study was likely minimal since dissipation was similar between the more acidic cannas and less acidic sweetflag mesocosms. This is further supported in follow-up lab dissipation studies that showed little effect of pH on dissipation of CBZ in DI water (Fig. S5). Moreover, chemical dissipation by photolysis should be minimal since mesocosm water surfaces were covered with black polyethylene sheeting film to limit light penetration into the water.

PFOA was the most persistent chemical in the mesocosms. During the entire 17 week study, < 15.5% of PFOA residues dissipated in the non-planted controls (Figs. 1 and 2). PFOA molecules are highly stable, due to strong electronegativity of fluorine atoms in long-chains with multiple carbon−fluorine bonds (Liu et al., 2019) that are resistant to biodegradation, hydrolysis, photolysis, pyrolysis, and even chemical oxidation (Guo et al., 2019; Liu et al., 2019). Overall efficiencies of planted FTWs for PFOA removal was lowest compared to those for the other CECs tested in this study. The FTWs planted with sweetflag removed relatively insignificant amounts of PFOA (15.0−20.6%) over the 17 week study (Fig. 1). Planting density did not consistently influence dissipation, being significant only at week 10. The extent of PFOA dissipation in canna-planted mesocosms during the first 3 weeks (17.1−20.9%; Fig. 2) was similar to that observed for sweetflag (19.1−24.5%) and the non-planted controls (15.5%), but was greater than the controls from week 6 through the end of the study. At week 6, 23.9−35.3% of the PFOA had dissipated, increasing to 60% by the end of the 17 week study. Planting density did not affect PFOA dissipation in canna-planted treatments.

Given that PFOA is highly resistant to degradation, any observed dissipation in the planted treatments relative to the non-planted controls may have likely been due to uptake and/or sorption by plants. Curiously, some dissipation (15.5%) was observed in the non-planted controls at weeks 3 and 6, which then decreased to 6% at week 17. Given the stability of PFOA, these phenomena may have likely been associated with sampling and analysis errors.

SMX within the test systems dissipated in both the planted and non-planted treatments. In the non-planted controls, 73.7% of the SMX was no longer detectable after 17 weeks, possibly due to biodegradation (Li et al., 2018, Figs. 1 and 2). Several species of bacteria, fungi, and algae have been reported to decompose SMX (Wang and Wang, 2018). Photodegradation was not likely significant since the mesocosms were covered with black plastic sheets. Dissipation of SMX increased when plants were present in the FTWs. In sweetflag-planted treatments, SMX concentrations decreased over 50% in two weeks and by 90% after 10 weeks (Fig. 1). SMX concentrations decreased even more in treatments planted with cannas (Fig. 2). SMX concentrations in canna treatments were reduced by 50% one week after treatment, by over 90% after three weeks, and were not detectable after 17 weeks. Microbially-mediated biodegradation was not as likely in the more acidic treatments (i.e., cannas) since such conditions are not optimal for microflora (Wang and Wang, 2018). However, SMX is susceptible to hydrolysis under acidic conditions, which could have contributed to the dissipation observed, especially with the canna treatments. Even though SMX has been reported to degrade more readily under acidic pH conditions (Białk-Bielińska et al., 2012), pH did not significantly impact dissipation in the follow-up study (Fig. S5). The pH within sweetflag-planted mesocosms was >5.9 during the majority of the study, while the pH in canna treatments was consistently 1.8 to 3.6 from two weeks through the end of the study.

While pH-mediated degradation may have occurred, other processes also likely contributed to the dissipation observed. Białk-Bielińska et al. (2012) reported a hydrolysis rate of 12% per 30 days for SMX. Using this rate, SMX concentrations would be expected to only decrease by 51% by the end of the study. Sorption may have also accounted for some of this dissipation. SMX has two acid dissociation constants (pKa) of 1.7 and 5.6, accounting for the protonation of the aniline N and deprotonation of the sulphonamide NH, respectively (Ndagijimana et al., 2019). These pKa values allow SMX to exist in three different ionic forms (anionic, SMX^-, pH > 5.6; neutral, SMX, 1.7 < pH < 5.6; and cationic, SMX^+, pH < 1.7) (Moral-Rodríguez et al., 2016). SMX was likely in the anionic form in the controls and sweetflag-planted mesocosms (pH ~5.9) and in the neutral form in the canna-planted mesocosms. Anionic species are very soluble in water due to interaction of their ionized functional groups with polar water molecules. In contrast, neutral functional groups do not interact as readily with water molecules. Sorption of the neutral form to non-polar surfaces is more likely due to the reduced solubility of the neutral molecules. Chen et al. (2015) showed the sorption of neutral SMX to the non-polar constituent graphene from pH 2−5 but no sorption of anionic SMX at pH 9.

Dissipation trends for E2 in the mesocosms were similar to those for APAP. After one week, concentrations of E2 in non-planted controls were reduced by 20.4%, while concentrations in the sweetflag-planted mesocosms were reduced by > 73.2% (Fig. 1). E2 was not detectable in any of the mesocosms planted with cannas (regardless of planting density) after one week (Fig. 2). After two weeks, no residues of E2 were detected in any of the planted treatments or non-planted controls. Generally, the hydrolysis of E2 is more rapid at relatively higher temperatures: 4 °C (DT_{50} = 40.9 d) and 21.5 °C (DT_{50} = 1.3 d) (Cormier et al., 2015). During this study, water temperature in mesocosms ranged from 20.5 to 29.3 °C, and the DT_{50} of E2 in the water without plants was 6.7 d. While E2 was not persistent in the controls, FTWs established with sweetflag or canna plants accelerated dissipation of E2 from the wastewater.

Overall results indicate that planting density did not influence dissipation of the CECs in the FTW systems. No other studies are available for comparison with these results.

3.4. Plant growth

Initial plant shoot and root lengths were 31.6 ± 3.7 cm and 22.9 ± 5.2 cm, respectively, for sweetflag; and 50.5 ± 5.9 cm and 20.6 ± 7.8 cm for cannas, respectively. Initial fresh weights of the sweetflag and canna plants were 33.4 ± 5.3 g and 54.8 ± 14.8 g, respectively; with corresponding dry weights of 6.23 ± 0.6 g (18.7% of initial weight) and 11.9 ± 1.3 g (21.7% of initial weight), respectively. During the study, plant lengths and biomass increased considerably (Fig. S6). Although shoot lengths (34.2 ± 1.5 cm) of sweetflag plants harvested right after the study termination were nearly similar to the initial lengths, their root lengths (46.0 ± 8.3 cm) were 2-fold longer. At the end of the 17 week study, lengths of shoots (107.7 ± 11.4 cm) and roots (46.8 ± 7.6 cm) for cannas also doubled from their initial lengths. Overall lengths of the harvested plants were statistically similar between all treatments and the planted controls, with no observable effects due to planting densities.

Plant densities influenced biomass production of canna plants and numbers of asexually produced offshoots. Dry weights of the canna plants harvested from the treatment grown with 20 plants (100% density; 120.2 ± 11.1 g) were smaller than those planted with 10 (50% density; 163.7 ± 23.8 g) or 15 plants (75% density; 167.8 ± 16.4). Likewise, fewer shoots were produced (sum of original and new asexually produced shoots) in the T-100 treatment (8.7 ± 3.0) during the 17 week study relative to the T-50 (11.5 ± 3.3) and T-75 (10.8 ± 2.7) treatments and controls (12.9 ± 3.4). These

results indicate that, relative to plant growth, there is no advantage to planting at the maximum density of 20 canna plants per mesocosm due to growth reductions. Planting densities of 50% or 75% did not restrict growth.

3.5. Model application

In general, dissipation of CECs in the highest planting density treatment (T-100) was best characterized using a DE model with correlation coefficients (R^2) of 0.76–1.00 with sweetflag and 0.95–1.00 with cannas (Fig. 3). Likewise, dissipation in the controls was generally best characterized using the DE model with R^2 values ranging from 0.42 to 0.97 across the CECs. The SO and FO models did not describe the data as well, having R^2 values ranging from −0.09 to 1.00 and −0.19 to 1.00, respectively (Table S1). Dissipation trends for PFOA observed in the non-planted control and sweetflag-planted treatment did not fit FO and SO models ($-0.19 < R^2 < -0.01$). Although those dissipation trends were fitted with the DE model ($R^2 = 0.42–0.76$), model accuracy was low. The relative lack of correlation between modeled and measured results is indicative of the low removal efficiency in these treatments.

The broad applicability of the DE model for describing chemical dissipation has been reported in other studies (Utture et al., 2011; Hwang et al., 2018). Using this parameterized model (Table 1), CEC half-lives (DT_{50}) were estimated for the mesocosms containing the highest density of plantings (T-100 treatment) (Fig. 3). The comparable data calculated by FO and SO kinetic models are shown in Supporting Information (Table S2). The aqueous DT_{50} values for canna were shorter than for sweetflag, having values of 2.4 h (APAP), 7.4 d (ATZ), 20.4 d (CBZ), 96.8 d (PFOA), 6.2 d (SMX), and 9.6 h (E2). In comparison, DT_{50} values for sweetflag were 4.0 d (APAP), 19.3 d (ATZ), 32.8 d (CBZ), 690 d (PFOA), 7.7 d (SMX), and 2.4 h (E2). Dissipation within the non-planted controls was characterized by DT_{50} values of 7.1 d (APAP), 1930.8 d (ATZ), 103.2 d (CBZ), 1228.8 d (PFOA), 28.9 d (SMX), and 6.7 d (E2). The DT_{50} values observed in the canna treatment were also shorter than those reported in other studies: 0.7–2.1 d (APAP); 14–742 d (ATZ); 69.7–∞ d (CBZ); stable (PFOA); 10.1–85 d (SMX); 1.3–40 d (E2) (Lam et al., 2004; Lin et al., 2010; Macbean, 2012; Cormier et al., 2015; Li et al., 2015; U.S. EPA, 2016; Hamann et al., 2016; IUPAC, 2018). These results indicate that cannas may be more useful than sweetflag for accelerating dissipation of these CECs from contaminated water. The differences in CEC dissipation between the two species is likely due to a combination of factors including increased transpiration associated with the broader leaves of cannas, as well as the larger amount of root surfaces/biomass for interception of contaminants and colonization by microflora.

3.6. Principle component analysis (PCA)

PCA was conducted based on the CEC residue data obtained with the non-planted control and T-100 treatments. Two principal

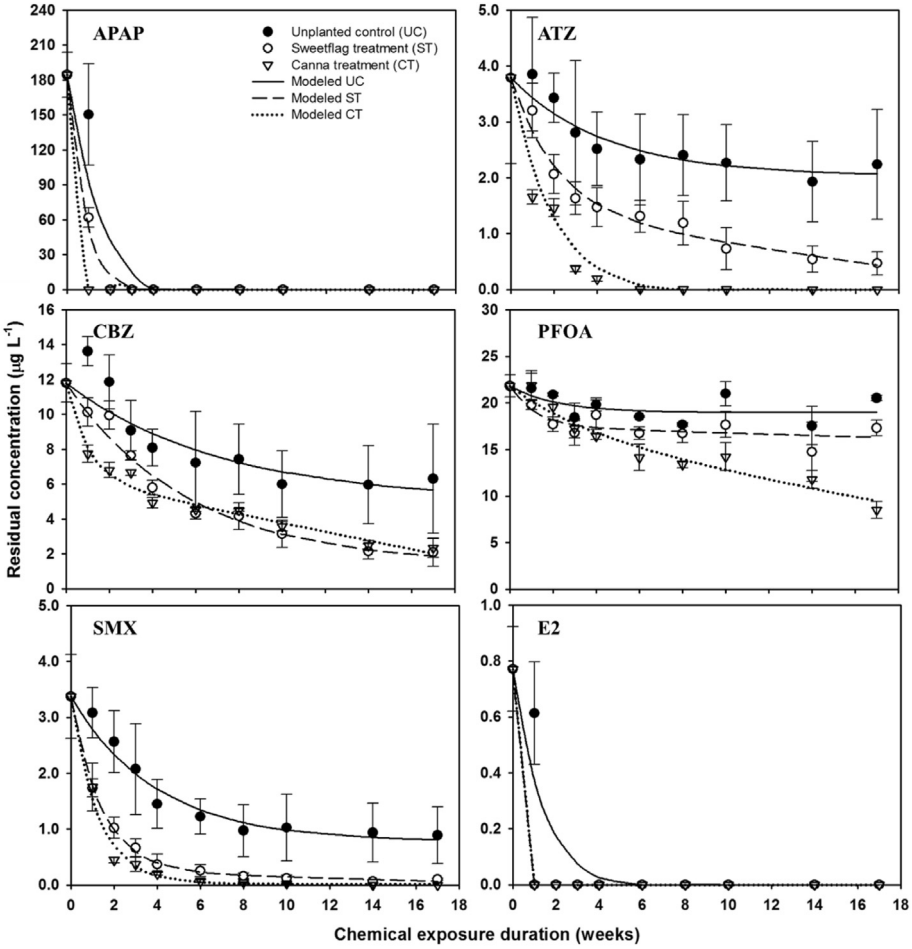

Fig. 3. Time-dependent dissipation trends for acetaminophen (APAP), atrazine (ATZ), carbamazepine (CBZ), perfluorooctanoic acid (PFOA), sulfamethoxazole (SMZ), and 17β-estradiol (E2) in T-100 treatment and control that did not include any of plants. Error bars represent standard deviations.

Table 1
Regression parameters and half-lives (DT_{50}) obtained from the dissipation curves of acetaminophen (APAP), atrazine (ATZ), carbamazepine (CBZ), perfluorooctanoic acid (PFOA), sulfamethoxazole (SMZ), and 17β-estradiol (E2) in water using a double-exponential (DE) model.

Target compound[a)]	Plant	DE model parameter				
		P_1[b)] (%)	P_2[b)] (%)	k_1[c)] (d^{-1})	k_2[c)] (d^{-1})	DT_{50}[d)] (d)
APAP	No plant	216.4	−116.4	8.2×10^{-2}	3.4×10^{-3}	7.1
	Sweetflag	191.3	−91.3	1.7×10^{-1}	8.6×10^{-4}	4.0
	Canna	184.5	−84.5	10.5	0.0	0.1
ATZ	No plant	1.7	98.3	3.2×10^{-2}	7.7×10^{-7}	1930.8
	Sweetflag	2.4	97.6	6.6×10^{-2}	8.1×10^{-5}	19.3
	Canna	3.8	96.2	9.4×10^{-2}	0.0	7.4
CBZ	No plant	6.8	93.2	2.0×10^{-2}	0.0	103.2
	Sweetflag	10.4	89.6	2.5×10^{-2}	0.0	32.8
	Canna	5.4	94.6	1.4×10^{-1}	3.9×10^{-4}	20.4
PFOA	No plant	2.8	97.2	6.5×10^{-2}	0.0	1228.8
	Sweetflag	4.4	95.6	1.2×10^{-1}	1.0×10^{-4}	960.0
	Canna	4.7	95.3	3.9×10^{-2}	7.1×10^{-4}	96.8
SMX	No plant	2.6	97.4	3.6×10^{-2}	0.0	28.9
	Sweetflag	3.1	96.9	1.0×10^{-1}	1.6×10^{-5}	7.7
	Canna	3.4	96.6	1.1×10^{-1}	8.7×10^{-7}	6.2
E2	No plant	0.8	99.2	9.9×10^{-2}	0.0	6.7
	Sweetflag	0.8	99.2	9.2	0.0	0.1
	Canna	0.8	99.2	1.9	0.0	0.4

a) APAP = acetaminophen; ATZ = atrazine; CBZ = carbamazepine; PFOA = perfluorooctanoic acid; SMX = sulfamethoxazole; E2 = 17β-estradiol.
b) P_1 and P_2, Proportions of first and second dissipation phases, respectively, in the DE model.
c) k_1 and k_2, Dissipation rate constants for first and second dissipation phases, respectively, in the DE model.
d) DT_{50}, Half-lives of CECs in the mesocosm water established with floating treatment wetlands.

components (PC1 and PC2) were extracted to explain 80.8% and 11.3% of total variance, respectively. PC1 was related to persistence of the chemical, while PC2 was related to the plant type. Correlation scores between respective factors (n = 18) and PCs were plotted (Fig. 4). PCA scores for APAP and E2, which dissipated the most rapidly in mesocosms, were mostly correlated with plant type (PC2), while PCA scores for ATZ, CBZ, and SMX-controls, CBZ-sweetflag, and PFOA-canna were more correlated with the persistence factor (PC1). The other treatments were horizontally distributed from left to right in the order of their dissipation rates (i.e., SMX > ATZ > CBZ). With the exception of PFOA, PCA scores for controls were most correlated with the persistence factor (PC1), scores for cannas were more correlated with the plant type factor (PC2), and scores for sweetflag were intermediate. PCA scores for PFOA did not follow this order of correlation, with the PCA score for cannas being similar to the SMX, ATZ, and CBZ controls. The PFOA controls were not related to any of the treatments and the sweetflag PCA scores intermediate between those of CBZ-canna and ATZ-canna. This atypical distribution may have resulted from the non-monotonic decreasing trends in concentrations detected throughout the study.

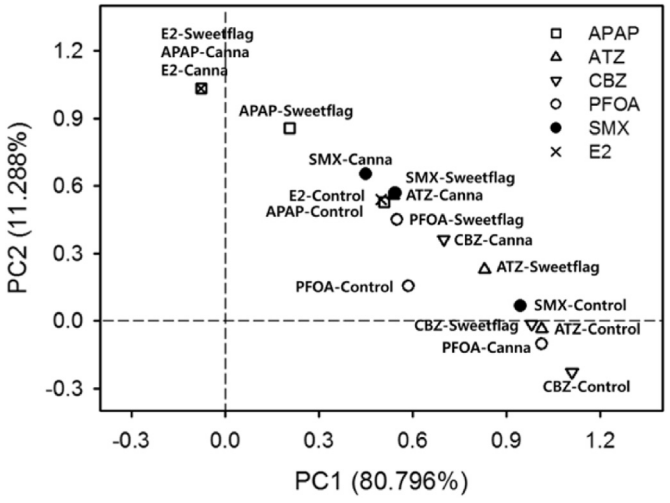

Fig. 4. Principle components analysis for CEC analysis data obtained from the non-planted controls and the T-100 treatments (with both sweetflag and canna) after the 17 week study.

4. Conclusions

In this study, the use of FTWs established with sweetflag (*Acorus gramineus* Sol. ex Aiton) or canna (*Canna hybrida* L. 'Orange King Humbert') plants at different planting densities were evaluated for their abilities to remove CECs from contaminated water. CEC removal efficiencies were highest in the treatments established with canna plants, and the planting density was not influential. APAP and E2 were most rapidly dissipated from the mesocosms established with sweetflag or canna plants, followed by SMX, ATZ, CBZ, and PFOA. Principle Components Analysis indicated that the most influential factors on the CEC removal by FTWs were the persistence of CECs in water and the type of plants established in the FTWs. Overall results show that cannas are a promising plant species for use in FTW systems designed to remove trace concentrations of CECs from surface water. Results also demonstrate that removal of CECs can vary significantly depending on the chemical, making it necessary to evaluate CEC removal on an individual basis. Further studies are needed to understand transfer and transformation of CEC residues in the water−canna uptake system.

CRediT author statement

Jeong-In Hwang: Methodology, Investigation, Formal analysis, Visualization, Writing − original draft, Writing − review & editing; Francisca Ordonez Hinz: Methodology, Formal analysis, Visualization, Writing − original draft, Writing − review & editing; Joseph P. Albano: Conceptualization, Resources; Patrick Christopher Wilson: Conceptualization, Resources, Writing − review & editing, Supervision, Finding acquisition.

Declaration of competing interest

The authors declare that they have no conflict of interests for this paper.

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Appendix B. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2020.129159.

Appendix A. Supporting information

Included as Supporting Information are descriptions of the LC–MS/MS analytical method used for quantifying CEC residues, tables including parameter values of various kinetic models for evaluation of CEC dissipation trends, and figures describing daily temperatures/precipitation/humidity onsite, changes of pH, EC and nutrition in mesocosms, and dried weight data for plants at the end of the study.

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