Ecological Engineering 175 (2022) 106477

Contents lists available at ScienceDirect

Ecological Engineering

journal homepage: www.elsevier.com/locate/ecoleng

# Effects of plants and biochar on the performance of treatment wetlands for removal of the pesticide chlorantraniliprole from agricultural runoff

Khalil Abas [a], Jacques Brisson [a], Marc Amyot [c], Jacques Brodeur [a], Veronika Storck [c], Juan Manuel Montiel-León [d], Sung Vo Duy [d], Sébastien Sauvé [d], Margit Kõiv-Vainik [a,b,*]

[a] Institut de Recherche en Biologie Végétale, Département de Sciences Biologiques, Université de Montréal, Montréal, Canada
[b] Department of Geography, Institute of Ecology and Earth Sciences, University of Tartu, Tartu, Estonia
[c] Département de Sciences Biologiques, Université de Montréal, Montréal, Canada
[d] Département de Chimie, Université de Montréal, Montréal, Canada

ARTICLE INFO

*Keywords:*
Pesticides
Macrophytes
Constructed wetlands
Phytoremediation
Subsurface flow
Substrate enhancement

ABSTRACT

Chlorantraniliprole (CAP), an emergent insecticide commonly replacing banned neonicotinoids, is used worldwide despite the risk of contaminating water bodies. Treatment wetlands (TWs) have shown great potential for mitigating various pesticides in agricultural runoff, but little is known about CAP removal. The aim of this study was to determine the effect of adding biochar to subsurface flow treatment wetlands (SSF TWs) and the performance of three macrophyte species (*Phragmites australis* subsp. *americanus, Scirpus cyperinus* and *Sporobolus michauxianus*) in CAP removal. Removal efficiency was monitored over a one-month period in water-saturated SSF mesocosms fed with synthetic agricultural runoff containing CAP. To reflect temporal changes in agricultural runoff dynamics, two CAP concentrations were used in influent: a peak concentration (4 μg/L) for the first week and a trace concentration (0.4 μg/L) for the three subsequent weeks. Results showed that mesocosms with biochar were very effective in removing CAP mass (90 to 99%) and remained so throughout the experimental period. On the other hand, the level of CAP removal achieved in planted mesocosms without biochar was low (less than 13%). Evapotranspiration contributed significantly to volume reduction, but no general pattern in CAP mass removal efficiency was detected among the planted treatments without biochar. However, planted treatments acted as buffer zones, accumulating CAP and reducing its peak mass in effluent. Evapotranspiration rates of *Scirpus* and *Phragmites* were higher than that of *Sporobolus*, resulting in a greater buffering effect. This study suggests that addition of biochar to SSF TW substrate is a promising approach for CAP mitigation in agricultural runoff, but long-term efficiency remains to be assessed.

## 1. Introduction

The extensive use of pesticides in agriculture contributes to water contamination and poses a significant threat to aquatic ecosystems, human health and biodiversity (Cimino et al., 2016; Dabrowski et al., 2002). In the last two decades, a wide variety of pesticides claimed to have a lesser impact on ecosystems have been approved (Umetsu and Shirai, 2020), despite the lack of in-depth knowledge of their ecotoxicological risk to the environment (Rortais et al., 2017). Chlorantraniliprole (CAP), an emerging insecticide commercialized in 2007, is part of the new chemical class anthranilic diamides (Lahm et al., 2007) and has been registered in many countries (Bassi et al., 2009; Lewis et al., 2016). It is commonly applied as a seed treatment to soil drenches, or through chemigation of a wide range of crops such as cereals, oilseeds, fruits, vegetables and pulses (United States Environmental Protection Agency, 2008). Chlorantraniliprole is xylem-mobile, allowing its absorption by the plant and translocation in aerial parts, thereby providing effective control against chewing insect pests (Lahm et al., 2007; Selby et al., 2017). CAP is intended to replace pyrethroids and neonicotinoids because of reduced toxicity to some Hymenopteran pollinators (Schmidt-Jeffris and Nault, 2016). However, it is toxic to several non-target vertebrates, such as fish (trout: CL50–96 h > 13.8 ppm; bluegill: CL50–96 h > 15.1 ppm), and highly toxic to freshwater invertebrates (CL50/CE50–48 h ranges from 11.6 to 8.59 ppb) (Lewis et al., 2016; SAgE pesticides, 2019; United States Environmental Protection Agency, 2008). Also, the Pesticide Properties DataBase (Lewis

* Corresponding author at: 46 Vanemuise St., 51003, Tartu, Estonia.
*E-mail address:* margit.koiv.vainik@ut.ee (M. Kõiv-Vainik).

https://doi.org/10.1016/j.ecoleng.2021.106477
Received 30 April 2021; Received in revised form 13 October 2021; Accepted 7 November 2021

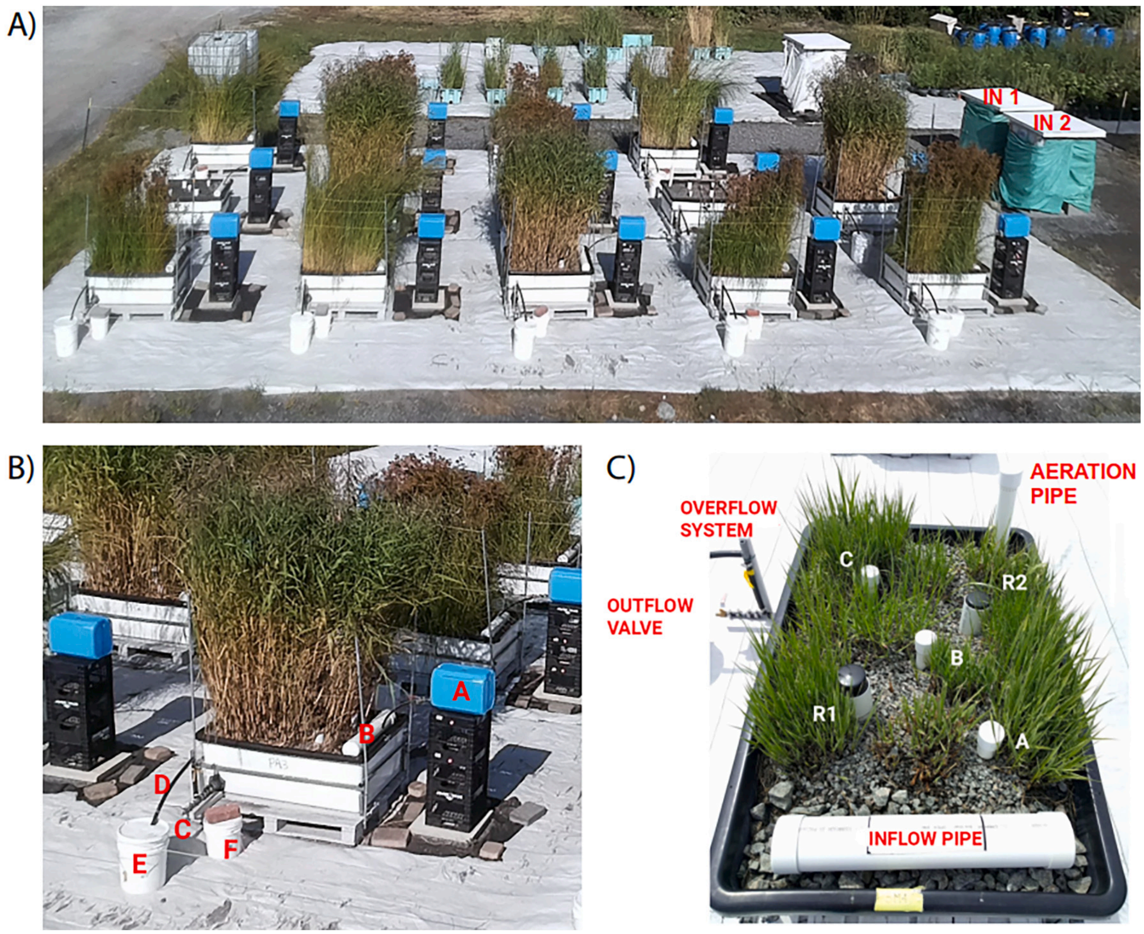


**Fig. 1.** Experimental setup and design. A: Aerial view of the experimental setup (IN1 and IN2: inflow tanks); B: Close-up view of a mesocosm: a) 20 L influent container; b) Perforated water inlet pipe; c) Water outlet valve for sampling and draining of the mesocosms; d) Overflow; e) 20 L effluent bucket; f) 10 L bucket for combined overflow sample collection; C: Top view of a mesocosm (A, B, C: piezometer pipes; R1, R2: rhizotron pipes).

et al., 2016) reports that several laboratory and field studies have shown that chlorantraniliprole biodegrades very slowly, with a typical half-life of 597 days in soil and 170 days in water and sediment. CAP poses a high risk of contaminating rivers and aquifers because it is a moderately mobile insecticide that persists in soil and water, with a high leaching potential (Lewis et al., 2016; Pandey et al., 2020). Also, this insecticide is increasingly detected in surface and groundwater in several regions of the world (Deng, 2019; Giroux, 2018; Lalonde and Garron, 2020; Malaj et al., 2020; Marsala et al., 2020; Redman et al., 2020). Its market share is expected to grow substantially over the next few years due to its wide application on rice, soy, fruits and vegetable, and the continuous development of new CAP-based products (360 Research Reports, 2021). Therefore, it is critical to develop and implement ecological and sustainable technologies for preventing and managing such pollution of the environment.

The use of treatment wetlands (TWs) in agricultural environments is an efficient and inexpensive management strategy to reduce the release of pesticides into the environment. They are operated as ecologically engineered systems that use natural processes involving vegetation, soils, and their associated microbial assemblages to improve water quality (Hammer, 1989; Kadlec and Wallace, 2009; Vymazal and Březinová, 2015). The effectiveness of subsurface flow treatment wetlands (SSF TWs) to mitigate pesticide contamination has drawn increasing attention (Gikas et al., 2018; Matamoros et al., 2007; Wu et al., 2017). These TWs have shown high potential for pesticide removal, mainly through microbial degradation (Lv et al., 2016; Mandal and Singh, 2017; Wu et al., 2017) and plant uptake (Vymazal and Březinová, 2015). Additionally, pesticide sorption can be achieved with substrate enhancements (e.g. addition of materials that have a high sorption capacity). The removal of several classes of pesticides (organophosphates, pyrethroids, organochlorine) has been tested in SSF TWs, but the efficiency and prominence of the different processes involved are variable (Liu et al., 2019; Tang et al., 2016; Wu et al., 2017). To the best of our knowledge, no study has yet investigated the efficiency of TWs in removal of CAP or other insecticides from the anthranilic diamide class.

One approach to increase the efficiency of SSF TWs is to enhance the substrate by adding a material such as biochar, a cost-effective and sustainable product that promotes adsorption and biodegradation (Spahr et al., 2020). Biochar is a stable by-product synthesized by pyrolysis, i.e. by carbonization of plant and/or animal biomass in the absence of oxygen (Ahmad et al., 2014). Its high microporosity and high carbon content allow high adsorption of organic contaminants and increase microbial biomass, activity and diversity in soil (Ahmad et al., 2014; Atkinson et al., 2010; Verheijen et al., 2010; Yu et al., 2010). In a TW context, biochar addition has been proven to promote microbial diversity (Ji et al., 2020; Sha et al., 2020) and to increase SSF TW efficiency in removing common agricultural pollutants, including nitrogen and phosphorus (Bolton et al., 2019; Dalahmeh et al., 2019; Gao et al., 2018; Gupta et al., 2015; Ji et al., 2020; Kasak et al., 2018).

A few recent studies have shown that adding biochar to the TW substrate can also improve pesticide removal (Ouertani, 2019; Sha et al., 2020; Tang et al., 2016; Ulrich et al., 2017). Other studies have tested CAP removal in agricultural soils amended with biochar (Sun et al., 2021; Wang et al., 2012a, 2012b; Wang et al., 2015). For instance, Wang

**Table 1**
Experimental setup and design information.

| Experimental period: | Summer 2019 | | |
|---|---|---|---|
| Location: | Latitude: 45°33′43.00″ N; longitude: 73°34′18.50″ W | | |
| Climatic conditions: | Humid continental climate; warm, humid summer; cold winter (Environment and Climate Change Canada, 2020). | | |
| Flow conditions in mesocosms: | Water-saturated subsurface flow | | |
| Number of mesocosms: | 14 | | |
| Dimensions of mesocosms | L 130 × W 80 × H 46 cm | | |
| Empty volume of the mesocosms | 0.43 $m^3$ | | |
| Height of filter material | 0.41 m | | |
| Water level in mesocosms | 0.39 m | | |
| Void volume of saturated layer | 0.12 $m^3$ (measured in May 2019) | | |
| Type of filter materials: | Granite gravel | Biochar (hardwood charcoal: 50% maple; 25% beech; 25% birch; pyrolysis at max. Temperature of 315 °C) | |
| Origin of the filter material | Agrebec Inc., Canada | Feuille d'Érable Inc., Canada | |
| Particle size of filter materials | Main media Ø 5–12 mm; Distribution and drainage zones Ø 20–28 mm | Inside main media Ø 3–7 mm | |
| Combination of filter materials in mesocosms: | Granite gravel 100% by volume | Granite gravel 75% + biochar 15% by volume | |
| No. of mesocosms with these filter materials | 9 planted 1 unplanted | 3 planted 1 unplanted | |
| Plant species: | *Phragmites australis* subsp. *americanus* (American reed) | *Scirpus cyperinus* (Woolgrass) | *Sporobolus michauxianus* (Prairie cordgrass) |
| No. of mesocosms per plant species | 3 | 3 | 3 |
| No. of planted mesocosms with biochar addition | 0 | 3 | 0 |
| Calculated hydraulic retention time per mesocosm: | 4.4 days | | |
| Mesocosm loading frequency | 2 applications/week | | |
| Loading days | Mondays and Thursdays | | |
| Loading per event per mesocosm | 120 L | | |
| Inflow distribution pipe | Diameter Ø 10.2 cm; Bottom-perforated (Ø 0.6 cm holes) | | |
| Outflow drainage pipe inside the mesocosms | Diameter Ø 5.1 cm; Perforated (Ø 1.3 cm holes) | | |
| Piezometer pipes for water sampling and water level measurements inside mesocosms | Perforated (holes Ø 1.3 cm); Covered with a plastic net | | |
| Rhizotron pipes for root zone monitoring | Diameter Ø 7 cm; Transparent acrylic tubes sealed on the bottom | | |

et al. (2015, 2012a, 2012b) observed that adding a biochar amendment to the soil significantly increases CAP sorption and decreases its bioavailability. These studies have shown that biochar addition could promote the removal of pesticides from agricultural runoff, but more studies are needed under TW conditions to evaluate the removal of emergent pesticides like CAP.

In addition to substrate properties, plants may play a critical role in SSF TWs by increasing pesticide removal (George et al., 2003; Liu et al., 2019; Vymazal and Březinová, 2015). Although plant uptake constitutes only temporary storage of contaminants, plants also provide a living environment for a microbial community, mainly in the rhizosphere zone (Kadlec and Wallace, 2009). Moreover, plants could contribute to pesticide removal through enzymatic activity (Dhir, 2020). The choice of wetland plant species to establish within a TW depends on characteristics such as tolerance to stress, large biomass and fast growth, and if they are native to the region (Gagnon et al., 2012; Rodriguez and Brisson, 2015; Vymazal, 2011). In their literature review, Brisson and Chazarenc (2009) showed that differences in plant performance are difficult to assess because they depend on the treatment context and the pollutants to be treated. Nevertheless, the identity of plant species influences the performance of TWs.

The objectives of the present study were to determine the effects of biochar addition and plant species selection on CAP removal from agricultural runoff. To achieve our objectives, a subsurface flow TW experiment was conducted in mesocosms using simulated agricultural runoff containing CAP. The mesocosms were planted with either *Phragmites australis* subsp. *americanus*, *Scirpus cyperinus* or *Sporobolus michauxianus*. These macrophyte species are native to Canada and have suitable characteristics for TWs, such as large biomass, rapid growth, tolerance to contamination and water saturation stresses, as well as adaptation to local climate. Hardwood biochar was added to the substrate of a subset of the mesocosms.

## 2. Materials and methods

### 2.1. Experimental setup and design

The experiment, conducted outdoor at the Montréal Botanical Garden (Canada), consisted of water-saturated subsurface flow treatment wetland (SSF TW) mesocosms organized following a randomized block a posteriori design (Fig. 1; Fig. S1). All the experimental design parameters are summarized in Table 1. Twelve of the mesocosms were planted and two were left unplanted. Three species of macrophytes were selected for this study: *Phragmites australis* subsp. *americanus* (American reed), *Scirpus cyperinus* (Woolgrass) and *Sporobolus michauxianus* (Prairie cordgrass).

Nine mesocosms contained a gravel substrate and were planted with one of the 3 species, resulting in 3 replicates per species. Three additional replicates of the *S. cyperinus* mesocosm contained gravel substrate with biochar addition. The two unplanted mesocosms were used as control: one with gravel substrate and another with gravel substrate with biochar addition.

In the text below, the name of the genus refers to the treatment in which the species was planted, and the name of the unplanted treatments are referred to as "unplanted". Therefore, the planted treatments are referred to as: *Phragmites*, *Scirpus* and *Sporobolus*. For mesocosms with added biochar, the treatment containing *Scirpus* is referred to as "*Scirpus* with biochar", and the unplanted treatment is referred to as "unplanted with biochar".

Each of the mesocosms consisted of a plastic tank equipped with inflow and outflow pipe systems (Fig. 1; Table 1; Fig. S2). The overflow system maintained the water level in the mesocosms two cm below the substrate surface. The overflow water was accumulated in a plastic bucket, from which effluent samples were collected. A valve connected to the outflow pipe was used for sampling water from inside the mesocosms.

In each mesocosm, three PVC piezometer pipes for sampling purposes (A, B and C) were placed diagonally at 3 different distances from the water inflow zone (Fig. 1; Table 1; Fig. S2). In this experiment, only the middle B piezometer pipe was used for sampling. In each mesocosm, two acrylic pipes were added for insertion of a rhizotron camera (CI-600 In-Situ Root Imager; CID Bio-Science) to take photographs (360°, total of 37 cm depth from the substrate surface) for the purposes of monitoring root system growth.

### 2.2. Experimental substrates

The main substrate used in our experiment was an inert gravel of granitic origin (Table 1). The entry and exit areas of the mesocosms contained a coarse gravel to facilitate even water distribution. The non-reactive gravel was chosen as main substrate to avoid additional variables in the mesocosm experiment from the chemical interactions of the gravel. At the same time, gravel is common TW substrate that facilitates biofilm growth and can be a growing media for the vegetation.

To determine the effect of biochar on CAP removal, hardwood biochar was mixed into the granite substrate of four mesocosms (three planted and one unplanted; Table 1). Extensive research, proven by several reviews, has been carried out with biochars made from different biomass feedstock (Mohan et al., 2014; Wang et al., 2020; Xiang et al., 2020). Several studies have confirmed the high efficiency of wood-based biochars for removal of different types of pollutants from water (Hagemann et al., 2020; Huff and Lee, 2016; Shaheen et al., 2019).

### 2.3. Selection of plant species

All three of the macrophyte species selected (Table 1, Fig. S3) are native to Canada (Brouillet et al., 2010) and have suitable characteristics for TWs, such as large biomass, rapid growth, tolerance to contamination and water saturation stresses, as well as adaptation to local climate (Mozdzer and Zieman, 2010; Quinn et al., 2015; United States Department of Agriculture - Natural Resources Conservation Service, 2020). The genera *Phragmites* and *Scirpus* are commonly planted in TWs because of their ability to effectively remove contaminants (Gaboutloeloe et al., 2009; Kadlec and Wallace, 2009; Vymazal, 2013; Vymazal, 2011). The exotic common reed *P. australis* subsp. *australis*, widely used for this purpose, is invasive in North America and other parts of the world (Saltonstall, 2002), and Rodriguez and Brisson (2016) suggested that native *P. australis* subsp. *americanus* is a good alternative candidate for TWs, since its effectiveness appears to be similar. Holdredge et al. (2010) showed that American reed rhizomes produce more roots than the common reed, which suggests that American reed competes well under nutrient-limited conditions. *Scirpus cyperinus* has been planted in several types of TWs (Behrends et al., 1996; Demchik and Garbutt, 1999; Kohler et al., 2004) and in roadway runoff management (Winston et al., 2012). It adapts well to stressful conditions and is efficient in removing fertilizers and trace metals from polluted water (Demchik and Garbutt, 1999). *Sporobolus michauxianus*, (syn. *Spartina pectinata*) has not yet been tested in TWs but should also be a good candidate for those treating agricultural runoff (Bonilla-Warford and Zedler, 2002). This species is used for bank stabilization (Weaver and Fitzpatrick, 1932) and biofuel production (Lee et al., 2011). It grows rapidly in early spring and produces a large amount of biomass (Madakadze et al., 1998).

### 2.4. Simulated agricultural runoff and loading of the mesocosms

According to several studies (George et al., 2003; Gupta et al., 2015; Vymazal and Březinová, 2015), the hydraulic retention time (HRT) in SSF TWs differs greatly (for example 2 to 20 days) depending on several factors: average precipitation amount, the number of rain events per week, the season, design, experimental setup, TW layout, etc. In our study, we used a theoretical HRT (Table 1) similar to that found in comparable mesocosm studies (Gikas et al., 2018; Gupta et al., 2015; Zhou et al., 2018).

Plants were given a full growing season (year 2018) to establish within the gravel substrate, in order to ensure they reached maturity before the beginning of the experiment (June 2019). Further information on plant preparation and fertilization prior to the experiment is presented in the Supplementary material (S4 and Table S4.1). To ensure normal plant growth in the inert gravel substrate, the nutrient concentrations in the influent were higher than those typically found in agricultural runoff (Kasak et al., 2018; Kato et al., 2009; Koskiaho et al., 2003). Feeding of the mesocosms with a fertilizer solution began in early spring 2019. The chemical composition of the influent prepared from tap water and nutritional additives is shown in Table 2 and the recipe for the fertilizer solution in Table S5.

**Table 2**
Average (X ± *SD*) concentration of nutrients measured in influent during the 2019 season.

| Elements | Concentration (mg/L) |
|---|---|
| N | 30.1 (13.8) |
| P | 6.0 (0.6) |
| K | 51.1 (3.3) |
| Ca | 57.5 (3.0) |
| Mg | 14.6 (1.1) |
| S | 0.03 (0.01) |
| C | 65.8 (6.8) |
| Fe | 0.75 (0.12) |

The synthetic fertilizer solution (influent; Table 2) was prepared on watering days (Mondays and Thursdays) in two 900 L polyethylene tanks, for a total of 1800 L of solution. The solution was mixed and then pumped, using an electrical pump and a hose, to 20 L containers, one of which was located near each mesocosm (Fig. 1). Watering was performed manually, in 20 L rounds for each of the 14 mesocosms, for a total of 6 rounds delivering 120 L per mesocosm. Each feeding event lasted 6 to 8 h. On each watering day, a random watering order was applied. Water level measurements were taken from the sampling piezometer B (Fig. 1; Fig. S2), before and after each watering, using a measuring stick and a measuring tape. After each round, the overflow water was collected in a 20 L graduated bucket and measured. These measurements were used to calculate water balance for each mesocosm for each watering day.

The experiment to determine the fate of chlorantraniliprole (CAP) in the experimental systems was carried out from August 8 to September 2, 2019. Two different concentrations of CAP (properties shown in Table S6) were added to the influent during these 4 weeks (8 applications in total). The concentrations were calculated and prepared from the commercial formulation Coragen©. A dilution of the commercial product (working solution) was prepared in order to transfer and mix the volumes of solution corresponding to the desired influent CAP concentrations in the influent tank. To simulate the dynamics of CAP in agricultural runoff after its field application, a “peak” concentration (4 μg CAP/L, equivalent to 480 μg per mesocosm) was used during the first week (two applications: P1 and P2), followed by a trace concentration (0.4 μg CAP/L, equivalent to 48 μg per mesocosm) during the three subsequent weeks (six applications: T1 to T6). In this experiment, the CAP “peak” concentration reproduced the agricultural runoff of stormwater flowing from agricultural lands during a rain event after pesticide application. To reproduce the CAP concentrations in agricultural runoff, we relied on data collected by Québec’s Ministry of the Environment and the Fight against Climate Change (MELCC), from the rivers of the Lac-Saint-Pierre watershed (Giroux et al., 2019). The peak concentration of 4 μg/L tested in our experiment was 10 times greater than the maximum concentration found in waterways (maximum river concentration determined 0.4 μg/L), in order to reproduce the runoff in drainage ditches next to agricultural fields shortly after pesticide application. This peak concentration was used during the first two applications (indicated with P1, P2).

### 2.5. Sample collection, monitoring and analysis

#### 2.5.1. Plant monitoring and sampling

Plants were measured throughout the growing season in order to monitor their health and growth. The height of shoots and flowers, base diameter and number of flowers and shoots were evaluated 4 times during the growing season (May, July, August and September). At the end of the season, the above-ground plant biomass of each mesocosm was cut down, collected and the wet weight was measured on the same day. Aerial parts of plants in 5 randomly selected zones within the mesocosm were dried (for 1 month in a greenhouse cubicle at 35 °C, then for 2 days in an oven at 70 °C) and the dry weight was measured (Starfrit digital scale, 1 g accuracy). The total above-ground plant biomass obtained from mesocosms was calculated using the average of dry and wet weight ratio of the 5 selected zones. Root and rhizome growth inside the mesocosms were monitored using the rhizotron pictures at the end of September, after the CAP application period.

### 2.5.2. Evapotranspiration rate measurement

Water loss through evapotranspiration (ET) was calculated twice weekly by measuring total inlet volume, the variation of volume inside the mesocosms and total outlet volume following Eq. (1).

$$ET = V_{in} - ((V_{t2} - V_{t1}) - V_{out}) \tag{1}$$

$V_{in}$ = Volume of influent and rain.
$V_{t1}$ = Volume inside mesocosm, before watering.
$V_{t2}$ = Volume inside mesocosm, before following watering.
$V_{out}$ = Volume collected from the outlet (overflow), between watering events.

Water volume inside the mesocosms was calculated using water level measurements (cm) inside the mesocosms and a correlation between water volume and depth of the mesocosms (void volumes measured at the beginning of the season; calculated pore factor 3.3 L/cm).

The volume of capillary water in the drained portion of the mesocosms was not included in the ET calculation, since it is considered negligible (Stefanakis and Tsihryintzis, 2011). Average evapotranspiration rate (cm/d) was calculated as the total volume lost by evapotranspiration divided by the surface of the mesocosm and by the number of days between watering events.

### 2.5.3. Water sampling and analysis

For water analyses, grab samples of the influent at the beginning of each watering day, samples of the water within the mesocosms before and after watering and combined overflow were collected. Combined overflow sampling was performed by collecting proportional subsamples of the effluent water after each watering round (Fig. 1). Effluent sampling was performed at the end of each watering day from the combined overflow.

Electrical conductivity (EC), pH, total dissolved solids (TDS) and redox potential (ORP) were measured from influent and overflow with a multiparametric probe (Hanna Instruments®), 24 h after sampling once a week, throughout the feeding period (May to October).

Chemical analyses of total suspended solids (TSS), chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), nitrate ($NO_3^-$) orthophosphate ($PO_4^{3-}$), total organic carbon (TOC), ammonium ($NH_4^+$), total phosphorus (TP), metals (Ca, K, Mg, Fe) and hydrogen sulfide ($H_2S$) were carried out throughout the season. For these parameters, samples were taken from the influent and the combined overflows of the mesocosms and analyzed in an accredited laboratory (Eurofins Environex, Longueuil, Canada). The chemical analyses were performed according to the standard methods (APHA et al., 2012; Centre d'expertise en analyse environnementale du Québec, 2019). To determine the general performance of the mesocosms, the influent and effluent concentrations of common agricultural pollutants and water balance were used to calculate the mass (mg) of pollutants discharged to the environment and mass removal efficiency.

To monitor CAP concentration in the water of the mesocosms, samples were collected from the influent, the water inside the mesocosms before and after watering, as well as the combined overflow. CAP samples of 25 mL were taken in amber glass bottles and stored in the freezer (at −18 °C), until analysis.

CAP level in the water of the mesocosms was monitored on a total of 9 dates. Sampling was conducted on each watering day, throughout the CAP application period, and additional sampling was done during the watering day that followed the last CAP application.

### 2.5.4. CAP analysis

Samples were analyzed by on-line solid-phase extraction (on-line SPE) coupled to liquid chromatography tandem mass spectrometry through a heated electrospray ionization source (LC-HESI-MS/MS). The instrumental method was adapted from Goeury et al. (2019). An Accela 600 quaternary pump (Thermo Finnigan, San Jose, CA) was used for the sample loading step (5 mL injection volume) onto an on-line Hypersil Gold aQ C18 column (20 mm × 2.1 mm, 12 μm particle size) for sample pre-concentration. The elution step was carried out using an Accela 1250 quaternary pump (Thermo Finnigan, San Jose, CA) and chromatographic separation was performed with a Hypersil Gold column C18 (50 mm × 2.1 mm, 1.9 μm particle size) maintained at 50 °C in a thermostated column compartment. A TSQ Quantiva triple-quadrupole mass spectrometer (Thermo Fisher Scientific, Waltham, MA) was used for analyte detection and quantification. The mass spectrometer was operated in selected reaction monitoring (SRM) mode and ionization was achieved in negative mode. The detection limit of CAP was 5 ng/L. More details on CAP analysis and quality control are presented in the Supplementary material (S7).

CAP removal was calculated for 4 applications (P1, P2, T1, T2; Eq. (2)). CAP concentration in effluent was monitored for 2 dates (P2 and T1) and an approximation was calculated for the two other applications (P1 and T2; Eq. S8) using the proportion of CAP concentration inside the water of the mesocosms before and after the watering. CAP removal values were corrected for water loss due to evapotranspiration. Water sample results for CAP were converted from units of concentration to mass using water level measurements and a correlation between water volume and depth of the mesocosms.

$$\text{Mass Removal} = M_{in} - ((M_{t2} - M_{t1}) - M_{out}) \tag{2}$$

$M_{in}$ = Mass of CAP in influent.
$M_{t1}$ = Mass of CAP in water inside the mesocosm, before watering.
$M_{t2}$ = Mass of CAP in water inside the mesocosm, before next watering.
$M_{out}$ = Mass of CAP in the water collected from the outlet, between watering events.

Percentage of removal for each watering event was calculated as the total mass removed, divided by the mass of CAP inside the mesocosm before watering. Cumulative CAP mass removal was calculated as the sum of CAP removal for each watering day.

### 2.5.5. Statistical analyses

All values are reported as mean ± the standard error of the mean unless otherwise noted. Comparison of the following parameters was tested statistically between treatments: dry above-ground biomass, CAP concentration and mass in effluent, CAP removal, CAP in water inside each mesocosm, season average of evapotranspiration. All statistical analyses were done on four treatments with replicas (Phrag, Sporob, Scirp, Scirp+bch). However, some results on CAP are presented separately in two sections, according to main objectives. Unplanted treatments were used for qualitative comparison without statistical analysis for lack of replication.

Where appropriate, repeated measures analysis of variance (ANOVA) with linear mixed modelling was applied to test for the significance of the interaction between treatment and time. Block, treatment and time effects were included in the model as random factors. When interaction was statistically significant, separate analyses were conducted for each sampling date. One-way ANOVA was used to determine if treatment differences were statistically significant ($\alpha$ = 0.05) followed by a post-hoc Tukey's Honestly Significant Difference (HSD) when the overall ANOVA was significant. All models were checked for normality and homogeneity of the variance by visual inspection of plots of residuals against fitted values. Variables that did not meet normality or heterogeneity assumptions were modified using the

**Table 3**
Average water and biomass parameters (X ± *SD*) during the growing season in 2019.

| Treatment | HRT (days) | Effluent (L/event) | ET minimum (cm/day) | ET average (cm/day) | ET maximum (cm/day) |
|---|---|---|---|---|---|
| Phrag | 6.9 (0.4) | 76.0 (4.0) | 0.2 | $1.6^{ab}$ (0.6) | 2.8 |
| Sporob | 6.3 (0.1) | 83.4 (1.2) | 0.1 | $1.3^{b}$ (0.6) | 2.5 |
| Scirp | 7.4 (0.3) | 70.9 (3.0) | 0.5 | $1.8^{a}$ (0.6) | 3.2 |
| Scirp + Bch | 6.8 (0.6) | 78.0 (6.9) | 0.2 | $1.5^{c}$ (0.5) | 2.7 |
| Unplant + Bch | 4.9 | 109.3 | 0.0 | 0.4 | 0.9 |
| Unplant | 4.7 | 112.5 | 0.0 | 0.3 | 0.9 |

| | Aboveground biomass (g/m$^2$) | Shoots length (cm) | Shoots (nb/m$^2$) | Flowers (nb/m$^2$) |
|---|---|---|---|---|
| Phrag | $2766^{a}$ (321) | 190 (8) | 570 (138) | 153 (44) |
| Sporob | $4493^{c}$ (126) | 165 (8) | 1281 (151) | 483 (72) |
| Scirp | $2578^{a}$ (279) | 142 (11) | 727 (56) | 286 (67) |
| Scirp + Bch | $1809^{b}$ (435) | 126 (7) | 713 (234) | 205 (141) |

Note: Different letters indicate significant differences between treatments based on one-way ANOVA at $p < 0.05$.
Hydraulic retention time (HRT), Evapotranspiration rate (ET), and treatments (e.g. Phrag) are described in the Materials and Methods section.

appropriate transformation (ln, square or Box-Cox). R (ver. 4.0.2) was used to perform statistical analyses.

## 3. Results

### 3.1. General performance

The experimental treatments performed well throughout the season in terms of removing the common agricultural pollutants measured (N, P, organic matter). In addition to CAP removal, a high level of mass removal was achieved for all the common agricultural pollutants (ranging between 73 and 97%) except for phosphorus (ranging between 25 and 68%) (Tables S9 - S12). The highest removal was achieved by the planted treatments for TKN, $NO_3^-$, $NH_4^+$, TP, $PO_4^{3-}$. For example, $NO_3^-$ removal ranged between 89% and 94% for the planted treatments, while it ranged between 67% and 69% for unplanted. On the other hand, there was no difference between the planted and unplanted treatments in removal of TSS, TOC and COD.

### 3.2. Plant biomass

During the experimental period, the plants were healthy and fully grown (Fig. S3). There were significant differences in plant biomass between species at the end of the season (Table 3). Total dry aboveground biomass ranged from 1.26 kg/m$^2$ to 4.26 kg/m$^2$ (Fig. S13). For *Sporobolus,* aboveground biomass was significantly greater than that of the other planted treatments, with an average of 4.13 kg/m$^2$. Also, *Sporobolus* had the highest density of shoots (1281 shoots/m$^2$) and flowers (483 flowers/m$^2$). It was followed by *Phragmites* and *Scirpus*, with 2.5 kg/m$^2$ and 2.2 kg/m$^2$ of biomass respectively, with no significant difference between them. The biomass of *Scirpus* with biochar, at 1.5 kg/m$^2$, was significantly lower than that of the other planted treatments (Table 3).

Rhizotron camera images taken on September 24, following CAP application, indicate that the plants were well established in the mesocosms. The root system of all the plant species appears dense and well developed. Visually, the roots of *Sporobolus* are shallower than those of *Phragmites* and *Scirpus* and do not reach the bottom of the mesocosms

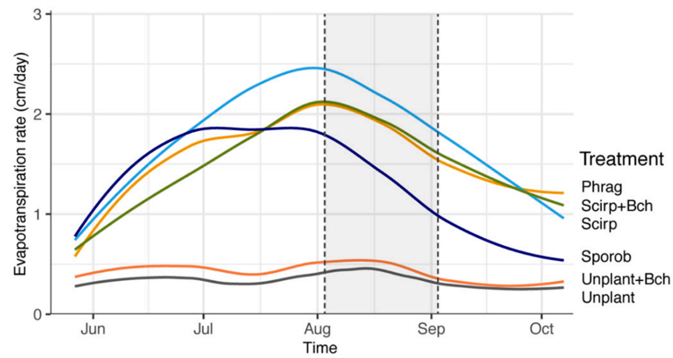


**Fig. 2.** Average evapotranspiration rate for all treatments in 2019. Dashed lines show the CAP application period. Smoothed conditional mean was applied using R function *geom_smooth* (method: loess; span 0.65).

(Fig. S14).

### 3.3. Evapotranspiration rate

For all the planted treatments, evapotranspiration (ET) rate varied throughout the season, increasing from the beginning to mid-season, then decreasing from August onward (Fig. 2). *Scirpus* without biochar had the highest ET rate of all the treatments (Table 3, Fig. 2). *Phragmites* and *Scirpus* with biochar had similar ET rates starting from mid-July until the end of the season. In contrast, *Sporobolus* had a similar initial ET rate increase to that of the other treatments, but reached a lower and earlier peak in the beginning of July, before starting to decrease at the beginning of August, and overall showing the lowest ET rate. The seasonal average ET rate was significantly different between planted treatments (Table 3). Although biomass and evapotranspiration rate varied between plant species, no correlation was found ($R^2 = 0.1$).

ET rate was strongly correlated with effluent volume ($R^2 = 0.998$) and the HRT ($R^2 = 0.971$). Increase in ET rate led to an increase in HRT and a decrease in effluent volume. Because the ET rate was high (Table 3), an average 35% of the water that entered the planted mesocosms (120*L*) was not released into the environment. In contrast, an average 92% of the water volume that entered the unplanted treatments was released into the environment.

### 3.4. Performance of mesocosms during chlorantraniliprole application

Chlorantraniliprole concentration in mesocosm effluent showed significant differences between planted treatments (Table S15). This was visible for both peak (e.g. P2 application of 4 μg CAP/L, equivalent to 480 μg per mesocosm) and trace applications (e.g. T1 application of 0.4 μg CAP/L, equivalent to 48 μg per mesocosm), with no general pattern (Table S15). On P2, *Phragmites* (0.79 μg/L) was significantly different from *Scirpus* (1.44 μg/L) and on T1, *Sporobolus* (2.10 μg/L) was significantly different from *Phragmites* (2.47 μg/L) and *Scirpus* (2.67 μg/L). However, because of the significant difference in evapotranspiration rate between the treatments (Fig. 2), the CAP mass balance provides a more accurate estimate of the systems' efficiency. Chlorantraniliprole mass in mesocosm effluent showed no significant difference between planted treatments for P2 and T1 (Table S15). Also, for those two applications, there was a significant difference in CAP mass in effluent between *Scirpus* with biochar (0.22 μg and 0.13 μg, for P2 and T1 respectively) and *Scirpus* without biochar (63 μg and 157 μg, respectively) (Table S15). In all the treatments containing biochar (*Scirpus* with biochar and unplanted mesocosm with biochar), for the first 4 applications, the CAP concentration and mass in effluent were very low (ranging between 0.001 and 0.026 μg/L and between 0.04 and 2.83 μg) with very small differences between them.

### 3.5. Effect of substrate enhancement with biochar on CAP removal

CAP cumulative removal was above 99% for the first four CAP applications for *Scirpus* with biochar and the unplanted mesocosm with biochar (Fig. 4). There was a significant difference in CAP mass removal between *Scirpus* with and without biochar under both high (P2, 480 μg of CAP added with influent per event) and low CAP addition. Whether planted or not, biochar treatments had a CAP mass removal ranging from 90 to 99% for second and third CAP applications (P2, T1). There was no difference in CAP mass removal efficiency between peak and trace applications. Also, CAP mass in water inside mesocosms containing biochar remained very low, with values ranging from 0.16 μg to 6.36 μg (Fig. 5) for the nine sampling dates. The difference between planted mesocosms with and without biochar in CAP mass in water inside mesocosms was significant for all dates. The cumulative mass removal of CAP in the mesocosms also confirms high and stable CAP removal in mesocosms containing biochar (Fig. 4).

### 3.6. Plant performance in CAP removal

The planted mesocosms showed limited CAP mass removal that was nonetheless better than that of the unplanted control, which removed nearly no CAP (Fig. 4). After the first four CAP applications, cumulative CAP mass removal for the unplanted treatment was only 9.7%, while it was 39%, 39% and 38% for *Phragmites*, *Scirpus* and *Sporobolus* respectively (Fig. 4). There was a small difference in CAP mass removal efficiency between peak and trace applications. The highest mass removal occurred during the first peak application (P1), but shortly after it reached a plateau for planted treatments without biochar (Fig. 4). In P1, removal reached 73% for *Phragmites*, 62% for *Scirpus* and 63% for *Sporobolus*. For the two following applications (P2, T1), despite a significant difference in removal, the actual difference was negligible (Fig. 5). Furthermore, starting with the second application (P2), negative values of CAP mass removal in the treatments were obtained.

While the CAP mass in the influent varied abruptly from peak (480 μg) to trace application (48 μg), the mass in water inside the planted mesocosms varied gradually. For instance, during T1, the CAP mass in the influent was 48 μg, while the CAP mass in water inside the planted mesocosms varied between 306 μg and 426 μg (Fig. 5). The CAP mass variation in the unplanted treatment was less progressive than that in the planted treatments. This is particularly evident beginning with the fifth application (T3), at which point the mass inside the unplanted treatment was 55 μg while the mass inside the planted treatments ranged from 101 μg to 166 μg.

Although biomass and ET rate varied between plant species, there was little difference in CAP mass removal between planted treatments without biochar. Significant differences were found between planted treatments in CAP mass removal for P2 and T1 applications. On P2, *Scirpus* showed significantly lower CAP mass removal (−4%) than *Phragmites* (12%) and *Sporobolus* (12%). Whereas on T1, *Scirpus* showed significantly higher CAP mass removal (9%) than *Phragmites* (−13%) and *Sporobolus* (−4%; Fig. 5). However, following the fourth application, all three planted treatments appeared to reach the same cumulative CAP removal average of 39% (Fig. 4). There was a small difference in CAP mass in water inside the mesocosms between the planted treatments (Fig. 5). Although the mass was significantly lower for the *Sporobolus* treatment compared to *Scirpus* and *Phragmites*, for most of the applications (T1, T2, T3, T4 and T5), this difference was negligible.

## 4. Discussion

All tested mesocosms successfully removed common agricultural pollutants similarly to previous research (Wang et al., 2018), but only those including biochar proved to be very effective in removing CAP. Although there was little difference in CAP removal between the three macrophyte species, based on mass balance, an attenuation of peak mass of CAP in effluent was particularly notable among these treatments.

### 4.1. Effect of biochar on CAP removal

#### 4.1.1. High effectiveness of biochar

Results showed that biochar addition to the substrate was very effective in improving CAP removal in SSF, resulting in reduced CAP mass and concentration in effluent from the systems. CAP mass removal was very high and similar in *Scirpus* with biochar and the unplanted with biochar (91 to 99%) compared to *Scirpus* without biochar (−4 to 9%). This is consistent with results from controlled laboratory batch and column experiments that have shown a direct positive link between biochar addition and the removal of various pesticides for treatment of contaminated water and soils (Deng et al., 2017; Jin et al., 2016; Mandal and Singh, 2017; Ulrich et al., 2015). Moreover, other studies on TW with biochar amendment have shown very efficient removal of various pesticides (ex: chlorpyrifos, endosulfan, fenvalerate, diuron, abamectin) (Sha et al., 2020; Tang et al., 2016; Ulrich et al., 2017). In our study, the specific mechanisms involved in CAP removal in the mesocosms were not determined. Biochar addition has been shown to promote microbial activity and diversity in TWs or in soil (Ahmad et al., 2014; Ji et al., 2020; Sha et al., 2020), suggesting that it may enhance biodegradation of organic pollutants. It is recognized that the main mechanisms for the removal of pesticides associated with biochar are microbial degradation and adsorption by the substrate which are mainly due to the high microporosity and hydrophobicity of biochar (Spahr et al., 2020). Nevertheless, CAP biodegrades slowly in soils and in water. Its half-life in soils ranges from 228 to 924 days (median 490 days) under aerobic conditions and is 208 days in the absence of oxygen (Lewis et al., 2016). In water, it is persistent under aerobic conditions with a half-life ranging from 125 to 231 days (median 178 d; Lewis et al., 2016). It is moderately persistent under anaerobic conditions (half-life = 42 d) at 25 °C (Lewis et al., 2016). The main degradation pathways of CAP are abiotic, either by alkaline-catalyzed hydrolysis or photodegradation in water (Lavtižar et al., 2014), which are not promoted under water-saturated sub-surface TW conditions. Thus, the biodegradation of CAP in our SSF mesocosms have probably been negligible. The high removal rate can more likely be explained by adsorption on the substrate of our mesocosm, which is consistent with results obtained by Wang et al. (2012a, 2012b, 2015). It has been shown that contaminants with high $K_{OC}$ are more likely adsorbed on substrate particles, plant surfaces and biofilm in TWs (Vymazal and Březinová, 2015). CAP is a moderately sorbed pesticide ($K_{OC}$ of 362 mL/g) and does not adsorb easily compared to other contaminants that have a $K_{OC} > 1000$ mL/g (Liu et al., 2019). Yet, our study shows that biochar appears to be very effective for its adsorption, as it is for several other types of pesticides. Jin et al. (2016) concluded that soil amendment composed of only a few percent of biochar greatly reduced the concentration of imidacloprid, isoproturon and atrazine. Also, it has been shown that biochar in infiltration systems can enhance atrazine and prometon adsorption under various conditions (Ulrich et al., 2015).

#### 4.1.2. Long term effectiveness of biochar

Results from our study showed stable and highly effective CAP cumulative removal for two weeks and an almost negligible concentration in water from biochar treatments for one month, suggesting that its effectiveness remained constant throughout the application period (Figs. 4 and 5). However, the long-term efficacy of biochar for CAP removal remains to be investigated since it varies with the properties of the biochar and organic contaminants present in the influent (Mia et al., 2017). Sun et al. (2021) found that biochar does not influence the degradation rate of CAP, whether or not it is adsorbed on biochar, suggesting that CAP accumulates in the system due to its very slow rate of degradation. In batch experiments, Ulrich et al. (2015) showed that biochar appears to remain effective at treating pesticide for several years. Our study was conducted on a single pesticide, but when several pesticides are present simultaneously in influent, as in the case of agricultural runoff, there may be competition for adsorption. For example, Zheng et al. (2010) found that when atrazine and simazine co-existed, a competitive sorption occurred between them on the biochar, reflecting a decrease in sorption capacity. Therefore, it would be important to confirm the effectiveness of biochar for CAP removal in combination with other pesticides with which it is often used.

#### 4.1.3. Biochar effect on plant growth

Biochar is often used in agriculture to improve soil properties, enhance abundance of microorganisms and promote plant growth (Jones et al., 2012; Kavitha et al., 2018; Lehmann et al., 2011; Palansooriya et al., 2019). Some studies (Elad et al., 2011; Kasak et al., 2018) showed that biochar addition to the TW substrate increased plants' above-ground biomass thereby increasing the performance of TWs in removing common agricultural pollutants (Kadlec and Wallace, 2009; Vymazal, 2013). However, in our study, biochar had a negative impact on the aboveground biomass and ET rate of *Scirpus* (Table 3; Fig. 2; Fig. S13), although there was no visual difference in the root system (Fig. S14) between *Scirpus* with and without biochar. This could be due to the efficiency of biochar for nutrient adsorption in mesocosms fed with influent that has a low nutrient concentration. Since our study took place over a single season, it would be necessary to test the effect of biochar on the biomass of other species and over the longer term.

### 4.2. Plant performance on CAP removal

#### 4.2.1. Limited effect of plants

Plants were healthy in all mesocosms, and their height at the end of the growing season was similar to that found in natural environments for mature populations of the same species (Rodriguez and Brisson, 2016; United States Department of Agriculture - Natural Resources Conservation Service, 2020). Yet, the presence of plants had a limited effect on CAP mass removal, which was only slightly higher than in the unplanted mesocosm, suggesting that removal mechanisms linked to the presence of plants do not seem to play an important role, at least, under the tested CAP concentrations and short HRT of our experiment. In TWs, plants can play a direct role in removing pesticides through uptake, or an indirect role by promoting microbial degradation and adsorption on roots and biofilm (Kochi et al., 2020). In this study, CAP removal mechanisms were not determined but CAP biodegradation was probably negligible in our mesocosms, since it biodegrades very slowly and its main degradation pathways are abiotic (photolysis and alkaline-catalyzed hydrolysis). Removal through plant uptake would be expected for a systemic insecticide like CAP (Cryder et al., 2021). Even though high and moderately hydrophobic pesticides seem more easily accumulated and transported in plants than highly lipophobic ones, plant uptake is generally weak and sorption via substrate is predominant (Liu et al., 2019; Vymazal and Březinová, 2015). Moreover, under the typically low pesticide concentrations of agricultural runoff and relatively short average HRT in agricultural TWs, plant uptake is unlikely to be important removal mechanisms, whether or not it is followed by biodegradation of CAP via enzymatic action. A possible explanation for the slightly higher performance of the planted treatments compared to the unplanted mesocosm in our study could be the adsorption of the pesticide to organic matter present in the mesocosms, such as roots and biofilm (Vymazal and Březinová, 2015). Since cumulative CAP mass removal reached a plateau from the first application (P1), the substrate seems to have become saturated at that point. This may be due to the low presence of organic matter in the substrate of our SSF systems, mainly composed of inert gravel.

Considering the limited effect of plants on mesocosm efficiency for removing CAP, an absence of difference between plant species would be expected. Indeed, the difference between species in CAP mass removal and in CAP mass in effluent was negligible, although differences were measured in some species' characteristics. *Sporobolus* biomass was higher than that of *Scirpus* and *Phragmites*. On the other hand, the ET rate of *Scirpus* and *Phragmites* was higher than that of *Sporobolus*. The difference in HRT between the planted treatments could have resulted in a difference in pollutant mass removal, as is often the case with biodegradable contaminants (Milani et al., 2019), which CAP is not. No general trend could be identified in the differences between species in CAP removal, although a significant difference was obtained between species for two application dates. This lack of difference between species is supported by CAP cumulative removal (Fig. 4), which was similar between the three species for the fourth application (T2).

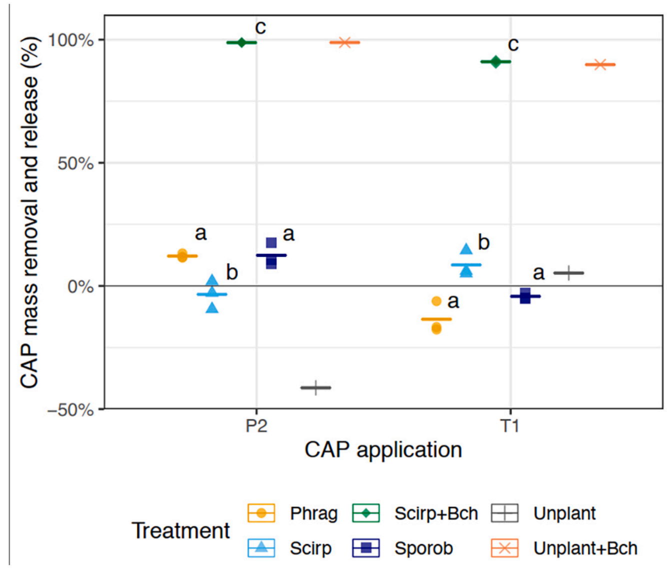


**Fig. 3.** Comparison of average CAP mass removal efficiency in mesocosms 3.5 days after application P2 and T1. Acronyms: P2 – second peak CAP application event; T1 – first trace application. Different letters indicate significant differences between treatments, for each application separately, based on one-way ANOVA at $p < 0.05$.

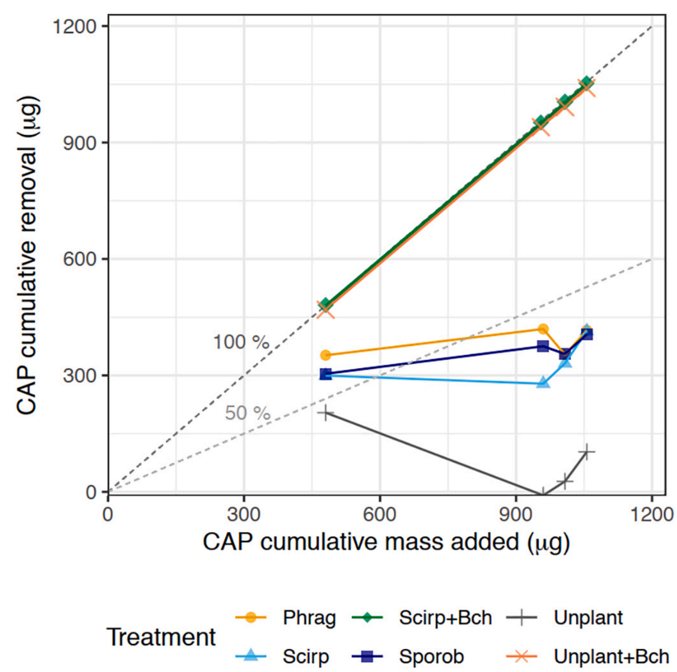


**Fig. 4.** Calculated cumulative CAP mass removal, for the first four events, according to treatments. Dashed lines indicate 50% and 100% CAP cumulative removal.

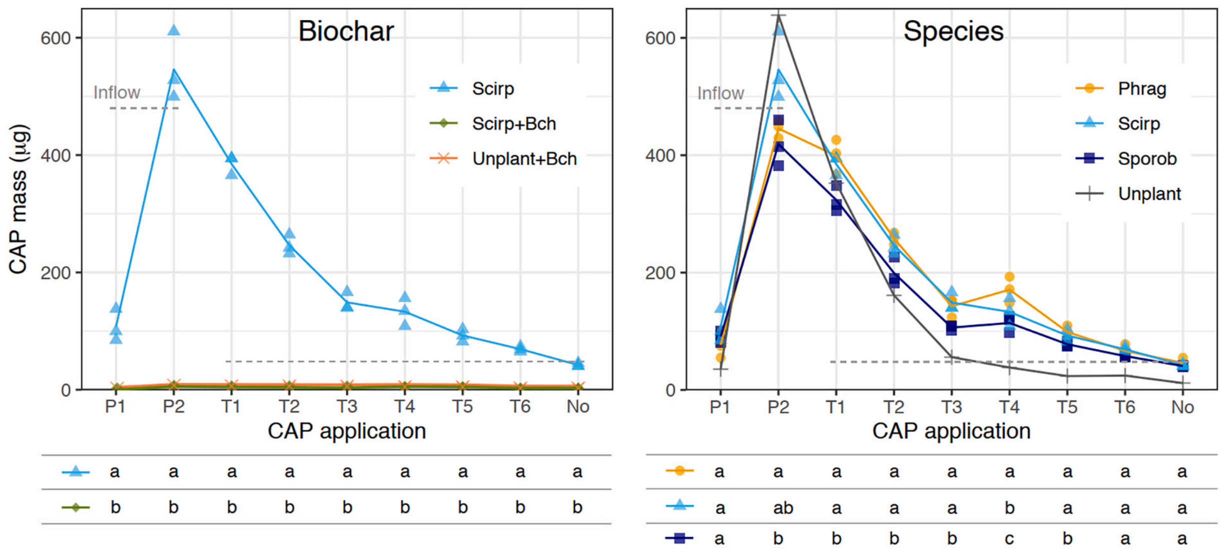


**Fig. 5.** Comparison of changes in CAP mass (calculated from the concentrations and water balances) in the water inside the mesocosms before vs after the watering throughout the application period. Acronyms: P1 and P2 - peak CAP application events; T1 to T6 - trace events; No - no CAP application. Different letters indicate significant differences between treatments, for each application separately, based on one-way ANOVA at $p < 0.05$.

### *4.2.2. Buffering effect of CAP peak mass*

Negative CAP mass removal values suggest that CAP previously retained in the mesocosms was released back into the water of the planted treatments and the unplanted mesocosm during both the second (P2) and third (T1) applications (Figs. 3 and 4). For example, following the second application (P2), *Scirpus* released an average of 4% of its retained CAP, and, following the third application (T1), *Phragmites* and *Sporobolus* released 13% and 4%, respectively (Table S15). Indeed, adsorption can be reversible, especially for molecules presenting a moderate adsorption coefficient (Passeport et al., 2013; Stehle et al., 2011), like CAP. Adsorption and desorption in TWs can be a temporary phenomenon that attenuates peak pesticide concentrations in runoff. Even if removal is temporary, reduction of peak pesticide concentrations could reduce the toxicity of pollutants in vulnerable aquatic environments (Tournebize et al., 2017). Results showed a reduction in CAP mass in effluent ranging from 83 to 91% for planted treatments during both peak applications (P1 and P2). This seems consistent with Elsaesser et al. (2011), who found that planted TWs reduced peak pesticide concentration more effectively than unplanted ones. Our results on CAP mass in the mesocosm water (Fig. 5) suggest that CAP accumulated from the P2 application. This phenomenon appears to be amplified in planted treatments, due to decreased water volume caused by their high ET rate (Beebe et al., 2014; Towler et al., 2004). This combination of peak concentration reduction and slow release of CAP in effluent suggests that the SSF mesocosms acted as buffers of CAP peak mass. This buffer effect seems to have differed between the three planted treatments. Our results showed that CAP mass inside the water of the mesocosms was significantly lower for *Sporobolus* compared to *Scirpus* and *Phragmites*, for the majority of the applications. The lower performance of *Sporobolus* seems to be related to its low ET rate compared to that of the other species. This suggests that SSF mesocosms planted with *Scirpus* and *Phragmites* were more efficient as buffers than *Sporobolus*, particularly from the beginning of August when the ET rate of the latter decreased compared to the other two species (Fig. 2).

Although plant species did not play an important role in CAP removal, their presence in SSF TWs has been shown to be effective in removing several other pollutants, including other pesticides (Vymazal and Březinová, 2015), and provides important ecological benefits, such as contributing to local biodiversity (Brix, 1994; Knight, 1997).

## 5. Conclusions

This study aimed to investigate TW improvement with biochar addition and plant species selection, for the removal of CAP, an emerging insecticide that is persistent in the environment, potentially toxic and has a high leaching potential. Our results showed high and consistent CAP removal from runoff with biochar addition. The low CAP removal in planted TW mesocosms without biochar suggests that a full-size TW would not be effective for CAP removal without the presence of an adsorbent substrate. But, as our experiment with CAP lasted only one month, the long-term effectiveness of biochar in removing CAP remains to be demonstrated. Further studies should test the removal of CAP in TWs together with other pesticides to understand their interaction, such as competition for adsorption sites.

## CRediT authorship contribution statement

**Khalil Abas:** Investigation, Formal analysis, Writing – original draft, Visualization. **Jacques Brisson:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Marc Amyot:** Conceptualization, Writing – review & editing, Funding acquisition. **Jacques Brodeur:** Conceptualization, Writing – review & editing, Funding acquisition. **Veronika Storck:** Conceptualization, Writing – review & editing. **Juan Manuel Montiel-León:** Methodology. **Sung Vo Duy:** Methodology, Writing – original draft. **Sébastien Sauvé:** Conceptualization, Methodology, Writing – review & editing, Visualization, Funding acquisition. **Margit Kõiv-Vainik:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

## Declaration of Competing Interest

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

## Acknowledgements

This research was supported by the Traversy-Langlois fund for the protection of ecosystems and Estonian Research Council grant no.

PUT1125. The authors would like to thank Mary Céline Traversy and Raymond Langlois for their generosity, Patrick Boivin and Benoît Saint-Georges for technical support, Stéphane Daigle and Uku Vainik for statistical help, and all the interns for assistance with field and lab work.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ecoleng.2021.106477.

### References

360 Research Reports, 2021. Global Chlorantraniliprole Industry Research Report, Growth Trends and Competitive Analysis 2021-2027 (No. QYR-18228895).
Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S., Ok, Y.S., 2014. Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere 99, 19–33. https://doi.org/10.1016/j.chemosphere.2013.10.071.
APHA, AWWA, WEF, 2012. Standard Methods for the Examination of Water and Wastewater, 22nd ed. American Public Health Association, American Water Works Association, Water Environment Federation, Washington D.C.
Atkinson, C.J., Fitzgerald, J.D., Hipps, N.A., 2010. Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review. Plant Soil 337, 1–18.
Bassi, A., Rison, J.L., Wiles, J.A., 2009. Chlorantraniliprole (DPX-E2Y45, Rynaxypyr®, Coragen®), a new diamide insecticide for control of codling moth (Cydia pomonella), Colorado potato beetle (Leptinotarsa decemlineata) and European grapevine moth (Lobesia botrana). Nova Gorica 4, 39–45.
Beebe, D.A., Castle, J.W., Molz, F.J., Rodgers, J.H., 2014. Effects of evapotranspiration on treatment performance in constructed wetlands: Experimental studies and modeling. Ecol. Eng. 71, 394–400. https://doi.org/10.1016/j.ecoleng.2014.07.052.
Behrends, L.L., Bailey, E., Bulls, M.J., Coonrod, H.S., Sikora, F.J., 1996. Seasonal Trends in Growth and Biomass Accumulation of Selected Nutrients and Metals in Six Species of Emergent Aquatic Macrophytes (Tennessee Valley Authority).
Bolton, L., Joseph, S., Greenway, M., Donne, S., Munroe, P., Marjo, C.E., 2019. Phosphorus adsorption onto an enriched biochar substrate in constructed wetlands treating wastewater. Ecol. Eng. X 1, 100005.
Bonilla-Warford, C.M., Zedler, J.B., 2002. Potential for Using Native Plant Species in Stormwater Wetlands, p. 10.
Brisson, J., Chazarenc, F., 2009. Maximizing pollutant removal in constructed wetlands: should we pay more attention to macrophyte species selection? Sci. Total Environ. 407, 3923–3930. https://doi.org/10.1016/j.scitotenv.2008.05.047. Thematic Papers: selected papers from the 2007 Wetland Pollutant Dynamics and Control Symposium.
Brix, H., 1994. Functions of macrophytes in constructed wetlands. Water Sci. Technol. 29, 71–78.
Brouillet, L., Coursol, F., Meades, S.J., Favreau, M., Anions, M., Bélisle, P., Desmet, P., 2010. VASCAN, the Database of Vascular Plants of Canada.
Centre d''expertise en analyse environnementale du Québec, 2019. Laboratory Analysis (Ministère de l'Environnement et de la Lutte contre les changements climatiques).
Cimino, A.M., Boyles, A.L., Thayer, K.A., Perry, M.J., 2016. Effects of neonicotinoid pesticide exposure on human health: a systematic review. Environ. Health Perspect. 125, 155–162.
Cryder, Z., Wolf, D., Carlan, C., Gan, J., 2021. Removal of urban-use insecticides in a large-scale constructed wetland. Environ. Pollut. 268, 115586.
Dabrowski, J.M., Peall, S.K.C., Reinecke, A.J., Liess, M., Schulz, R., 2002. Runoff-related pesticide input into the Lourens River, South Africa: basic data for exposure assessment and risk mitigation at the catchment scale. Water Air Soil Pollut. 135, 265–283.
Dalahmeh, S.S., Assayed, A., Stenström, Y., 2019. Combined vertical-horizontal flow biochar filter for onsite wastewater treatment—removal of organic matter, nitrogen and pathogens. Appl. Sci. 9, 5386.
Demchik, M., Garbutt, K., 1999. Growth of woolgrass in acid mine drainage. J. Environ. Qual. 28, 243–249.
Deng, X., 2019. Study Number 304: Surface Water Monitoring for Pesticides in Agricultural Areas in the Central Coast and Southern California, 2018. Environmental Monitoring Branch, California Department of Pesticide Regulation.
Deng, H., Feng, D., He, J., Li, F., Yu, H., Ge, C., 2017. Influence of biochar amendments to soil on the mobility of atrazine using sorption-desorption and soil thin-layer chromatography. Ecol. Eng. 99, 381–390. https://doi.org/10.1016/j.ecoleng.2016.11.021.
Dhir, B., 2020. Chapter 21 - Green technologies for the removal of agrochemicals by aquatic plants. In: Prasad, M.N.V. (Ed.), Agrochemicals Detection, Treatment and Remediation. Butterworth-Heinemann, pp. 569–591. https://doi.org/10.1016/B978-0-08-103017-2.00021-0.
Elad, Y., Cytryn, E., Harel, Y.M., Lew, B., Graber, E.R., 2011. The Biochar effect: plant resistance to biotic stresses. Phytopathol. Mediterr. 50, 335–349.
Elsaesser, D., Blankenberg, A.-G.B., Geist, A., Mæhlum, T., Schulz, R., 2011. Assessing the influence of vegetation on reduction of pesticide concentration in experimental surface flow constructed wetlands: Application of the toxic units approach. Ecol. Eng. 37, 955–962. https://doi.org/10.1016/j.ecoleng.2011.02.003.
Environment and Climate Change Canada, 2020. Weather, Climate and Hazards [WWW Document]. https://www.canada.ca/en/services/environment/weather.html.
Gaboutloeloe, G.K., Chen, S., Barber, M.E., Stöckle, C.O., 2009. Combinations of horizontal and vertical flow constructed wetlands to improve nitrogen removal. Water Air Soil Pollut. Focus 9, 279–286.
Gagnon, V., Chazarenc, F., Kõiv, M., Brisson, J., 2012. Effect of plant species on water quality at the outlet of a sludge treatment wetland. Water Res. 46, 5305–5315. https://doi.org/10.1016/j.watres.2012.07.007.
Gao, Y., Zhang, W., Gao, B., Jia, W., Miao, A., Xiao, L., Yang, L., 2018. Highly efficient removal of nitrogen and phosphorus in an electrolysis-integrated horizontal subsurface-flow constructed wetland amended with biochar. Water Res. 139, 301–310. https://doi.org/10.1016/j.watres.2018.04.007.
George, D., Stearman, G.K., Carlson, K., Lansford, S., 2003. Simazine and metolachlor removal by subsurface flow constructed wetlands. Water Environ. Res. 75, 101–112. https://doi.org/10.2175/106143003X140881.
Gikas, G.D., Vryzas, Z., Tsihrintzis, V.A., 2018. S-metolachlor herbicide removal in pilot-scale horizontal subsurface flow constructed wetlands. Chem. Eng. J. 339, 108–116. https://doi.org/10.1016/j.cej.2018.01.056.
Giroux, I., 2018. État de Situation sur la Présence de Pesticides Dans le Lac Saint-Pierre. Ministère du Développement Durable, de l'Environnement et de la Lutte Contre les Changements Climatiques, Direction de L'information Sur les Milieux Aquatiques.
Giroux, I., Auteuil-Potvin, F., Doussantousse, É., 2019. Présence de Pesticides dans L'eau au Québec: Portrait et Tendances Dans les Zones de Maïs et de Soya – 2015 à 2017. Ministère de l'Environnement et de la Lutte contre les changements climatiques, Direction générale du suivi de l'état de l'environnement, Quebec.
Goeury, K., Duy, S.V., Munoz, G., Prévost, M., Sauvé, S., 2019. Analysis of Environmental Protection Agency priority endocrine disruptor hormones and bisphenol a in tap, surface and wastewater by online concentration liquid chromatography tandem mass spectrometry. J. Chromatogr. A 87–98.
Gupta, P., Ann, T., Lee, S.-M., 2015. Use of biochar to enhance constructed wetland performance in wastewater reclamation. Environ. Eng. Res. 21, 36–44 (doi: 2015.21.1.36).
Hagemann, N., Schmidt, H.-P., Kägi, R., Böhler, M., Sigmund, G., Maccagnan, A., McArdell, C.S., Bucheli, T.D., 2020. Wood-based activated biochar to eliminate organic micropollutants from biologically treated wastewater. Sci. Total Environ. 730, 138417. https://doi.org/10.1016/j.scitotenv.2020.138417.
Hammer, D.A. (Ed.), 1989. Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural. CRC Press.
Holdredge, C., Bertness, M.D., Von Wettberg, E., Silliman, B.R., 2010. Nutrient enrichment enhances hidden differences in phenotype to drive a cryptic plant invasion. Oikos 119, 1776–1784.
Huff, M.D., Lee, J.W., 2016. Biochar-surface oxygenation with hydrogen peroxide. J. Environ. Manag. 165, 17–21. https://doi.org/10.1016/j.jenvman.2015.08.046.
Ji, B., Chen, J., Mei, J., Chang, J., Li, X., Jia, W., Qu, Y., 2020. Roles of biochar media and oxygen supply strategies in treatment performance, greenhouse gas emissions, and bacterial community features of subsurface-flow constructed wetlands. Bioresour. Technol. 122890 https://doi.org/10.1016/j.biortech.2020.122890.
Jin, J., Kang, M., Sun, K., Pan, Z., Wu, F., Xing, B., 2016. Properties of biochar-amended soils and their sorption of imidacloprid, isoproturon, and atrazine. Sci. Total Environ. 550, 504–513. https://doi.org/10.1016/j.scitotenv.2016.01.117.
Jones, D.L., Rousk, J., Edwards-Jones, G., DeLuca, T.H., Murphy, D.V., 2012. Biochar-mediated changes in soil quality and plant growth in a three year field trial. Soil Biol. Biochem. 45, 113–124.
Kadlec, R.H., Wallace, S., 2009. Treatment Wetlands, 2nd ed. CRC Press, Boca Raton, FL.
Kasak, K., Truu, J., Ostonen, I., Sarjas, J., Oopkaup, K., Paiste, P., Kõiv-Vainik, M., Mander, Ü., Truu, M., 2018. Biochar enhances plant growth and nutrient removal in horizontal subsurface flow constructed wetlands. Sci. Total Environ. 639, 67–74. https://doi.org/10.1016/j.scitotenv.2018.05.146.
Kato, T., Kuroda, H., Nakasone, H., 2009. Runoff characteristics of nutrients from an agricultural watershed with intensive livestock production. J. Hydrol. 368, 79–87. https://doi.org/10.1016/j.jhydrol.2009.01.028.
Kavitha, B., Reddy, P.V.L., Kim, B., Lee, S.S., Pandey, S.K., Kim, K.H., 2018. Benefits and limitations of biochar amendment in agricultural soils: a review. J. Environ. Manag. 227, 146–154.
Knight, R.L., 1997. Wildlife habitat and public use benefits of treatment wetlands. Water Sci. Technol. 35, 35–43.
Kochi, L.Y., Freitas, P.L., Maranho, L.T., Juneau, P., Gomes, M.P., 2020. Aquatic macrophytes in constructed wetlands: a fight against water pollution. Sustainability 12, 9202.
Kohler, E.A., Poole, V.L., Reicher, Z.J., Turco, R.F., 2004. Nutrient, metal, and pesticide removal during storm and nonstorm events by a constructed wetland on an urban golf course. Ecol. Eng. 23, 285–298.
Koskiaho, J., Ekholm, P., Räty, M., Riihimäki, J., Puustinen, M., 2003. Retaining agricultural nutrients in constructed wetlands—experiences under boreal conditions. Ecol. Eng. 20, 89–103. https://doi.org/10.1016/S0925-8574(03)00006-5.
Lahm, G.P., Stevenson, T.M., Selby, T.P., Freudenberger, J.H., Cordova, D., Flexner, L., Benner, E.A., 2007. RynaxypyrTM: a new insecticidal anthranilic diamide that acts as a potent and selective ryanodine receptor activator. Bioorg. Med. Chem. Lett. 17, 6274–6279.
Lalonde, B., Garron, C., 2020. Temporal and spatial analysis of surface water pesticide occurrences in the maritime region of Canada. Arch. Environ. Contam. Toxicol. 79 (1), 12–22. https://doi.org/10.1007/s00244-020-00742-x.
Lavtižar, V., Gestel, C.A., Dolenc, D., Trebše, P., 2014. Chemical and photochemical degradation of chlorantraniliprole and characterization of its transformation products. Chemosphere 95, 408–414.

Lee, D.K., Boe, A., Owens, V., Gonzalez-Hernandez, J., Rayburn, A.L., 2011. Developing prairie cordgrass (Spartina pectinata) as a new bioenergy crop. Asp. Appl. Biol. 112, 197–201.
Lehmann, J., Rillig, M.C., Thies, J., Masiello, C.A., Hockaday, W.C., Crowley, D., 2011. Biochar effects on soil biota–a review. Soil Biol. Biochem. 43, 1812–1836.
Lewis, K.A., Tzilivakis, J., Warner, D., Green, A., 2016. An international database for pesticide risk assessments and management. Hum. Ecol. Risk Assess. Int. J. 22, 1050–1064.
Liu, T., Xu, S., Lu, S., Qin, P., Bi, B., Ding, H., Liu, Y., Guo, X., Liu, X., 2019. A review on removal of organophosphorus pesticides in constructed wetland: Performance, mechanism and influencing factors. Sci. Total Environ. 651, 2247–2268. https://doi.org/10.1016/j.scitotenv.2018.10.087.
Lv, T., Zhang, Y., Zhang, L., Carvalho, P.N., Arias, C.A., Brix, H., 2016. Removal of the pesticides imazalil and tebuconazole in saturated constructed wetland mesocosms. Water Res. 91, 126–136. https://doi.org/10.1016/j.watres.2016.01.007.
Madakadze, I.C., Coulman, B.E., Mcelroy, A.R., Stewart, K.A., Smith, D.L., 1998. Evaluation of selected warm-season grasses for biomass production in areas with a short growing season. Bioresour. Technol. 65, 1–12. https://doi.org/10.1016/S0960-8524(98)00039-X.
Malaj, E., Liber, K., Morrissey, C.A., 2020. Spatial distribution of agricultural pesticide use and predicted wetland exposure in the Canadian Prairie Pothole Region. Sci. Total Environ. 718, 134765.
Mandal, A., Singh, N., 2017. Optimization of atrazine and imidacloprid removal from water using biochars: Designing single or multi-staged batch adsorption systems. Int. J. Hyg. Environ. Health 220, 637–645. https://doi.org/10.1016/j.ijheh.2017.02.010. Special Issue: Eighth PhD students workshop: Water and Health – Cannes 2016.
Marsala, R.Z., Capri, E., Russo, E., Bisagni, M., Colla, R., Lucini, L., Suciu, N.A., 2020. First evaluation of pesticides occurrence in groundwater of Tidone Valley, an area with intensive viticulture. Sci. Total Environ. 736, 139730.
Matamoros, V., Puigagut, J., García, J., Bayona, J.M., 2007. Behavior of selected priority organic pollutants in horizontal subsurface flow constructed wetlands: a preliminary screening. Chemosphere 69, 1374–1380. https://doi.org/10.1016/j.chemosphere.2007.05.012.
Mia, S., Dijkstra, F.A., Singh, B., 2017. Long-term aging of biochar: a molecular understanding with agricultural and environmental implications. Adv. Agron. 141, 1–51.
Milani, M., Marzo, A., Toscano, A., Consoli, S., Cirelli, G.L., Ventura, D., Barbagallo, S., 2019. Evapotranspiration from Horizontal subsurface flow constructed wetlands planted with different perennial plant species. Water 11, 2159. https://doi.org/10.3390/w11102159.
Mohan, D., Sarswat, A., Ok, Y.S., Pittman, C.U., 2014. Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent – a critical review. Bioresour. Technol. 160, 191–202. https://doi.org/10.1016/j.biortech.2014.01.120. Special Issue on Biosorption.
Mozdzer, T., Zieman, J., 2010. Ecophysiological differences between genetic lineages facilitate the invasion of non-native Phragmites australis in north American Atlantic coast wetlands. J. Ecol. 98, 451–458. https://doi.org/10.1111/j.1365-2745.2009.01625.x.
Ouertani, S., 2019. Effet de L'ajout de Biochar sur les Microorganismes des Marais Filtrants Artificiels Traitant des Effluents de Serre (doctoral thesis,). Université Laval.
Palansooriya, K.N., Ok, Y.S., Awad, Y.M., Lee, S.S., Sung, J.K., Koutsospyros, A., Moon, D.H., 2019. Impacts of biochar application on upland agriculture: a review. J. Environ. Manag. 234, 52–64.
Pandey, N., Rana, D., Chandrakar, G., Gowda, G.B., Patil, N.B., Annamalai, M., Adak, T., 2020. Role of climate change variables (standing water and rainfall) on dissipation of chlorantraniliprole from a simulated rice ecosystem. Ecotoxicol. Environ. Saf. 205, 111324.
Passeport, E., Tournebize, J., Chaumont, C., Guenne, A., Coquet, Y., 2013. Pesticide contamination interception strategy and removal efficiency in forest buffer and artificial wetland in a tile-drained agricultural watershed. Chemosphere 91, 1289–1296.
Quinn, L.D., Straker, K.C., Guo, J., Kim, S., Thapa, S., Kling, G., Voigt, T.B., 2015. Stress-tolerant feedstocks for sustainable bioenergy production on marginal land. BioEnergy Res. 8, 1081–1100.
Redman, Z.C., Anastasio, C., Tjeerdema, R.S., 2020. Quantum yield for the aqueous photochemical degradation of chlorantraniliprole and simulation of its environmental fate in a model California rice field. Environ. Toxicol. Chem. 39, 1929–1935.
Rodriguez, M., Brisson, J., 2015. Pollutant removal efficiency of native versus exotic common reed (Phragmites australis) in north American treatment wetlands. Ecol. Eng. 74, 364–370. https://doi.org/10.1016/j.ecoleng.2014.11.005.
Rodriguez, M., Brisson, J., 2016. Does the combination of two plant species improve removal efficiency in treatment wetlands? Ecol. Eng. 91, 302–309. https://doi.org/10.1016/j.ecoleng.2016.02.047.
Rortais, A., Arnold, G., Dorne, J.L., More, S.J., Sperandio, G., Streissl, F., Verdonck, F., 2017. Risk assessment of pesticides and other stressors in bees: principles, data gaps and perspectives from the European Food Safety Authority. Sci. Total Environ. 587, 524–537.
SAgE pesticides, 2019. Effets Toxiques des Matières Actives: Chlorantraniliprole.
Saltonstall, K., 2002. Cryptic invasion by a non-native genotype of the common reed, Phragmites australis, into North America. Proc. Natl. Acad. Sci. 99, 2445–2449.
Schmidt-Jeffris, R.A., Nault, B.A., 2016. Anthranilic diamide insecticides delivered via multiple approaches to control vegetable pests: a case study in snap bean. J. Econ. Entomol. 109, 2479–2488.
Selby, T.P., Lahm, G.P., Stevenson, T.M., 2017. A retrospective look at anthranilic diamide insecticides: discovery and lead optimization to chlorantraniliprole and cyantraniliprole. Pest Manag. Sci. 73, 658–665.
Sha, N.Q., Wang, G.H., Li, Y.H., Bai, S.Y., 2020. Removal of abamectin and conventional pollutants in vertical flow constructed wetlands with Fe-modified biochar. RSC Adv. 10, 44171–44182.
Shaheen, S.M., Niazi, N.K., Hassan, N.E.E., Bibi, I., Wang, H., Tsang, D.C.W., Ok, Y.S., Bolan, N., Rinklebe, J., 2019. Wood-based biochar for the removal of potentially toxic elements in water and wastewater: a critical review. Int. Mater. Rev. 64, 216–247. https://doi.org/10.1080/09506608.2018.1473096.
Spahr, S., Teixidó, M., Sedlak, D.L., Luthy, R.G., 2020. Hydrophilic trace organic contaminants in urban stormwater: Occurrence, toxicological relevance, and the need to enhance green stormwater infrastructure. Environ. Sci. Water Res. Technol. 6, 15–44.
Stefanakis, A.I., Tsihryintzis, V.A., 2011. Dewatering mechanisms in pilot-scale sludge drying reed beds: effect of design and operational parameters. Chem. Eng. J. 172, 430–443.
Stehle, S., Elsaesser, D., Gregoire, C., Imfeld, G., Niehaus, E., Passeport, E., Payraudeau, S., Schäfer, R.B., Tournebize, J., Schulz, R., 2011. Pesticide risk mitigation by vegetated treatment systems: a meta-analysis. J. Environ. Qual. 40, 1068–1080. https://doi.org/10.2134/jeq2010.0510.
Sun, C., Bei, K., Xu, Y., Pan, Z., 2021. Effect of biochar on the degradation dynamics of chlorantraniliprole and acetochlor in Brassica chinensis L. and soil under field conditions. ACS Omega 6, 217–226. https://doi.org/10.1021/acsomega.0c04268.
Tang, X., Yang, Y., Tao, R., Chen, P., Dai, Y., Jin, C., Feng, X., 2016. Fate of mixed pesticides in an integrated recirculating constructed wetland (IRCW). Sci. Total Environ. 571, 935–942.
Tournebize, J., Chaumont, C., Mander, Ü., 2017. Implications for constructed wetlands to mitigate nitrate and pesticide pollution in agricultural drained watersheds. In: Ecol. Eng., Wetlands and Buffer Zones in Watershed Management, 103, pp. 415–425. https://doi.org/10.1016/j.ecoleng.2016.02.014.
Towler, B.W., Cahoon, J.E., Stein, O.R., 2004. Evapotranspiration crop coefficients for cattail and bulrush. J. Hydrol. Eng. 9, 235–239.
Ulrich, B.A., Im, E.A., Werner, D., Higgins, C.P., 2015. Biochar and activated carbon for enhanced trace organic contaminant retention in stormwater infiltration systems. Environ. Sci. Technol. 49, 6222–6230.
Ulrich, B.A., Loehnert, M., Higgins, C.P., 2017. Improved contaminant removal in vegetated stormwater biofilters amended with biochar. Environ. Sci. Water Res. Technol 3, 726–734.
Umetsu, N., Shirai, Y., 2020. Development of novel pesticides in the 21st century. J. Pestic. Sci. 45, 54–74.
United States Department of Agriculture - Natural Resources Conservation Service, 2020. PLANTS Database - USDA PLANTS [WWW Document]. https://plants.sc.egov.usda.gov/java/ (accessed 1.12.21).
United States Environmental Protection Agency, 2008. Pesticides Fact Sheet for Chlorantraniliprole. Office of Prevention, Pesticides and Toxic Substances (7505P).
Verheijen, F., Jeffery, S., Bastos, A.C., Velde, M., Diafas, I., 2010. Biochar application to soils. A critical scientific review of effects on soil properties, processes, and functions. EUR 24099, 162.
Vymazal, J., 2011. Plants used in constructed wetlands with horizontal subsurface flow: a review. Hydrobiologia 674, 133–156. https://doi.org/10.1007/s10750-011-0738-9.
Vymazal, J., 2013. The use of hybrid constructed wetlands for wastewater treatment with special attention to nitrogen removal: a review of a recent development. Water Res. 47, 4795–4811. https://doi.org/10.1016/j.watres.2013.05.029.
Vymazal, J., Březinová, T., 2015. The use of constructed wetlands for removal of pesticides from agricultural runoff and drainage: a review. Environ. Int. 75, 11–20. https://doi.org/10.1016/j.envint.2014.10.026.
Wang, T.T., Cheng, J., Liu, X.J., Jiang, W., Zhang, C.L., Yu, X.Y., 2012a. Effect of biochar amendment on the bioavailability of pesticide chlorantraniliprole in soil to earthworm. Ecotoxicol. Environ. Saf. 83, 96–101.
Wang, Y., Tao, L., Chen, M., Li, F., 2012b. Effects of the feii/cuii interaction on copper aging enhancement and pentachlorophenol reductive transformation in paddy soil. J. Agric. Food Chem. 60, 630–638. https://doi.org/10.1021/jf2040093.
Wang, T.T., Li, Y.S., Jiang, A.C., Lu, M.X., Liu, X.J., Yu, X.Y., 2015. Suppression of chlorantraniliprole sorption on biochar in soil–biochar systems. Bull. Environ. Contam. Toxicol. 95, 401–406.
Wang, M., Zhang, D., Dong, J., Tan, S.K., 2018. Application of constructed wetlands for treating agricultural runoff and agro-industrial wastewater: a review. Hydrobiologia 805, 1–31. https://doi.org/10.1007/s10750-017-3315-z.
Wang, X., Guo, Z., Hu, Z., Zhang, J., 2020. Recent advances in biochar application for water and wastewater treatment: a review. PeerJ 8. https://doi.org/10.7717/peerj.9164.
Weaver, J.E., Fitzpatrick, T.J., 1932. Ecology and relative importance of the dominants of tall-grass prairie. Bot. Gaz. 93, 113–150.
Winston, R.J., Hunt, W.F., Kennedy, S.G., Wright, J.D., Lauffer, M.S., 2012. Field evaluation of storm-water control measures for highway runoff treatment. J. Environ. Eng. 138, 101–111.
Wu, J., Li, Z., Wu, L., Zhong, F., Cui, N., Dai, Y., Cheng, S., 2017. Triazophos (TAP) removal in horizontal subsurface flow constructed wetlands (HSCWs) and its accumulation in plants and substrates. Sci. Rep. 7, 5468.
Xiang, W., Zhang, X., Chen, J., Zou, W., He, F., Hu, X., Tsang, D.C.W., Ok, Y.S., Gao, B., 2020. Biochar technology in wastewater treatment: a critical review. Chemosphere 252, 126539. https://doi.org/10.1016/j.chemosphere.2020.126539.

Yu, X., Pan, L., Ying, G., Kookana, R.S., 2010. Enhanced and irreversible sorption of pesticide pyrimethanil by soil amended with biochars. J. Environ. Sci. (China) 22, 615–620. https://doi.org/10.1016/s1001-0742(09)60153-4.
Zheng, W., Guo, M., Chow, T., Bennett, D.N., Rajagopalan, N., 2010. Sorption properties of greenwaste biochar for two triazine pesticides. J. Hazard. Mater. 181, 121–126. https://doi.org/10.1016/j.jhazmat.2010.04.103.
Zhou, X., Jia, L., Liang, C., Feng, L., Wang, R., Wu, H., 2018. Simultaneous enhancement of nitrogen removal and nitrous oxide reduction by a saturated biochar-based intermittent aeration vertical flow constructed wetland: Effects of influent strength. Chem. Eng. J. 334, 1842–1850.